

Electron-beam-induced quantum interference effects in a multilevel quantum emitterH. B. Crispin^{✉*} and N. Talebi^{✉†}*Institute for Experimental and Applied Physics, Christian Albrechts University, Leibnizstrasse 19, 24118 Kiel, Germany*

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Cathodoluminescence spectroscopy has recently emerged as a novel platform for nanoscale control of nonclassical features of light. Here, we propose a theoretical model for cathodoluminescence from a multilevel quantum emitter. Employing a master equation approach and treating the electron-beam excitation as an incoherent broadband field source, we show that quantum interference can arise between the different relaxation pathways. The induced interference can significantly modify the time-dependent spectra resulting in the enhancement or suppression of cathodoluminescence. We find that the excitation rate, initial state of the emitter, and excited level spacing play a crucial role in determining the influence of interference. Our findings shed light on electron-beam-induced quantum interference in cathodoluminescence and provides a theoretical basis for exploring quantum optical phenomena in electron-driven multilevel systems.

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Free-electron and matter interactions and their associated phenomena have attracted the attention of scientists for more than a century [1–7]. A well-known effect is cathodoluminescence (CL), in which electrons incident on a material induce light emission [6]. Recently, photon antibunching from nitrogen-vacancy (NV^0) centers in diamond nanoparticles has been observed while exciting them with electron beams [8]. This demonstrates the excitation of a two-level quantum emitter by fast electrons, thus paving the way for quantum optical studies with deep-subwavelength resolution. Subsequent works have shown the versatile nature of the CL photon statistics [9–11]. For instance, by varying the electron-beam current, a transition from sub-Poissonian to super-Poissonian behaviour was observed in the case of few emitters [9,11]. Moreover, superbunching effects emerge when multiple defect centers are excited, in contrast to the corresponding photoluminescence experiments [9]. The tunability of the photon statistics makes CL spectroscopy a novel technique for single-photon state generation, an essential requirement in quantum computing and quantum information [12,13]. Therefore, a physical understanding of the nonclassical aspects of the CL emission is important from a theoretical and experimental perspective.

Several models have been proposed to understand the photon correlations in CL [9,14–17]. The majority of these theoretical works, however, rely on classical models

[9,14–16]. Recently, an intuitive master equation approach was introduced to explain the superbunching effect [17], where a phenomenological description of CL from two-level quantum emitters was provided. The nature of the optical state of the radiation field was also discussed based on heuristic arguments. However, the focus has been on the electron-beam excitations of only two-level systems so far. In a recent study of the dephasing of hBN color centers [18], a novel time-resolved CL spectroscopy technique has revealed the role of additional transition pathways in single emitters. Therefore, exploring the dynamics of multilevel quantum emitters under electron-beam excitations is already within experimental reach but a theoretical model for such systems is absent.

In this work, we propose a theoretical framework for the electron-beam excitations of a single multilevel quantum emitter. We assume the system is continuously excited by incident electrons and undergoes radiative decay via spontaneous emission that is detected as CL. Our analysis relies on a quantum optical master equation that is derived from a model Hamiltonian describing the electron-emitter interaction. The resulting dynamical equations for the system naturally consist of the electron-beam-excitation part introduced phenomenologically in Ref. [17]. In addition, the broad spectral nature of the CL emission is predicted. Moreover, a remarkable feature is the possibility of quantum interference between different transition pathways. The interference significantly alters the dynamics of the emitter and the time-dependent spectra leading to enhancement or suppression of spectral peaks. We find that the excitation rate, the initial state of the system, and the energy splitting between the excited levels play a crucial role in determining the influence of induced interference. In general, our master equation can be applied to an N -level quantum emitter and the choice of the relevant energy levels, e.g., two levels or more, may depend on the material system and the transitions that are involved.

Our work is organized as follows. In Sec. II, we discuss the theoretical formalism for the free electron-emitter interaction

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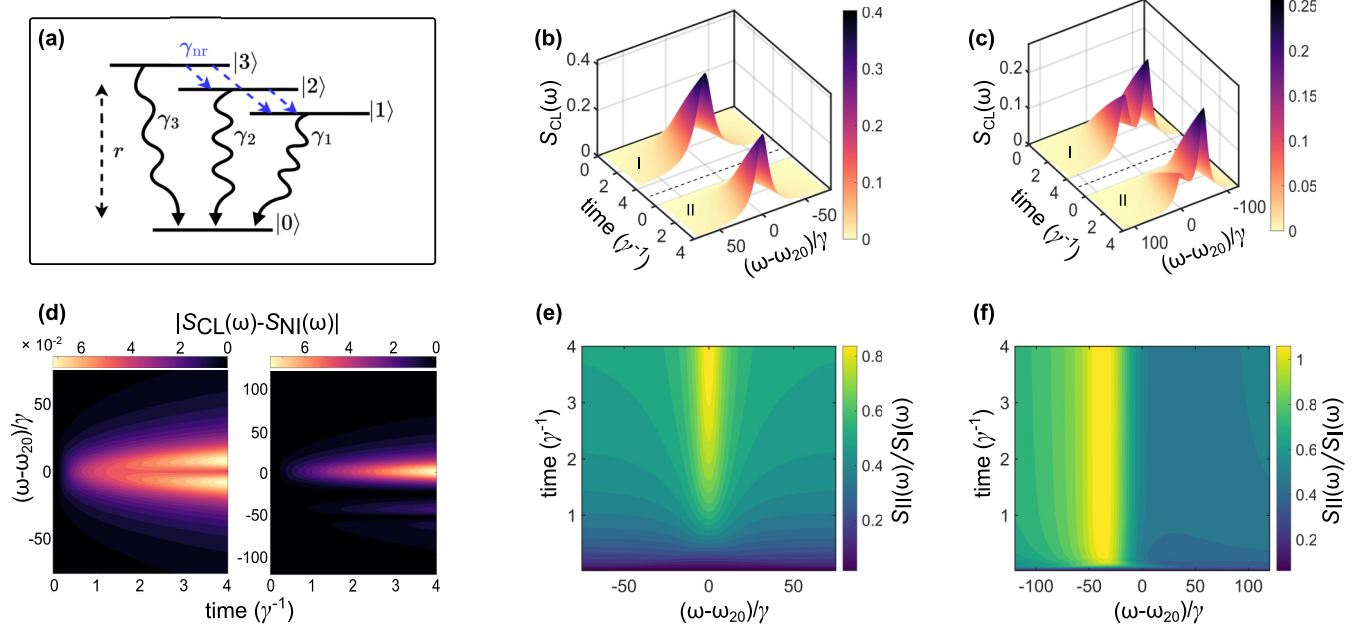


FIG. 1. (a) A four-level V-type configuration of the quantum emitter under consideration. The energy levels $|1\rangle$, $|2\rangle$, and $|3\rangle$ denote the excited states with decay rates γ_1 , γ_2 , and γ_3 , respectively. The states $|3\rangle$ and $|2\rangle$ can also undergo nonradiative decay with rate γ_{nr} to the states $|2\rangle$ and $|1\rangle$, as indicated by the blue arrows. The electron-beam excitation modeled as an incoherent broadband field couples to the transitions $|0\rangle \longleftrightarrow |1\rangle$, $|0\rangle \longleftrightarrow |2\rangle$, and $|0\rangle \longleftrightarrow |3\rangle$ with r being the excitation rate. In (b) and (c), the time-dependent spectra is plotted in the presence (curve II) and absence (curve I) of interference, where the emitter initial state is considered to be the ground state. The considered parameters for simulations are $\gamma = 1$, $r = 5\gamma$, $\gamma_{nr} = 3\gamma$ for two different excited level spacing of (b) $\omega_{21} = \omega_{32} = 0.05\gamma$ and (c) $\omega_{21} = 50\gamma$, $\omega_{32} = 0.05\gamma$. (d) The interference contribution $|S_{CL}(\omega) - S_{NI}(\omega)|$ to the spectra as a function of time and frequency for $\omega_{21} = \omega_{32} = 0.05\gamma$ (left panel) and $\omega_{21} = 50\gamma$, $\omega_{32} = 0.05\gamma$ (right panel). (e) and (f) show the relative intensity of the spectral peaks $[S_{II}(\omega)/S_I(\omega)]$ associated with the time-dependent spectra (a) and (b), respectively.

and derive the master equation for an electron-driven multi-level quantum emitter. Section III is devoted to a discussion of the time-dependent spectra. In Sec. IV, the numerical results are presented with an analysis of the interference effects in the emission spectra and the density matrix dynamics of the quantum emitter. Section V contains a discussion of the parameter regimes and schemes for experimental realization. We conclude in Sec. VI.

II. THEORETICAL FORMALISM

We consider the emitter to be a four-level quantum system in a V-type configuration [see Fig. 1(a)]. The excited states are denoted as $|1\rangle$, $|2\rangle$, and $|3\rangle$ that can spontaneously decay to the ground state $|0\rangle$ with rates γ_1 , γ_2 , and γ_3 , respectively. We also allow for nonradiative decay channels $|3\rangle \rightarrow |1\rangle$, $|3\rangle \rightarrow |2\rangle$, and $|2\rangle \rightarrow |1\rangle$ with γ_{nr} being the nonradiative decay rate. This could represent the fast relaxation to the lower excited levels, e.g., via phonons. For simplicity, we assume this decay rate γ_{nr} to be the same for all the nonradiative channels throughout our analysis. A typical quantum system with such specifications could be defects in two-dimensional materials coupled to nonradiative phonon excitations [19].

The master equation for the radiative decay of a single multilevel quantum emitter can be found in standard references [20,21]. Here, we focus on the electron-beam-induced dynamics of the system. Several studies motivate our theoretical model [8,22–26]. Although electron excitation is

fundamentally different from optical excitation [6,27,28]—due to its higher energy and momentum—the close relation between photoluminescence (PL) and incoherent CL has been noted [22,23], especially the free electron acting as a broadband optical source of excitation [23,24]. In addition, master equation approaches employing incoherent pumping schemes have been successful in describing the PL spectra [25,26]. Since CL at the nanoscale can be viewed as an analog of photoluminescence [8], we model the electron-emitter interaction by an incoherent broadband pump field driving the quantum emitter. The corresponding electric field can be written as

$$\vec{E}(t) = \mathcal{E}_e(t)e^{-i\omega_e t}\hat{e} + \text{c.c.} \quad (1)$$

Here, $\mathcal{E}_e(t)$ is the field amplitude, ω_e is the central frequency, and $\hat{e}$ denotes the polarization vector. Since the field is incoherent, the amplitude $\mathcal{E}_e(t)$ is assumed to be δ correlated at different times and having zero mean value,

$$\langle \mathcal{E}_e(t)\mathcal{E}_e^*(t') \rangle = \mathcal{R}\delta(t - t'), \quad \langle \mathcal{E}_e(t) \rangle = 0, \quad (2)$$

where $\mathcal{R}$ denotes the incoherent excitation strength. The influence of incoherent fields on atomic systems has been previously explored in a different context in quantum optics [29–32]. Here, we apply it to model the dynamics of the emitter under electron-beam excitations. The interaction Hamiltonian for our system reads

$$H_I = -\sum_{i=1}^3 \mathcal{E}_e(t)(\vec{d}_{i0} \cdot \hat{e} A_{i0})e^{-i\omega_e t} + \text{H.c.}, \quad (3)$$

where $\vec{d}_{i0}$ ($i = 1, 2, 3$) are the transition dipole moments and $A_{i0} = |i\rangle\langle 0|$ ($i = 1, 2, 3$) denote the transition operators. In this work, it is assumed that the dipole moments are real and mutually orthogonal. The equations of motion for the combined state of the emitter and the field is given by the Liouville-von Neumann equation

$$\frac{\partial \tilde{\rho}}{\partial t} = -\frac{i}{\hbar}[\tilde{H}_I(t), \tilde{\rho}(t)]. \quad (4)$$

In the above equation, the density operator $\tilde{\rho}(t) = U(t)\rho(t)U^\dagger(t)$ and the Hamiltonian $\tilde{H}_I(t) = U(t)H_I(t)U^\dagger(t)$ are expressed in the interaction picture according to $U(t) = \exp\{iH_0t/\hbar\}$, where $H_0 = \sum_i \hbar\omega_{i0}|i\rangle\langle i|$ ($i = 1, 2, 3$) is the system Hamiltonian and $\omega_{i0} = \omega_i - \omega_0$ is the transition frequency. To derive the equations of motion for the quantum emitter, we proceed within the framework of the generalized reservoir theory and the Born approximation [31,32]. For the complete derivation, we refer the reader to Appendix A 1. Here we present the final master equation that governs the time evolution of the reduced density operator $\rho(t)$ of the quantum emitter in the Schrödinger picture, given by

$$\begin{aligned} \frac{d\rho}{dt} = & -\frac{i}{\hbar}[H_0, \rho] - \sum_i (\gamma_i + \mathbf{r}_i) \left[\frac{1}{2}\{S_i^+ S_i^-, \rho\} - S_i^- \rho S_i^+ \right] \\ & - \sum_i \mathbf{r}_i \left(\frac{1}{2}\{S_i^- S_i^+, \rho\} - S_i^+ \rho S_i^- \right) \\ & - \sum_{\substack{i,j \\ i \neq j}} \mathbf{r}_{ij} \left(\frac{1}{2}\{S_i^+ S_j^- + S_j^- S_i^+, \rho\} - S_j^- \rho S_i^+ - S_i^+ \rho S_j^- \right) \\ & + \mathcal{L}_{\text{nr}}\rho, \end{aligned} \quad (5)$$

where γ_i is the radiative decay rate of the i th transition, $S_i^+ \equiv A_{i0} = |i\rangle\langle 0|$ [$S_i^- = (S_i^+)^\dagger$, $i = 1, 2, 3$] is the raising (lowering) operator for our system, and the nonradiative decay of the excited levels ($|3\rangle \rightarrow |1\rangle$, $|3\rangle \rightarrow |2\rangle$, and $|2\rangle \rightarrow |1\rangle$) is incorporated phenomenologically into the master equation according to the Lindblad operator

$$\begin{aligned} \mathcal{L}_{\text{nr}}\rho = & -\gamma_{\text{nr}} \left[\frac{1}{2}\{A_{22}, \rho\} - A_{12}\rho A_{21} \right] \\ & - \gamma_{\text{nr}} [A_{33}, \rho] - A_{13}\rho A_{31} - A_{23}\rho A_{32}, \end{aligned} \quad (6)$$

where γ_{nr} denotes the nonradiative decay rate.

The quantum optical master equation (5) models the dynamics of an electron-driven N -level quantum emitter. The first and second terms in the master equation (5) describe the free evolution of the system and the familiar radiative decay of the excited levels [20,32], respectively. More importantly, the third term in Eq. (5) offers a key insight. It describes the electron-beam excitation of the system (see Ref. [17]), where the parameter $\mathbf{r}_i$ is the excitation rate of the emitter due to incident electrons. The derivation of this excitation part naturally follows from the interaction Hamiltonian (3). Our focus throughout this article is the influence of the cross terms ($i \neq j$) in Eq. (5). They indicate the possibility of electron-beam-induced quantum interference between different transition pathways. The interference amongst the i th and j th ($i \neq j$) transition is denoted by the cross term $\mathbf{r}_{ij} = p\sqrt{\mathbf{r}_i \mathbf{r}_j}$ [31,32]. Here, we have introduced the interference parameter p .

$p = \pm 1$ indicates maximal interference whereas $p = 0$ implies no interference. Experimentally, the interference parameter can be controlled by tailoring the local density of states of the emitter and employing novel electron-driven photon sources with tunable wavelengths [33–37] to control the interaction between the electron beam and the different transitions. These sources utilize either the Smith-Purcell effect or a fabricated metamaterial lens, where the latter comprises an array of nanoholes in order to produce focused broadband coherent radiation under electron excitation. In particular, the incident electron energy serves as a control parameter for tuning the wavelength of the emitted light, particularly for the Smith-Purcell effect. We show here that the presence of interference can greatly modify the CL emission and the emitter dynamics. Note that, in the simple case of a two-level system, quantum interference is absent and we obtain the phenomenological CL model [17] with $(\gamma + \mathbf{r}) \rightarrow \gamma$.

III. TIME-DEPENDENT SPECTRA

To study the effects of interference, we numerically compute the time-dependent CL spectrum of the quantum emitter. Following Refs. [38,39], the spectra for our system can be expressed in the form

$$\begin{aligned} S_{\text{CL}}(\omega) = & \text{Re} \int_0^t dt_2 \int_0^{t-t_2} d\tau e^{-\Gamma(t-t_2)} e^{(\Gamma/2-i\omega)\tau} \\ & \times \sum_{i,j=1}^3 \gamma_{ij} \langle A_{i0}(t_2 + \tau) A_{0j}(t_2) \rangle, \end{aligned} \quad (7)$$

where Γ is the filter bandwidth, ω is the observed frequency, t is the elapsed time after the interaction, $\gamma_{ij} \equiv 2\gamma_i$ for $i = j$, and $\gamma_{ij} \equiv -\sqrt{\gamma_i \gamma_j}$ for $i \neq j$. In a multilevel emitter, the density matrix equations (5) for the populations and two-photon coherences are coupled due to interference, thereby leading to interesting effects in the dynamics and the spectra. In Appendix A 2, we outline the calculation of the one-time averages that determine the density matrix elements, while Appendix B presents the derivation of the spectrum (7), along with details of the detection scheme and the evaluation of the two-time correlations.

In the following, we explore the influence of interference on the CL emission for different excited level separations, initial state conditions, and excitation rates using Eqs. (5)–(7). For the numerical analysis, we set $\gamma_1 = \gamma_2 = \gamma_3 = \gamma$ and $\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}_3 = \mathbf{r}$, i.e., assuming equal decay and excitation rates. Physically, this implies that the electron beam couples identically to all transitions in the multilevel emitter, resulting in equal excitation probabilities. Here, we mention that the electron excitation is highly localized and typically involves multiple elementary processes, such as plasmons, surface plasmon polaritons, excitons, and secondary electrons [1,6], which collectively result in an incoherent excitation of the emitter. Therefore, it is reasonable to consider that all relevant transitions are excited at the same rate.

In all figures, the values of γ_{nr} and Γ are fixed as $\Gamma = 0.1\gamma$ and $\gamma_{\text{nr}} = 3\gamma$ ($\gamma_{\text{nr}} > \gamma$), respectively. The filter bandwidth is chosen to ensure that the spectral peaks are well resolved ($\Gamma < \gamma$), particularly in the parameter regime $\mathbf{r} > \gamma$. The

influence of the nonradiative decay rate on the interference effects is discussed in Appendix C. We additionally scale all the parameters such as the excitation rate r , nonradiative decay rate γ_{nr} , and frequencies $(\omega, \omega_{32}, \omega_{21})$ in units of γ . Unless stated otherwise, the initial state of the emitter is always considered to be the ground state.

IV. NUMERICAL RESULTS

A. CL spectra for different excited-state splitting

First, we analyze the spectra (7) for different energy splitting of the excited levels. In Fig. 1(b), a 3d contour plot of the CL spectra is displayed for small energy splitting between the three upper levels ($\omega_{21}, \omega_{32} \ll \gamma$). To highlight the interference effects, we plot Eq. (7) for the parameter values $p = 0$ (without interference) and $p = 1$ (with interference), indicated by I and II, respectively, in Fig. 1(b). The time-dependent spectra is single peaked and centered around $\omega = \omega_{20}$, as expected for the near-degenerate case of the upper energy levels. We find that the quantum interference effect in the CL emission leads to the suppression of the central peak. This feature is more prominent for times $t \leq \gamma^{-1}$ whereas at longer times $t > \gamma^{-1}$, the influence of interference diminishes. To see this temporal behavior of the induced interference, we plot the relative intensity I of the spectral peaks of curves II and I in Fig. 1(e) with I being the ratio $I = S_{\text{II}}(\omega)/S_{\text{I}}(\omega)$ evaluated at a particular frequency ω and time t . Here, $S_{\text{II}}(\omega)$ and $S_{\text{I}}(\omega)$ denote the spectra in the presence and absence of interference, respectively. The contour clearly shows the time dynamics of the influence of interference in the CL emission. For times less than or comparable to the radiative lifetime of the excited-state levels ($t \leq \gamma^{-1}$), the relative intensity around $\omega = \omega_{20}$ is $I < 1$ [see Fig. 1(e)], depicted as shades of green in the plot. Therefore, the interference effects play a significant role at shorter time scales $t \leq \gamma^{-1}$. In contrast, for longer times $t > \gamma^{-1}$, the relative intensity is $I \approx 1$, as can be seen from the transition from green to yellow in the contour in Fig. 1(e). These results show the time-dependent behavior of the induced interference.

We consider now the case of large splitting between only two upper energy levels ($\omega_{21} \gg \gamma$) while the excited level $|3\rangle$ is near degenerate with state $|2\rangle$ ($\omega_{32} \ll \gamma$). Figure 1(c) shows the corresponding CL spectra. The emission at the central frequency stems from the decay of transitions $|2\rangle \rightarrow |0\rangle$ and $|3\rangle \rightarrow |0\rangle$ whereas the sideband originates from the transition $|1\rangle \rightarrow |0\rangle$. Interestingly, the strong suppression of the central peak due to interference is evident for both $t \leq \gamma$ and $t > \gamma$, in contrast to the near-degenerate case [see Fig. 1(c)]. The contour plot in Fig. 1(f) shows the corresponding relative intensity of the curves II and I. The interference effects modify the emission at the central frequency $I < 1$ whereas the sideband is almost unaffected $I \approx 1$ [see Fig. 1(f)]. Our analysis reveals that the quantum interference is not only sensitive to the level splitting but the time scale of its influence can significantly change accordingly.

To gain more understanding of these results, we write the spectra as the sum of two parts $S_{\text{CL}}(\omega) = S_{\text{INT}}(\omega) + S_{\text{NI}}(\omega)$. Here, $S_{\text{INT}}(\omega)$ is the interference contribution to the total spectra and $S_{\text{NI}}(\omega)$ is referred to as the noninterfering part

that can be obtained by setting $p = 0$ in Eq. (7). It is useful to visualize only the interference contribution by plotting the quantity $|S_{\text{CL}}(\omega) - S_{\text{NI}}(\omega)|$. The corresponding contour plot is shown in Fig. 1(d) for the two cases of excited level splitting discussed in Figs. 1(b)–1(c). For closely spaced upper energy levels [left panel in Fig. 1(d)], note that the interference contribution is at the central frequency only up to times $t = 2\gamma^{-1}$ but shifts to $\omega = \omega_{20} \pm \omega_s$ for $t > 2\gamma^{-1}$. In contrast, for the nondegenerate case, we have the maximum interference contribution always centered around $\omega = \omega_{20}$, as shown in Fig. 1(d) (right panel).

B. Initial-state dependence of the spectra

We now proceed to study the spectra for various initial conditions. Specifically, we are interested in the role of interference when the emitter is prepared in a different quantum state prior to the interaction. This can be achieved experimentally using electron-driven photon sources (EDPHS) in CL spectroscopy, as demonstrated recently [18]. The numerical results are displayed in Figs. 2(a)–2(b). In Fig. 2(a), the time-dependent spectra for four different initial states of the quantum emitter is plotted, taking into account the effects of interference ($p = 1$). Figure 2(b) shows the respective CL spectra in the absence of quantum interference ($p = 0$). Comparing Fig. 2(a) and 2(b), the spectra strongly depends on the initial state of the system when considering interference effects. At short timescales $t \leq \gamma^{-1}$, we find that the spectra changes drastically if the emitter is prepared in an initial coherent superposition state rather than the ground state [compare the colored curves to the solid black curve in Fig. 2(a)]. Tuning the relative phase of the initial superposition allows us to control the quantum interference effect. This is shown in Fig. 2(a) (compare orange curve to solid red curve for time $t = 0.5\gamma^{-1}$), where the emission from the upper levels ($|2\rangle, |3\rangle \rightarrow |0\rangle$) is significantly enhanced, even in the presence of nonradiative decay. Although these modifications are less prominent for $t = 2\gamma^{-1}$, a notable difference between the spectra for the ground state and that of the superposition state [compare solid black and red curves in Fig. 2(a)] is still evident. On the contrary, the CL emission is almost independent of the initial state in the absence of interference [compare solid black and red curves in Fig. 2(b) for $t = 2\gamma^{-1}$]. We may thus consider the initial-state dependence of the spectra as a strong signature of the electron-beam-induced interference in time-resolved CL.

C. Spectra for different excitation rates

An important parameter in CL experiments that can be controlled is the electron-beam current I_e . One can relate it to the excitation rate r [17]. We now consider different excitation rates and analyze the CL emission. Figures 2(c)–2(d) display the spectra for weak ($r \leq \gamma$) and strong excitations ($r > \gamma$). Following a similar analysis like in our previous discussion, we plot the spectra for both the interference parameter values $p = 1$ [Fig. 2(c)] and $p = 0$ [Fig. 2(d)]. A common characteristic feature seen in both scenarios is the broadening of the spectral peaks. For larger values of the excitation rate, we find that the effect is stronger [compare red curve to solid

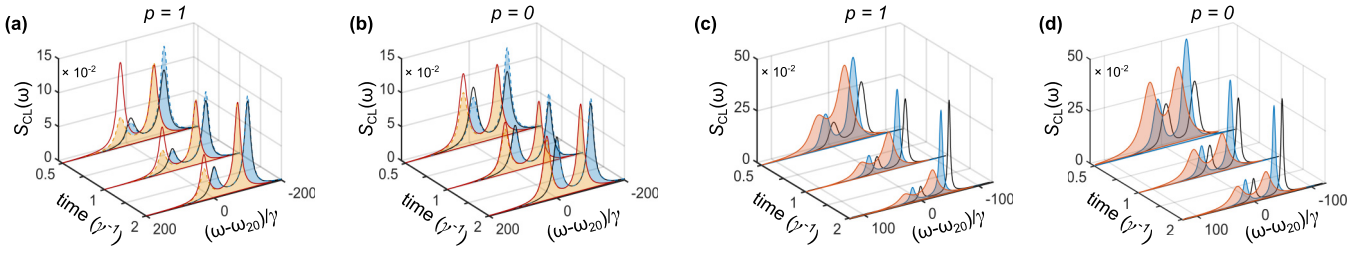


FIG. 2. The evolution of the spectra for different initial states of the emitter is plotted in (a) (with interference, $p = 1$) and (b) [without interference, $p = 0$] at times $t = 0.5$, $t = 1$, and $t = 2$ (units of γ^{-1}). The parameters are $\gamma = 1$, $r = 5\gamma$, and $\omega_{21} = 100\gamma$, $\omega_{32} = 0.05\gamma$. The solid black and red curves show the spectra computed with the initial state as the ground state $|\psi(t_0)\rangle = |0\rangle$ and an equally weighted superposition state $|\psi(t_0)\rangle = \sum_{i=0}^3 c_i e^{i\delta_i} |i\rangle$ ($c_i = 1/2$, $\delta_{12} = 0$, $\delta_{13} = \delta_{23} = \pi$), respectively. The blue and orange shaded curves show the spectra for the initial states $|\psi(t_0)\rangle = [|0\rangle + |1\rangle]/\sqrt{2}$ and $|\psi(t_0)\rangle = \sum_{i=0}^3 c_i e^{i\delta_i} |i\rangle$ ($c_i = 1/2$, $\delta_i = 0$), respectively. For clarity, the orange (shaded) and red (solid) curves are shifted by 30 units along the ω axis, and the spectra at times $t = 0.5$ and $t = 1$ are multiplied by a factor of 4 and 1.5, respectively. The dependence on the excitation rate in (c) the presence and (d) absence of interference and the spectra at times $t = 0.5$, $t = 1$, and $t = 2$ (units of γ^{-1}). The parameters are $r = 0.5\gamma$ (solid black), $r = \gamma$ (shaded blue), $r = 5\gamma$ (shaded red), and $\omega_{21} = 50\gamma$, $\omega_{32} = 0.05\gamma$ with the initial state as the ground state. For clarity, the blue and red curves (shaded) are shifted by 15 and 45 units along the ω axis, respectively, and the spectra at times $t = 0.5$ and $t = 1$ are multiplied by a factor of 15 and 3, respectively.

black curve in Figs. 2(c)–2(d)]. This behavior can be easily understood from the master equation (5). It can be clearly seen that the radiative decay width of the excited levels is the sum of the natural line width and the excitation rate $\gamma_i + r_i$. The electron-beam excitation therefore leads to broad spectral features in the CL emission.

D. Density matrix dynamics of the quantum emitter

Next, we investigate the corresponding density matrix dynamics of the emitter. In Figs. 3(a)–3(b), we plot the populations and the two-photon coherences for the near-degenerate and nondegenerate cases explored earlier in Figs. 1(b)–1(c). A 3d bar chart of the density matrix elements and its time evolution is shown in Fig. 3(d) considering the same parameters as in Fig. 3(a). The interference leads to population transfer between the excited levels, as seen from nonzero values of two-photon coherences $|\rho_{ij}|$ ($i, j = 1, 2, 3$) in Figs. 3(a)–3(b) (dashed curves). The two-photon coherences grow from zero to a maximum value before starting to decay and reaching a steady-state value. On shorter time scales $t < 1/r$, there can be strong interference even for large splitting between the two excited levels [see Fig. 3(b)]. To better understand the dynamics of the quantum path interferences, we compute the ratio $C = |\rho_{ij}|/(\rho_{ii} + \rho_{jj})$. Figure 3(c) shows the parameter C for three different energy splitting of the excited-state levels. In the situation where at least two upper levels are near-degenerate [curves I and II in Fig. 3(c)], the interference effects do play an important role, as the parameter C saturates at a steady-state (red curve in I and II) leading to observable effects in the spectra [Figs. 1(b)–1(c)]. However, for a large splitting between all the excited levels, the ratio C rapidly decays to zero [curve III in Fig. 3(c)]. The interference effects are therefore negligible in such cases.

V. DISCUSSION

We now discuss the possible experimental scenarios and parameter regimes to test the predictions. In CL, the excitation process usually involves additional elementary

processes mediated by secondary electrons or phonons [10,40]. The timescale associated with the excitation of the emitter is very small, ranging from femtoseconds to picoseconds. In comparison to the radiative lifetime of the emitter that is of the order of nanoseconds, the excitation timescale is much shorter, i.e., $t_{\text{exc}} \ll t_{\text{rad}}$. Therefore the relevant parameter regime to explore would be $r \gg \gamma$, where r is the excitation rate and γ represents the radiative decay rate of the emitter. Note that the excitation rate r can be controlled via the electron beam current I_e in experiments. In our analysis, we have chosen the optimal parameters for the excitation rate ($r \leq 10\gamma$), excited level separation, and filter bandwidth to clearly highlight the role of interference. Importantly, we have verified that the interference effects persist even at high excitation rates $r > 10\gamma$, and under conditions of unequal excitation rates r_1, r_2, r_3 . For the experimental realization, the time-resolved CL spectroscopic technique based on electron-driven photon sources would be a suitable choice [35–37,41]. Particularly, the spectra for different initial conditions can be explored using this setup. This is realized by a tailored metamaterial for illuminating the sample with focused coherent radiation. The system can therefore be excited to an initial coherent superposition state prior to the electron-beam excitations. In addition, to probe the dynamics of a single emitter, subnanometer resolution is required, as demonstrated in Ref. [8]. The investigation of quantum interference phenomena is therefore feasible with current CL spectroscopic techniques.

VI. CONCLUSION

In conclusion, we have developed a theoretical framework for cathodoluminescence from a quantum emitter. Modeling the electron-emitter interaction by an incoherent broadband field driving the system, we derive a quantum optical master equation for an electron-driven multilevel emitter. The master equation accounts for the electron-beam excitation of the emitter and the broad spectral nature of CL light emission. The present work therefore provides a new insight into the electron-matter interactions in CL and goes beyond previous

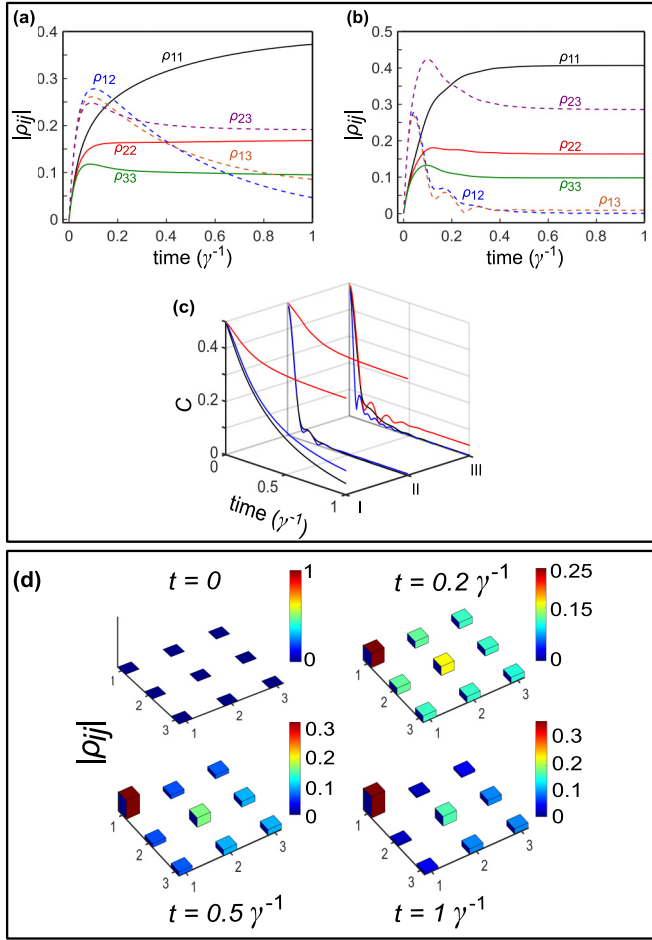


FIG. 3. The excited-state populations and the coherence dynamics plotted in (a) and (b). The parameters are $\gamma = 1$, $r = 5\gamma$, (a) $\omega_{21} = \omega_{32} = 0.05\gamma$ and (b) $\omega_{21} = 50\gamma$, $\omega_{32} = 0.05\gamma$. The initial state is considered to be the ground state in all subplots. For clarity, the coherences (dashed curves) in (a) and (b) are multiplied by a factor of 2 and 3, respectively. The 3d plot in (c) shows the time evolution of the ratio $C = |\rho_{ij}|/(\rho_{ii} + \rho_{jj})$ ($i \neq j$) of the two-photon coherences to the populations for different excited level separations: (I) $\omega_{21} = \omega_{32} = 0.05\gamma$, (II) $\omega_{21} = 50\gamma$, $\omega_{32} = 0.05\gamma$, and (III) $\omega_{21} = \omega_{32} = 50\gamma$. The solid black, blue, and red curves show the parameter C computed for two-photon coherences ρ_{12} , ρ_{13} , and ρ_{23} , respectively. (d) The magnitude of the density matrix elements $|\rho_{ij}|$ ($i, j = 1, 2, 3$) at times $t = 0$, $t = 0.2$, $t = 0.5$, and $t = \gamma$ with the parameters being the same as in (a).

phenomenological approaches. A novel result is the possibility of electron-beam-induced quantum interference between different transition pathways. We find that induced interference leads to significant modifications of the spectra and the emitter dynamics. Depending on the initial state preparation and the splitting between the excited levels, the quantum interference may either enhance or suppress the CL emission. These results can be crucial for time-resolved measurements of CL at the nanometer scale. Our findings open up the exploration of electron-beam-induced interference phenomena and provides a theoretical basis for investigating quantum optical effects in spectroscopic CL. Further generalization of this scheme, considering multiple emitters, paves the way towards exploring many-body correlations and superradiance features.

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APPENDIX A: DERIVATION OF THE MASTER EQUATION AND DENSITY MATRIX DYNAMICS

1. Master equation for the electron beam excitation of a multilevel quantum emitter

In this section we derive the incoherent broadband field contribution to the master equation presented in Eq. (5). We continue from Eq. (4) whose solution can be expressed as

$$\tilde{\rho}(t) = \tilde{\rho}(t_0) - \frac{i}{\hbar} \int_{t_0}^t dt' [\tilde{H}_I(t'), \tilde{\rho}(t')], \quad (\text{A1})$$

where we performed a formal integration of Eq. (4). Substituting the above expression back in Eq. (4) results in an integrodifferential equation of the form

$$\begin{aligned} \frac{\partial \tilde{\rho}(t)}{\partial t} = & -\frac{i}{\hbar} [\tilde{H}_I(t), \tilde{\rho}(t_0)] - \frac{1}{\hbar^2} \int_{t_0}^t dt' [\tilde{H}_I(t), \\ & \times [\tilde{H}_I(t'), \tilde{\rho}(t')]]. \end{aligned} \quad (\text{A2})$$

Since we are mainly interested in the dynamics of the emitter rather than the combined quantum state of the emitter and the field, we perform a partial trace over the variables of the subsystem corresponding to the incoherent field. The time evolution of the reduced density operator is then given by

$$\begin{aligned} \frac{\partial \tilde{\rho}_{\text{qe}}(t)}{\partial t} = & -\frac{i}{\hbar} \text{Tr} [\tilde{H}_I(t), \tilde{\rho}(t_0)] \\ & - \frac{1}{\hbar^2} \text{Tr} \int_{t_0}^t dt' [\tilde{H}_I(t), [\tilde{H}_I(t'), \tilde{\rho}(t')]], \end{aligned} \quad (\text{A3})$$

where $\tilde{\rho}_{\text{qe}}(t) = \text{Tr}[\tilde{\rho}(t)]$ is the state of the emitter. Within the framework of the generalized reservoir theory and the Born approximation [31,32], the incoherent broadband field is considered to be a large reservoir characterized by infinite degrees of freedom that is weakly coupled to the emitter. Therefore, the dynamics of the emitter is significantly modified by its interaction with the broadband field whereas the influence of the emitter on the field is assumed to be negligible. We can thus approximate the total density operator as $\tilde{\rho}(t) = \tilde{\rho}_{\text{qe}}(t) \otimes \rho_p(t_0)$ at all times [31], where $\rho_p(t_0)$ is the state of the broadband field reservoir. With these assumptions and making use of Eqs. (1)–(3) in Eq. (A3), we obtain the following equation for the density operator $\tilde{\rho}_{\text{qe}}(t)$,

$$\begin{aligned} \frac{\partial \tilde{\rho}_{\text{qe}}(t)}{\partial t} = & -\frac{1}{2} \sum_{i,j} \left[\frac{(\hat{d}_{i0} \cdot \hat{e})(\hat{d}_{j0} \cdot \hat{e})^* \mathcal{R}}{\hbar^2} (\{S_i^+ S_j^-, \tilde{\rho}_{\text{qe}}\} \right. \\ & - 2S_j^- \tilde{\rho}_{\text{qe}} S_i^+) e^{i\omega_{ijt}} + \frac{(\hat{d}_{i0} \cdot \hat{e})^* (\hat{d}_{j0} \cdot \hat{e}) \mathcal{R}}{\hbar^2} \\ & \left. \times (\{S_i^- S_j^+, \tilde{\rho}_{\text{qe}}\} - 2S_j^+ \tilde{\rho}_{\text{qe}} S_i^-) e^{-i\omega_{ijt}} \right]. \end{aligned} \quad (\text{A4})$$

Dropping the subscripts and undoing the unitary transformation $U = \exp\{iH_0t/\hbar\}$, we can write the equation for the density operator in the Schrodinger picture as

$$\begin{aligned} \frac{\partial \rho}{\partial t} = & -\frac{i}{\hbar}[H_0, \rho] - \sum_i \mathbf{r}_i \left[\frac{1}{2} \{S_i^+ S_i^-, \rho\} - S_i^- \rho S_i^+ \right] \\ & - \sum_i \mathbf{r}_i \left(\frac{1}{2} \{S_i^- S_i^+, \rho\} - S_i^+ \rho S_i^- \right) \\ & - \sum_{\substack{i,j \\ i \neq j}} \mathbf{r}_{ij} \left(\frac{1}{2} \{S_i^+ S_j^- + S_j^- S_i^+, \rho\} \right. \\ & \left. - S_j^- \rho S_i^+ - S_i^+ \rho S_j^- \right). \end{aligned} \quad (\text{A5})$$

The above expression gives the incoherent broadband field contribution to the master equation of the system with $\mathbf{r}_{ij} = p_{ij} \sqrt{\mathbf{r}_i \mathbf{r}_j}$ and excitation rate $\mathbf{r}_i = |\vec{d}_{i0} \cdot \hat{e}|^2 \mathcal{R}/\hbar^2$, where $p_{ij} = (\vec{d}_{i0} \cdot \hat{e})(\vec{d}_{j0} \cdot \hat{e})^*/(|\vec{d}_{i0} \cdot \hat{e}| |\vec{d}_{j0} \cdot \hat{e}|)$ is the introduced interference parameter [32]. For our calculations, we consider $|\vec{d}_{10}| = |\vec{d}_{20}| = |\vec{d}_{30}| = |d|$ and $\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}_3 = \mathbf{r}$. Therefore, as mentioned in the main text, we have $p_{ij} = p$ ($i, j = 1, 2, 3, i \neq j$). The second term in Eq. (A5) is responsible for the radiative broadening while the third term describes the electron-beam excitation of the emitter. The cross terms $i \neq j$ lead to quantum interference effects. We include the nonradiative decay of the excited levels ($|3\rangle \rightarrow |1\rangle$, $|3\rangle \rightarrow |2\rangle$, and $|2\rangle \rightarrow |1\rangle$) phenomenologically into the above master equation according to the Lindblad operator

$$\begin{aligned} \mathcal{L}_{\text{nr}} \rho = & -\gamma_{\text{nr}} \left[\frac{1}{2} \{A_{22}, \rho\} - A_{12} \rho A_{21} \right] \\ & - \gamma_{\text{nr}} \left[\{A_{33}, \rho\} - A_{13} \rho A_{31} - A_{23} \rho A_{32} \right], \end{aligned} \quad (\text{A6})$$

where the nonradiative decay rate $\gamma_{\text{nr}} > \gamma$. Thus we obtain the final master equation used in our analysis,

$$\begin{aligned} \frac{\partial \rho}{\partial t} = & -\frac{i}{\hbar}[H_0, \rho] - \sum_i (\gamma_i + \mathbf{r}_i) \left[\frac{1}{2} \{S_i^+ S_i^-, \rho\} - S_i^- \rho S_i^+ \right] \\ & - \sum_i \mathbf{r}_i \left(\frac{1}{2} \{S_i^- S_i^+, \rho\} - S_i^+ \rho S_i^- \right) \\ & - \sum_{\substack{i,j \\ i \neq j}} \mathbf{r}_{ij} \left(\frac{1}{2} \{S_i^+ S_j^- + S_j^- S_i^+, \rho\} \right. \\ & \left. - S_j^- \rho S_i^+ - S_i^+ \rho S_j^- \right) + \mathcal{L}_{\text{nr}} \rho. \end{aligned} \quad (\text{A7})$$

2. Density matrix dynamics: calculation of the one-time averages

To solve for the excited-state populations and the coherence dynamics of the emitter, we define a column vector of the one-time averages

$$\begin{aligned} \Psi(t) = & (\langle A_{11} \rangle, \langle A_{22} \rangle, \langle A_{33} \rangle, \langle A_{12} \rangle, \langle A_{21} \rangle, \langle A_{13} \rangle, \langle A_{31} \rangle, \\ & \langle A_{23} \rangle, \langle A_{32} \rangle, \langle A_{10} \rangle, \langle A_{01} \rangle, \langle A_{20} \rangle, \langle A_{02} \rangle, \langle A_{30} \rangle, \\ & \langle A_{03} \rangle, \langle A_{00} \rangle)^T, \end{aligned} \quad (\text{A8})$$

where $\rho_{ij} = \langle A_{ji} \rangle$. The column vector $\Psi(t)$ satisfies the equation

$$\frac{d\Psi(t)}{dt} = M\Psi(t). \quad (\text{A9})$$

Here, M is a 16×16 square matrix whose elements are coefficients that appear in the density matrix equations (5). It is now convenient to solve the matrix differential equation (A9) numerically and find the time evolution of the density matrix elements. In addition, we can use it to evaluate the two-time correlation functions in the time-dependent spectra (see Appendix B).

APPENDIX B: TIME-DEPENDENT SPECTRA AND EVALUATION OF THE TWO-TIME CORRELATIONS

Here we first derive the time-dependent CL spectra presented in Eq. (7) and discuss the detection scheme used in our analysis. We then outline the calculation of the two-time correlations that appear in the spectra. A rigorous theoretical description of the time-dependent spectrum was given by Eberly and Wódkiewicz [38,39]. This generalization of the steady-state spectra takes into account the filtering of the light field, e.g., by a Fabry-Perot interferometer, prior to detection. The physical spectrum depends on the first-order correlation functions of the electric-field operator and has been studied in the context of spontaneous emission [39,42,43] and resonance fluorescence from two-level and three-level systems [39,44,45]. More recently, the Eberly-Wódkiewicz spectrum was used to investigate the time dynamics of the photoluminescence spectra of a hBN color center [46]. In general, the time-dependent spectrum can be written as

$$\begin{aligned} S(\omega, \Gamma; t) = & \Gamma \int_{t_0}^t dt_1 \int_{t_0}^t dt_2 e^{-(\Gamma/2 - i\omega)(t-t_1)} e^{-(\Gamma/2 + i\omega)(t-t_2)} \\ & \times \langle \hat{E}^{(-)}(\vec{r}, t_1) \cdot \hat{E}^{(+)}(\vec{r}, t_2) \rangle, \end{aligned} \quad (\text{B1})$$

where ω is the observed frequency, Γ is the spectral bandwidth of the filter, and $t_0 = 0$ is considered the initial time. We adopt the shorthand notation $S(\omega, \Gamma) \equiv S(\omega, \Gamma; t)$ hereafter, as it is understood that we focus solely on the time-dependent spectra. For the four-level V-type system under consideration, the negative frequency part of the electric-field operator [47] at the position $\vec{r} = r\hat{r}$ of the detector in the far-field reads

$$\hat{E}^{(-)}(\vec{r}, t) = -\frac{\eta}{c^2 r} \sum_{i=1}^3 \omega_i^2 \{\hat{r} \times (\hat{r} \times \vec{d}_i)\} S_i^+(t - r/c) e^{ikr}, \quad (\text{B2})$$

where $\eta = 1/4\pi\epsilon_0$, $\omega_i \equiv \omega_{i0}$ ($i = 1, 2, 3$) denotes the transition frequency, $\vec{d}_i \equiv \vec{d}_{i0}$ ($i = 1, 2, 3$) is the transition dipole moment, and $S_i^+ \equiv A_{i0} \equiv |i\rangle\langle 0|$ denotes the raising operators. We consider a general detection scheme in which all the cross correlations $\langle A_{i0}(t_2 + \tau) A_{0j}(t_2) \rangle$ ($i \neq j$) also contribute to the emission spectra (B1) by choosing the unit vector $\hat{r}$ in the direction of observation to be $\hat{r} \cdot \vec{d}_i = |d| \cos \alpha = |d|/\sqrt{3}$, where $|\vec{d}_{10}| = |\vec{d}_{20}| = |\vec{d}_{30}| = |d|$. Substituting now the expression for the electric field operator (B2) in the spectra (B1)

and making a change of variables $t_1 \rightarrow t_2 + \tau$ [39], we find

$$S(\omega, \Gamma) = \phi \operatorname{Re} \int_0^t dt_2 \int_0^{t-t_2} d\tau e^{-\Gamma(t-t_2)} e^{(\Gamma/2-i\omega)\tau} \times \left(\sum_{i=1}^3 2\gamma \langle A_{i0}(t_2 + \tau) A_{0i}(t_2) \rangle - \gamma \sum_{\substack{i,j=1 \\ i \neq j}}^3 \langle A_{i0}(t_2 + \tau) A_{0j}(t_2) \rangle \right), \quad (\text{B3})$$

where we have assumed $\omega_{i0}/\omega_{j0} \approx 1$ ($i \neq j$) in arriving at the above equation with a prefactor $\phi = \Gamma \hbar \omega_{10}/(2cr^2)$ and the decay rate defined as $\gamma = |d|^2 \omega_{10}^3/(3\pi \epsilon_0 \hbar c^3)$. We scale $S(\omega, \Gamma)$ with respect to ϕ and express the time-dependent CL spectra as

$$S_{\text{CL}}(\omega) \equiv S(\omega, \Gamma)/\phi = \operatorname{Re} \int_0^t dt_2 \int_0^{t-t_2} d\tau e^{-\Gamma(t-t_2)} e^{(\Gamma/2-i\omega)\tau} \times \sum_{i,j=1}^3 \gamma_{ij} \langle A_{i0}(t_2 + \tau) A_{0j}(t_2) \rangle, \quad (\text{B4})$$

where the two-time correlations are written in a compact form by defining $\gamma_{ij} \equiv 2\gamma_i$ for $i = j$ and $\gamma_{ij} \equiv -\sqrt{\gamma_i \gamma_j}$ for $i \neq j$. Equation (B4) gives the form of the time-dependent CL spectra used in the main text [see Eq. (7)].

To calculate the two-time correlation functions in Eq. (B4), we introduce a column vector of the two-time averages given by

$$\begin{aligned} \vec{Y}^{mn}(t_2, \tau) = & [Y_{11}(t_2, \tau), Y_{22}(t_2, \tau), Y_{33}(t_2, \tau), Y_{12}(t_2, \tau), \\ & \times Y_{21}(t_2, \tau), Y_{13}(t_2, \tau), Y_{31}(t_2, \tau), Y_{23}(t_2, \tau), \\ & \times Y_{32}(t_2, \tau), Y_{10}(t_2, \tau), Y_{01}(t_2, \tau), Y_{20}(t_2, \tau), \\ & \times Y_{02}(t_2, \tau), Y_{30}(t_2, \tau), Y_{03}(t_2, \tau), Y_{00}(t_2, \tau)]^T, \\ & \times m, n = 0, 1, 2, 3 \end{aligned} \quad (\text{B5})$$

with

$$Y_{ij}(t_2, \tau) = \langle A_{ij}(t_2 + \tau) A_{mn}(t_2) \rangle. \quad (\text{B6})$$

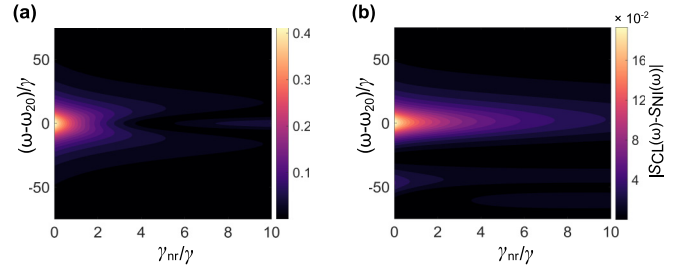


FIG. 4. The interference contribution ($|S_{\text{CL}}(\omega) - S_{\text{NI}}(\omega)|$) to the spectra shown as a function of the nonradiative decay rate (γ_{nr}) and frequency. The considered parameters for simulations are $\gamma = 1$, $r = 5\gamma$, $t = 4\gamma^{-1}$ for two different excited level spacing of (a) $\omega_{21} = \omega_{32} = 0.05\gamma$ and (b) $\omega_{21} = 50\gamma$, $\omega_{32} = 0.05\gamma$.

Applying the quantum regression theorem [48] results in

$$\frac{d\vec{Y}^{mn}(t_2, \tau)}{d\tau} = M\vec{Y}^{mn}(t_2, 0). \quad (\text{B7})$$

The solution can be expressed as $\vec{Y}(t_2, \tau) = e^{M\tau}\vec{Y}(t_2, 0)$, where $\vec{Y}(t_2, 0)$ is determined from the differential equations governing the one-time averages (A9). Following Ref. [39], we can introduce a matrix $\mathcal{T}^{mn}$ such that $\vec{Y}^{mn}(t_2, 0) = \mathcal{T}^{mn}\Psi(t_2)$, which allows us to conveniently evaluate the integral in Eq. (B4) given the initial conditions $\Psi(t_0)$.

APPENDIX C: EFFECTS OF NONRADIATIVE DECAY PROCESSES ON INTERFERENCE

In this section, we analyze the influence of nonradiative decay on the interference effects in the CL spectra. In Fig. 4, we plot the interference contribution ($|S_{\text{CL}}(\omega) - S_{\text{NI}}(\omega)|$) to the spectra as a function of the nonradiative decay rate γ_{nr} and frequency for excitation rate $r = 5\gamma$ and time $t = 4\gamma^{-1}$ with the initial state of the emitter being the ground state. As expected, the influence of interference is maximum when $\gamma_{\text{nr}} = 0$ for both the near-degenerate $\omega_{21} = \omega_{32} = 0.05\gamma$ [Fig. 4(a)] and the nondegenerate case $\omega_{21} = 50\gamma$, $\omega_{32} = 0.05\gamma$ [Fig. 4(b)]. For increasing nonradiative decay rates of the excited levels, the interference contribution is reduced, as can be seen in Figs. 4(a)–4(b). In the case of closely spaced upper energy levels, the influence of interference is negligible, notably for $\gamma_{\text{nr}} > r$ [see Fig. 4(a)]. For the nondegenerate case [Fig. 4(b)], in contrast, we find that the interference effects survive even for $\gamma_{\text{nr}} > r$. Our analysis indicates that the induced interference is robust and can significantly modify the spectra even in the presence of nonradiative decay processes.

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