Intensified blinking, continuous memory loss, and fluorescence enhancement of interacting light-emission quantum dots

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We propose a microscopic quantum-mechanical model for describing the nonstochastic dynamics of the nanoscopic light-emissive quantum dot. The model is extended beyond a single quantum dot to consider the Coulomb repulsion between neighboring quantum dots in the ionic states caused by the random fluctuations of charge carriers. We find that the interaction gives rise to intensified blinking intermittency, continuous memory loss of the dynamics, and fluorescence enhancement in an ensemble of light-emissive quantum dots, which explains the recent experimental results. Our findings clarify the nature of the interaction underlying in the ensemble.

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I. INTRODUCTION

Semiconductor quantum dots (QDs) are attracting much attention for possible use in controllable nanoscopic light emitters and their related applications.[1] One of the most intriguing features is the blinking behavior of the fluorescence from such nanoscopic light sources, which is found in a wide variety of natural and artificial nanostructures.[2–4] Under continuous-wave (cw) laser excitation, the fluorescence from a single QD or nanostructure randomly switches between "on" and "off." Those bright (on) and dark (off) periods last from a microsecond to many minutes, respectively. Analysis of time-series data of fluorescence from a single QD could give the characteristic blinking statistics, i.e., the probability of the "on" or "off" times follows the power law of $P(\tau_{\mathrm{on/off}}) \propto \tau_{\mathrm{on/off}}^{-\theta_{\mathrm{on/off}}}$, where $\tau_{\mathrm{on/off}}$ is the length of the on/off sojourn time and the exponent $\theta_{\mathrm{on/off}}$ lies between 1 and 2.[3–5]

The power-law statistics imply scale invariance in the critical phenomena of solid-state physics.[6] Such scale invariance could be understood as the dynamics to keep the long memory in the present case. It was also observed that the power-law statistics crossed over to a bending tail of $\exp(-\Gamma\tau_{\mathrm{on/off}})$ as time goes.[7] This suggests a crossover from long memory to memoriless (i.e., Markov process) dynamics. Beyond single isolated QDs, QDs can assemble into solids or close-packed clusters so that the ensemble of QDs should be considered where interaction between QDs would be important. The electronic coupling between QDs has been studied in view of energy transfer[8] or exciton transfer.[9] Yu and Orden[10] have examined the coupling effect on the blinking behavior of CdSe-ZnS QDs in their assemblies and found enhanced blinking compared to single QDs but they could not clarify the nature of the coupling. Theoretically, the prevailing power-law behavior has been reproduced by the distributed tunneling model with random switching between a neutral (bright) and an ionic (dark) state,[11] or by the diffusion-controlled transfer of the ejected electron in the dielectric media.[12] However, theoretical efforts to go beyond the single QDs have been hardly tried. Furthermore, most of the theoretical efforts were based on stochastic approaches, and thus they could not elucidate the underlying mechanism and explain some of the experimental observations at the quantum-mechanical microscopic level.

In this paper, we propose a microscopic quantum-mechanical model for describing nonstochastic dynamics of light-emissive QDs under cw excitation. A crossover from the long memory to the memoriless dynamics is found and the crossover time τ_C is determined by the tunneling or trapping probability to the ionic state. The model can be readily extended to the interacting QDs when the Coulomb repulsion between the ionized QDs is considered. From the interacting light-emissive QDs, we find intensified blinking intermittency, continuous memory loss, and fluorescence enhancement compared to the single QDs, which explains recent experimental findings.[10] This finding reveals the nature of the interaction between the clustered QDs and implies the possibility of a functional property controlled by the QD density.

The paper is organized as follows. In Sec. II, we introduce a model for the single quantum dot and describe the formulation. The blinking statistics and dynamical scaling are discussed. In Sec. III, we extend the model to include two quantum dots and the interaction between them. The blinking statistics, memory, coherence, and fluorescence intensity for the interacting quantum dots are discussed. Finally, in Sec. IV, we provide a summary and conclusion.

II. ISOLATED SINGLE QUANTUM DOT

Considering the three-state model for a single QD, as illustrated in Fig. 1(a), originally introduced by Kuno *et al.*,[13] we propose the following Hamiltonian $\mathcal{H}$ for the description of the microscopic quantum mechanics relevant for QD excitation under cw irradiation,

$$\mathcal{H} = E_\alpha c_\alpha^\dagger c_\alpha + E_\beta c_\beta^\dagger c_\beta + E_\gamma c_\gamma^\dagger c_\gamma + v[c_\beta^\dagger c_\gamma + c_\gamma^\dagger c_\beta] + A[e^{i\omega\tau} c_\alpha^\dagger c_\beta + e^{-i\omega\tau} c_\beta^\dagger c_\alpha]. \quad (1)$$

E_α and E_β are the energies of two internal (neutral) levels of the QD and E_γ is the ionic level. $c_\alpha^\dagger(c_\alpha)$, $c_\beta^\dagger(c_\beta)$, and $c_\gamma^\dagger(c_\gamma)$ are the creation (annihilation) operators of the corresponding three states, respectively. v is the tunneling or capturing probability to the ionic level. The last term of $\mathcal{H}$ is the external optical pumping by cw excitation. A is the field strength, and ω is the energy of the external optical pumping.

For theoretical treatment of the photoinduced fluorescence of the QD, we solve the time-dependent Schrödinger equa-

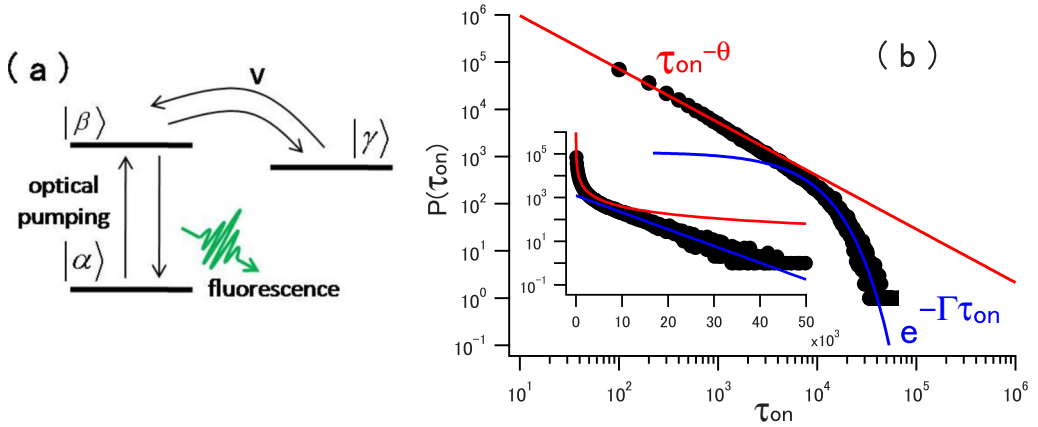

FIG. 1. (Color online) (a) Schematics of the three-state model for a single QD. (b) Unnormalized probability of the "on" sojourn time. A change from the power-law to the exponential behavior is clearly illustrated; the inset is a semilog plot. $\theta=1.15$ and $\Gamma=0.18$ are obtained. $v_0=1$ is used.

tion. In particular, this idea can be immediately extended to the many-body case by considering the many-body Hilbert-space spanning the whole system,[14] which will be adopted hereafter for the interacting QDs. The quantum-mechanical state vector $|\psi(\tau)\rangle$ is written as

$$|\psi(\tau)\rangle = C_\alpha(\tau)|\alpha\rangle + C_\beta(\tau)|\beta\rangle + C_\gamma(\tau)|\gamma\rangle,$$

where we have $|\alpha\rangle=c_\alpha^\dagger|0\rangle$, $|\beta\rangle=c_\beta^\dagger|0\rangle$, and $|\gamma\rangle=c_\gamma^\dagger|0\rangle$, respectively, and $|0\rangle$ is the vacuum. The initial state $|\Psi(0)\rangle$ should be the ground state, i.e., $|\Psi(0)\rangle=|\alpha\rangle$. The time-dependent Schrödinger equation $i\partial/\partial\tau|\Psi(\tau)\rangle=\mathcal{H}|\Psi(\tau)\rangle$ results in coupled differential equations for the coefficients $C_\alpha(\tau)$, $C_\beta(\tau)$, and $C_\gamma(\tau)$,

$$i\frac{\partial}{\partial\tau}C_\alpha(\tau) = E_\alpha C_\alpha(\tau) + Ae^{i\tau}C_\beta(\tau),$$

$$i\frac{\partial}{\partial\tau}C_\beta(\tau) = E_\beta C_\beta(\tau) + Ae^{-i\tau}C_\alpha(\tau) + vC_\gamma(\tau),$$

$$i\frac{\partial}{\partial\tau}C_\gamma(\tau) = E_\gamma C_\gamma(\tau) + vC_\beta(\tau), \quad (2)$$

where we note the energy or time quantities to be scaled by ω and redefine them to be dimensionless, that is, $\omega\tau\rightarrow\tau$, $E_\alpha/\omega\rightarrow E_\alpha$, $E_\beta/\omega\rightarrow E_\beta$, $E_\gamma/\omega\rightarrow E_\gamma$, $A/\omega\rightarrow A$, and $v/\omega\rightarrow v$. The microscopic randomness is implemented in v as $v(\tau)=\ldots,0,0,v_0,0,v_0,v_0,0,0,v_0,\ldots$ in the time series with a step of $d\tau$, that is, the random switch on and switch off of the tunneling probability to the ionic level.[15] We fix the parameters $E_\alpha=0$, $E_\beta=0.8$, $E_\gamma=1$, and $A=0.25$ unless mentioned otherwise.[16]

We have solved the coupled differential equations of Eq. (2) for $0<\tau<10^9$ with a time step of $d\tau=0.01$ and a bin time of $\delta\tau=100$. Remembering the dynamic interchange between the neutral (on) and the ionic (off) states, we calculated the unnormalized probability of the "on" sojourn time $P(\tau_{\rm on})$ by counting the number of "on" events from the time-series fluorescence intensity $\mathcal{I}(\tau)$. $\mathcal{I}(\tau)$ is defined by $\zeta(\tau)\Theta[\zeta(\tau)]$ with $\zeta(\tau)=|C_\alpha(\tau)|^2+|C_\beta(\tau)|^2-0.65$, where $\Theta(x)$ is the Heaviside step function.[17] In Fig. 1(b), we displayed the behavior of $P(\tau_{\rm on})$ with $\tau_{\rm on}$. First, we find that the power-law behavior is well reproduced with our approach. Furthermore, we find that the power-law behavior changes to exponential at τ_C ($\sim$12 000). The exponential tail is evident from the semilog plot in the inset. This implies that a crossover from the long memory to the memoriless process occurs in the system. The crossover time τ_C carries the key element for understanding the dynamic nature of the system. We find that it is the value of v_0 that predominantly determines τ_C. This is reasonable because only tunneling to the ionic level can provide the fundamental origin of the blinking dynamics. Figure 2 shows the dynamic crossover appearing in $P(\tau_{\rm on})$ with various values of v_0. In particular, we find a relation that τ_C is linearly proportional to $1/v_0$, i.e., $\tau_C\propto 1/v_0$.

III. INTERACTING QUANTUM DOTS

When the QDs are condensed into solids or clusters, the interaction between those becomes nontrivial. The interaction stems from the Coulomb repulsion between ionized QDs, i.e., electrically charged QDs. In the next-higher order, the dipole terms due to the QD polarization might be consid-

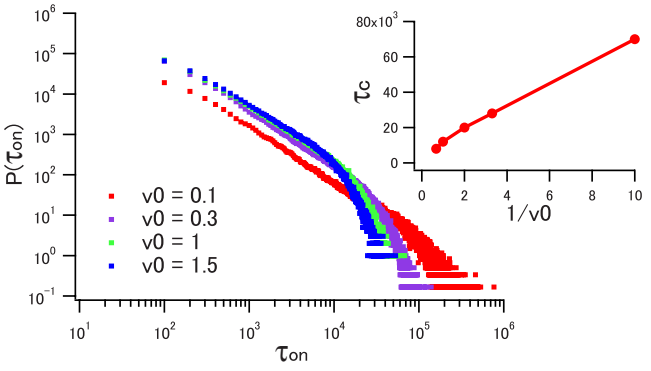

FIG. 2. (Color online) Probability of the on sojourn time $P(\tau_{\rm on})$ with respect to v_0. Inset: crossover time τ_C shows a linear behavior with $1/v_0$, except for $v_0\gg 1$.

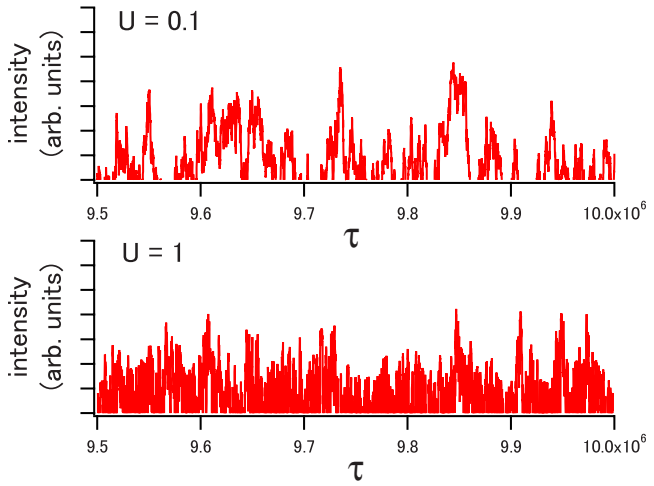

FIG. 3. (Color online) Fluorescence intensity $\mathcal{I}(\tau)$ from the weakly or strongly interacting QDs. The blinking becomes faster and more intensified for $U=1$ than $U=0.1$. $v_0=1$ is used.

ered but are neglected here for the simplicity. It is interesting and important to investigate the interaction effects on the clustered light-emissive QDs. We can treat the problem of interacting QDs on an equal footing with a single QD in the same formulation. We can readily extend the model of Eq. (1) for many interacting QDs and rewrite $\mathcal{H}$ as

$$\mathcal{H} = E_\alpha \sum_i c_{\alpha i}^\dagger c_{\alpha i} + E_\beta \sum_i c_{\beta i}^\dagger c_{\beta i} + E_\gamma \sum_i c_{\gamma i}^\dagger c_{\gamma i} + v \sum_i [c_{\beta i}^\dagger c_{\gamma i} + c_{\gamma i}^\dagger c_{\beta i}] + U \sum_{i>j} c_{\gamma i}^\dagger c_{\gamma i} c_{\gamma j}^\dagger c_{\gamma j} + A \sum_i [e^{i\tau} c_{\alpha i}^\dagger c_{\beta i} + e^{-i\tau} c_{\beta i}^\dagger c_{\alpha i}], \tag{3}$$

where i is the index of the QD ($i=1,2,3,\ldots$) and U (made dimensionless by dividing by ω) is the Coulomb repulsion between QDs being at the ionic levels. For the simplicity, in the study, we consider only two interacting QDs. $|\Psi(\tau)\rangle$ can then be extended to

$$\begin{aligned}|\Psi(\tau)\rangle = {} & C_{\alpha\alpha}(\tau)|\alpha\rangle|\alpha\rangle + C_{\alpha\beta}(\tau)|\alpha\rangle|\beta\rangle + C_{\alpha\gamma}(\tau)|\alpha\rangle|\gamma\rangle \\ & + C_{\beta\alpha}(\tau)|\beta\rangle|\alpha\rangle + C_{\beta\beta}(\tau)|\beta\rangle|\beta\rangle + C_{\beta\gamma}(\tau)|\beta\rangle|\gamma\rangle \\ & + C_{\gamma\alpha}(\tau)|\gamma\rangle|\alpha\rangle + C_{\gamma\beta}(\tau)|\gamma\rangle|\beta\rangle + C_{\gamma\gamma}(\tau)|\gamma\rangle|\gamma\rangle.\end{aligned}$$

The time-dependent Schrödinger equation should be solved under the initial condition of $|\Psi(0)\rangle=|\alpha\rangle|\alpha\rangle$. The calculation is performed for $0\leq\tau\leq10^8$ with $d\tau=0.01$ and $\delta\tau=100$. Similarly to the single QD case, the fluorescence intensity $\mathcal{I}(\tau)$ for one of two QDs can be defined from the solution of the time-dependent Schrödinger equation as $\zeta(\tau)\Theta[\zeta(\tau)]$ with $\zeta(\tau)=|C_{\alpha\alpha}(\tau)|^2+|C_{\alpha\beta}(\tau)|^2+|C_{\alpha\gamma}(\tau)|^2+|C_{\beta\alpha}(\tau)|^2+|C_{\beta\beta}(\tau)|^2+|C_{\beta\gamma}(\tau)|^2-0.65$. We then count the "on" events and calculate $P(\tau_{\rm on})$ in the same way as the previous single QD case.

In Fig. 3, we show the time-series fluorescence intensity $\mathcal{I}(\tau)$ in a given fixed time interval for $U=0.1$ and 1. The blinking becomes rapid and intensified as the interaction U increases; that is, the blinking of one QD alters the blinking of the other through the strong interaction U. The physical

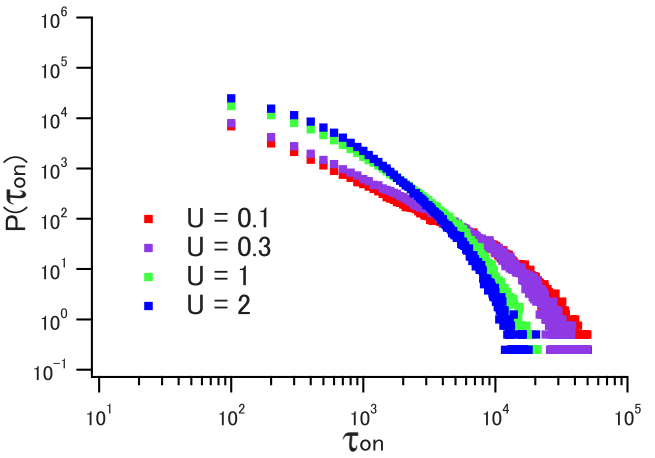

FIG. 4. (Color online) Probability of the "on" sojourn time $P(\tau_{\rm on})$ with respect to the interacting strength U. $v_0=1$ is used.

meaning of this intensified blinking can be sought in a few different directions. First, in Fig. 4, the probability $P(\tau_{\rm on})$ of the strong interaction $U=1$ or 2 is distinguished from the weak interaction. The probability of $U=1$ or 2 in the strong-interaction case does not clearly seem to follow the power-law behavior even in the short-time range of $10^2\lesssim\tau_{\rm on}\lesssim10^3$, possibly because the strong-interaction cases lose much of the long-memory characteristics of the dynamics. Second, in Fig. 5, we provide the correlation function $g(\tau)$ defined by $g(\tau)=\langle\mathcal{I}(\tau')\mathcal{I}(\tau'+\tau)\rangle/\langle\mathcal{I}(\tau')^2\rangle$, where $\langle\cdots\rangle$ means an average with respect to the time τ'. In this figure, just as in Fig. 4, it is immediately observed that the case with $U=1$ or 2 is different from that with $U=0.1$ or 0.3. For $U=0.1$ or 0.3, the curvature of the correlation function $g(\tau)$ changes around $\tau\approx2\times10^4$ (for $U=0.1$) or 10^4 (for $U=0.3$) and those time scales are found to be nothing else but the crossover time τ_C defined from the change from the power-law to the exponential behavior of $P(\tau_{\rm on})$ monitored from Fig. 4. On the other hand, for both $U=1$ and 2, the change in curvature of $g(\tau)$ is not clearly seen. This is consistent with Fig. 4. Hence, it is understood that the interaction U between QDs changes their dynamics qualitatively. Further, it should be stressed that the results of Figs. 3–5 directly reproduce

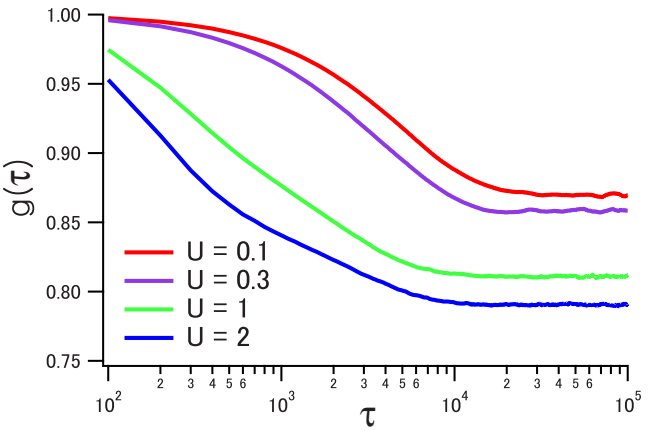

FIG. 5. (Color online) Correlation function $g(\tau)$ with respect to the interacting strength U. $v_0=1$ is used.

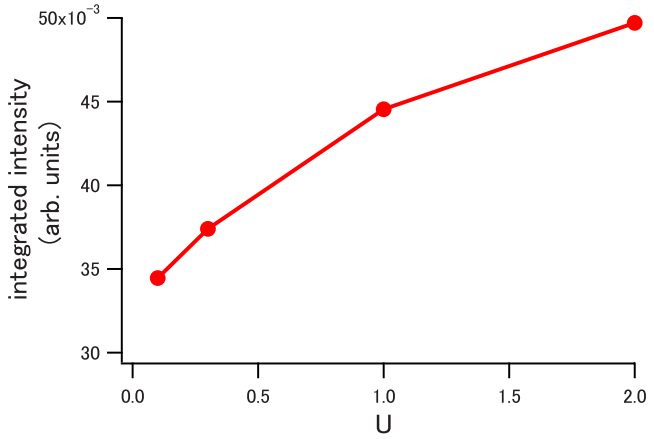

FIG. 6. (Color online) Integrated fluorescence intensity $\bar{\mathcal{I}}$ with respect to U. $v_0=1$ is used.

and explain the experimental observation by Yu and Orden.[10] Finally, we give the integrated fluorescence intensity $\bar{\mathcal{I}}$, defined by $\bar{\mathcal{I}}=\int_0^{\tau_{\max}} d\tau \mathcal{I}(\tau)/\tau_{\max}$ with $\tau_{\max}=10^8$ in Fig. 6 and find that $\bar{\mathcal{I}}$ enhances monotonically with U. This is important because it implies that the interaction U could be a possible origin of the photoinduced fluorescence enhancement (PFE).[11,18] It is known that the nonergodic long-memory dynamics (i.e., corresponding to the case with a small U) lead to the fluorescence decreasing with time because of statistical aging.[19] However, we treat the Hamiltonian system to guarantee energy conservation so that the fluorescence does not decrease with time for both small and large U. Instead, PFE can be naturally understood in the present study as an interaction effect. Due to the repulsion U between ionic states of two QDs, the probability for both QDs to fall in neighboring ionic states, i.e., $|\gamma\rangle|\gamma\rangle$, is not energetically favored. Suppression of such probability contributes to fluorescence enhancement compared to two isolated QDs. Recently, Wang *et al.*[20] have reported the blinking statistics correlated with the nanoparticle number. They have found that τ_C changes significantly with the number of particles for clusters of five or more particles, implying the importance of remnant interactions between particles or between particle and matrix environment or energy transfer between particles.

Our investigation suggests that functional properties or physical properties be created in a systematic fashion by clustering QDs. By controlling the density of QDs in the cluster (or generally, ensemble), one may control and optimize the interaction strength U. In particular, Figs. 4 and 5 figuratively illustrate the continuous memory loss of the dynamics and the consequent change in the dynamic characteristics with increasing U. The memoriless dynamics with a large U prevent the photoexcited electron from being trapped in the ionic state, or generally, in the defect-related or surface-related states so that they are expected to increase the electron mobility as well as the fluorescence intensity. Because of the interaction between QDs, electron transport would become coherent and mobility would increase.[21] This implies that one would have another controllable option, that is, the QD density in addition to the QD size, toward application of promising building blocks for modern electrical or optoelectrical devices.

IV. SUMMARY

To summarize, we propose a microscopic quantum-mechanical model for a nanoscopic light-emissive QD. The model can describe its nonstochastic dynamics under photoexcitation. A crossover from the long-memory to memoriless dynamics is described as time goes. Beyond a single QD, the model is extended to consider the Coulomb interaction between QDs being in the ionic states. It is found that the interaction gives rise to intensified blinking, continuous memory loss (i.e., continuous change in the blinking statistics), and fluorescence enhancement. The agreement with a recent experimental observation is good. Our theoretical findings uncover the nature of the interaction underlying in the QD ensemble.

ACKNOWLEDGMENTS

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[15] A given time series of $v(\tau)$ is not the only possible one showing the blinking statistics, consistent with the experimental observa-

tion. For example, $v(\tau)=v_0\times\eta(\tau)$, where $\eta(\tau)$ is a continuous random number $\in[0,1]$, can also give qualitatively same statistics and scaling behavior.

[16] In the problem, the free controllable parameters are now ω and v_0. In order to be more practical and realistic in the energy and time scales, one may first take $\omega\sim 1$ eV$\sim 10^{15}$ s^{-1}. When $v_0=1\sim 10^{15}$ s^{-1} and $\tau_C\sim 10^4\sim 10^{-11}$ s from Fig. 2. Instead, however, if taking $v_0=10^{-11}\sim 10^4$ s^{-1}, we get $\tau_C\sim 1$ s from a scaling relation of $\tau_C\propto 1/v_0$.

[17] The "on" event is determined by $|C_\alpha(\tau)|^2+|C_\beta(\tau)|^2\gg|C_\gamma(\tau)|^2$, i.e., $|C_\alpha(\tau)|^2+|C_\beta(\tau)|^2\gg 0.5$ from $|C_\alpha(\tau)|^2+|C_\beta(\tau)|^2+C_\gamma(\tau)|^2=1$. A practical criterion is chosen to be $|C_\alpha(\tau)|^2+|C_\beta(\tau)|^2>0.65$ and is also applied to the two interacting QDs.

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