Excitonic exchange effects on the radiative decay time of monoexcitons and biexcitons in quantum dots

Gustavo A. Narvaez,* Gabriel Bester, Alberto Franceschetti, and Alex Zunger†
National Renewable Energy Laboratory, Golden, Colorado 80401, USA
(Received 30 June 2006; published 17 November 2006)

Electron-hole exchange interaction splits the exciton ground state into "dark" and "bright" states. The dynamics of those states depends on the internal relaxation time between bright and dark states (spin-flip time), and on the radiative recombination time of the bright states. On the other hand, the calculated values of these recombination times depend not only on the treatment of correlation effects, but also on the accuracy of the electron and hole wavefunctions. We calculate the radiative decay rates for monoexcitons and biexcitons in (In,As)Ga/GaAs self-assembled and colloidal CdSe quantum dots from atomistic correlated wave functions. We show how the radiative decay time $\tau_R(X^0)$ of the monoexciton depends on the spin-flip relaxation time between bright and dark states. In contrast, a biexciton has no bright-dark splitting, so the decay time of the biexciton $\tau_R(XX^0)$ is insensitive to this spin-flip time. This results in ratios $\tau_R(X^0)/\tau_R(XX^0)$ of 4 in the case of fast spin flip, and a ratio of 2 in the case of slow spin flip. For (In,Ga)As/GaAs, we compare our results with the model calculation of Wimmer *et al.* [Phys. Rev. B **73**, 165305 (2006)]. When the same spin-flip rates are assumed, our predicted $\tau_R(X^0)/\tau_R(XX^0)$ agrees with that of Wimmer *et al.*, suggesting that our treatment of correlations is adequate to predict the ratio of monoexciton and biexciton radiative lifetimes. Our results agree well with experiment on self-assembled quantum dots when assuming slow spin flip. Conversely, for colloidal dots the agreement with experiment is best for fast spin flip.

DOI: 10.1103/PhysRevB.74.205422 PACS number(s): 73.21.La, 71.35.−y, 78.60.−b

I. INTRODUCTION: RELATION BETWEEN APPARENT AND MICROSCOPIC CARRIER DECAY

We address here the subject of how to compare measured exciton $\tau_R(X^0)$ and biexciton $\tau_R(XX^0)$ radiative relaxation times with calculated values. Experimentally, an ensemble of quantum dots is excited by an optical pump-pulse and the photons subsequently emitted are counted as a function of time. The photon emission rate vs time is often not a simple exponential. The reason for this is that even in a single dot the monoexciton ground state is not a single state but a manifold of exchange and fine-structure split states with internal carrier dynamics. In III-V and II-VI dots the monoexciton ground state originates from $e_0^1h_0^1$, where e_0 and h_0 are, respectively, the lowest- and highest-energy confined electron and hole states. Due to the electron-hole exchange interaction, this state is not fourfold degenerate but splits into four lines [Fig. 1(a)].[1–3] For the C_{2v} symmetry of (In,Ga)As/GaAs self-assembled quantum dots, the four states are the high-energy bright state B which consists of a pair b and b' split by a few μeV and the low-energy dark state D which consists of a pair d and d' that is quasidegenerate. B and D are split by a few hundred μeV due to exchange effects. For colloidal CdSe quantum dots with the C_{6v} symmetry the internal d-d' and b-b' splittings of the two pairs is small, with the b-b' recently measured to be about 1–2 meV.[4] In turn, the b-d splitting between the dark and the bright states is an order of magnitude larger than in self-assembled dots, ranging from 2–20 meV.[4,5] In both self-assembled and colloidal dots, the biexciton ground state $e_0^2h_0^2$ state has no fine structure and corresponds to a single bright state that can decay to the four states of $e_0^1h_0^1$ in the monoexciton [Fig. 1(c)].

In this paper we show that (i) due to exchange and fine-structure in the monoexciton, the measured apparent radiative recombination time $\tau_R(X^0)$ depends on the bright-to-dark spin-flip relaxation time τ_{BD} with rate $R_{BD}=\tau_{BD}^{-1}$. By using an atomistic pseudopotential-based approach combined with the configuration-interaction method,[6] we calculate the characteristic radiative recombination rates between B and the ground state (R_{B0}) and between D and the ground state (R_{D0}) and input them in a set of rate equations with varying R_{BD} rates. We find that the photon emission rate decays as a single-exponential with rate$\simeq R_{B0}$ for slow spin flip times, as a biexponential for intermediate τ_{BD}, and as a single-exponential with rate $R_{B0}/2$ for fast spin flip times. (ii) Within the same approach used for the monoexciton, we calculate the characteristic recombination rates R_{0B} and R_{0D} of the biexciton ground state into the bright and dark states of the monoexciton. We find that $R_{0B}\simeq R_{B0}$ and $R_{0D}\simeq R_{D0}$, and that the biexciton radiative decay is a single exponential with a decay time $\tau(XX^0)\simeq 2R_{0B}^{-1}$ regardless of R_{BD}. (iii) We show that due to the aforementioned dependence of the monoexciton decay time on R_{BD}, the ratio $\tau_R(X^0)/\tau_R(XX^0)$ has the values of 4 and 2 for the limiting cases of fast and slow spin flip, respectively. We thus resolve the apparent contradiction between the recent model calculations of Wimmer and co-workers,[7] who found $\tau_R(X^0)/\tau_R(XX^0)\simeq 2$, and our previous atomistic-based realistic calculations of $\tau_R(X^0)$ and $\tau_R(XX^0)$ in which we found[8] $\tau_R(X^0)/\tau_R(XX^0)\simeq 4$. We illustrate our findings with atomistic, pseudopotential-based calculations for a prototypical self-assembled $In_{0.6}Ga_{0.4}As/GaAs$ dot and a CdSe colloidal dot, comparing with available data.

II. RATE EQUATIONS FOR THE RADIATIVE DECAY OF THE MONOEXCITON

Figure 1(a) shows the monoexciton and biexciton energy levels that enter our calculations. We do not consider higher-

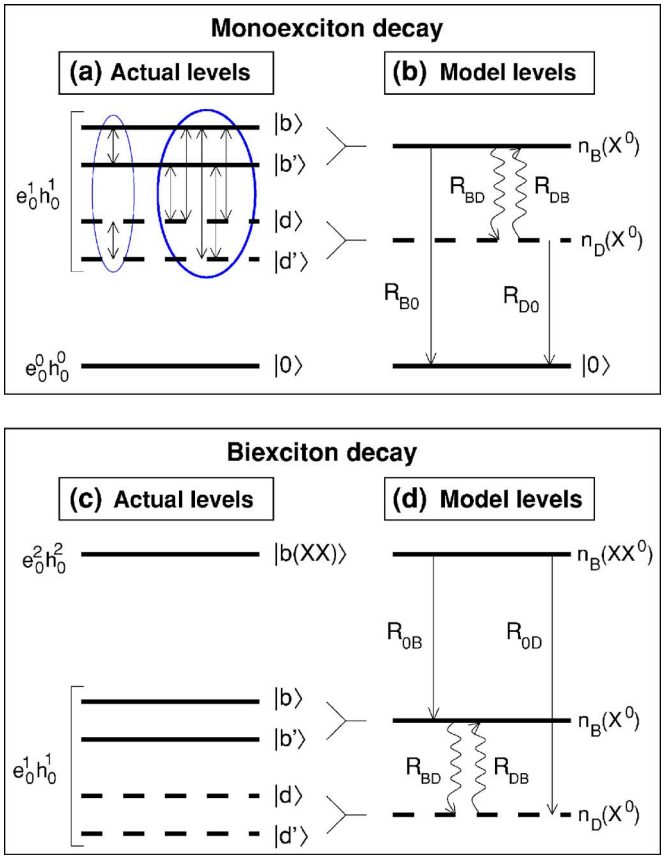

FIG. 1. (Color online) Sketch of (a) the four states that encompass the monoexciton ground state $e_0^1h_0^1$ and $e_0^0h_0^0$. Thin- and thick-line ellipses indicate, respectively, nonradiative thermalization as well as spin-flip channels. (b) The model three-level system for the monoexciton decay. R_{BD} (R_{DB}) is the bright-dark (dark-bright) rate while R_{B0} and R_{D0} are radiative decay rates for the bright and dark (model) state, respectively. (c) The same as (a) for the biexciton ground state $e_0^2h_0^2$ and $e_0^1h_0^1$, and (d) model representation, with radiative decay rates R_{0B} and R_{0D}.

lying states because most time-resolved photoluminescence experiments are conducted at temperatures such that the occupation of those states is negligible. From Fig. 1(a) we see that there are a number of discrete transitions channels denoted below by rates R_{ij}. We next set up a set of channel-specific rate equations describing how the individual levels of Fig. 1(a) "communicate," from which we will deduce the global decay of the ground state $n_0(t)$ which is measured. Using the characteristic radiative rates of the four excitonic states of $e_0^1h_0^1$ and the ground state $e_0^0h_0^0$ we establish the following system of rate equations:

$$dn_b/dt = -(R_{bb'} + R_{bd} + R_{bd'} + R_{b0})n_b + R_{d'b}n_{d'} + R_{db}n_d + R_{b'b}n_{b'},$$

$$dn_{b'}/dt = -(R_{b'b} + R_{b'd} + R_{b'd'} + R_{b'0})n_{b'} + R_{d'b'}n_{d'} + R_{db'}n_d + R_{bb'}n_b,$$

$$dn_d/dt = -(R_{db} + R_{d'b'} + R_{dd'} + R_{d0})n_d + R_{d'd}n_{d'} + R_{b'd}n_{b'} + R_{bd}n_b,$$

$$dn_{d'}/dt = -(R_{14} + R_{13} + R_{12} + R_{10})n_{d'} + R_{dd'}n_d + R_{b'd'}n_{b'} + R_{bd'}n_b,$$

$$dn_0/dt = R_{d'0}n_{d'} + R_{d0}n_d + R_{b'0}n_{b'} + R_{b0}n_b, \quad (1)$$

where R_{ij} are the characteristic recombination rates from the level i to level j. The five-level system of rate equations [Eq. (1)] that describe the radiative decay of X^0 can be reduced to a three-level system when (i) the thermalization rate [Fig. 1(a)] within the b-b' bright and within the d-d' dark states is assumed equal

$$R_{bb'} = R_{b'b} = R_{dd'} = R_{d'd} = R_{th}; \quad (2)$$

(ii) spin-flip rates between the dark and the bright states [Fig. 1(a)] are assumed to be independent on the index of the bright or dark state while keeping the distinction between bright-dark and dark-bright transition rates

$$R_{bd} = R_{bd'} = R_{b'd} = R_{b'd'} = R_{BD}, \quad (3)$$

$$R_{db} = R_{db'} = R_{d'b} = R_{d'b'} = R_{DB}; \quad (4)$$

and (iii) the decay rate of b and b' to $e_0^0h_0^0=|0\rangle$ are equal, and so are the decays of d and d' to $|0\rangle$

$$R_{b0} = R_{b'0} = R_{B0}, \quad R_{d0} = R_{d'0} = R_{D0}. \quad (5)$$

Assumption (i) is justified in different range of temperatures determined by the magnitude of the small splittings between b-b' and d-d': $T \gtrsim 2$ K in self-assembled dots and $T \gtrsim 20$ K in CdSe colloidal dots. Regarding (ii), the small fine-structure bright-dark splittings (10–300 μeV) in (In,Ga)As/GaAs dots allows us to make the assumption $R_{BD}=R_{DB}$. For CdSe colloidal dots the bright-dark splitting is about an order of magnitude larger[4,5] and therefore $R_{BD}=R_{DB}$ for $T \gtrsim 30$ K. (In the results discussed in Sec. V we adopt the regime in which $R_{BD}=R_{DB}$.) Assumption (iii) is supported by our atomistic pseudopotential-based calculations (see Sec. IV). Assuming Eqs. (2)–(5), we simplify Eq. (1) to

$$\frac{dn_B}{dt} = -(R_{B0} + 2R_{BD})n_B + 2R_{DB}n_D,$$

$$\frac{dn_D}{dt} = -(R_{D0} + 2R_{DB})n_D + 2R_{BD}n_B,$$

$$\frac{dn_0}{dt} = R_{B0}n_B + R_{D0}n_D, \quad (6)$$

where $n_B=n_b+n_b'$ is the occupation of the bright states and $n_D=n_d+n_{d'}$ the occupation of the dark states. We will calculate R_{B0} and R_{D0} from the electronic structure of the dot and vary R_{BD} in a wide range from very fast to very slow spin-flip rates to examine different regimes of behavior. We will

TABLE I. Calculated values for the radiative characteristic rates R_{i0} and R_{bi} $(i=b,b',d,d')$ for the monoexciton (X^0) and biexciton (XX^0), respectively, in an alloyed $In_{0.6}Ga_{0.4}As/GaAs$ dot (base diameter $b=252$ Å and height $h=35$ Å) and a CdSe colloidal dot (diameter $D=38$ Å). The approximate rates R_{B0}, R_{D0} that enter the model three-level system of rate equations [Eq. (6)] are also shown, as well as the rates R_{0B} and R_{0D} for the biexciton.

		$In_{0.6}Ga_{0.4}As/GaAs$			CdSe	
X^0	R_{b0}	$0.89\ ns^{-1}$	$R_{B0}=0.9\ ns^{-1}$	R_{b0}	$0.12\ ns^{-1}$	$R_{B0}=0.12\ ns^{-1}$
	$R_{b'0}$	$0.91\ ns^{-1}$		$R_{b'0}$	$0.12\ ns^{-1}$	
	R_{d0}	$0.65\times10^{-5}\ ns^{-1}$	$R_{D0}=0$	R_{d0}	$0.04\times10^{-6}\ ns^{-1}$	$R_{D0}=0$
	$R_{d'0}$	$0.53\times10^{-4}\ ns^{-1}$		$R_{d'0}$	$0.22\times10^{-6}\ ns^{-1}$	
XX^0	R_{bb}	$0.83\ ns^{-1}$	$R_{0B}=0.84\ ns^{-1}$	R_{bb}	$0.13\ ns^{-1}$	$R_{0B}=0.13\ ns^{-1}$
	$R_{bb'}$	$0.85\ ns^{-1}$		$R_{bb'}$	$0.13\ ns^{-1}$	
	R_{bd}	$0.67\times10^{-5}\ ns^{-1}$	$R_{0D}=0$	R_{bd}	$0.04\times10^{-6}\ ns^{-1}$	$R_{0D}=0$
	$R_{bd'}$	$0.46\times10^{-4}\ ns^{-1}$		$R_{bd'}$	$0.53\times10^{-6}\ ns^{-1}$	

then solve Eq. (6) and calculate the photon emission rate $I(t)=R_{B0}\,n_B(t)+R_{D0}\,n_D(t)$, which is directly comparable to time-resolved photoluminescence (PL) experiments.

III. RATE EQUATION FOR THE RADIATIVE DECAY OF THE BIEXCITON

The biexciton has a nondegenerate state without *B-D* splitting and it decays into the bright and dark states of the monoexciton. This decay can be modeled, similarly to the monoexciton decay, with a three-level system [Fig. 1(d)], yielding a single rate equation describing the population of the biexciton ground state:

$$\frac{dn_B(XX^0)}{dt} = -2(R_{0B}+R_{0D})n_B(XX^0). \tag{7}$$

As in the monoexciton case, we will calculate R_{0B} and R_{0D} from the electronic structure of the dot.

IV. CALCULATION OF BRIGHT AND DARK RECOMBINATION RATES FROM ELECTRONIC STRUCTURE

We use the empirical pseudopotential method where a superposition of screened atomic pseudopotentials are used to describe the quantum dot potential.[6] We take spin-orbit interaction into account and the method naturally includes interband coupling and intervalley coupling. Following the diagonalization of the single-particle Hamiltonian, we use a configuration-interaction (CI) approach[3] to obtain correlated monoexciton and biexciton wave functions $|\Psi^{(\nu)}(\chi)\rangle$ $(\chi=X^0,XX^0)$. The characteristic radiative recombination rates $R_{if}(\chi)$ are calculated using Fermi's golden rule from the correlated exciton wave functions as follows. For a transition $|\Psi^{(i)}(\chi)\rangle\rightarrow|\Psi^{(f)}(\chi-1)\rangle$, $R_{if}(\chi)$ follows from both the magnitude of the dipole matrix element of the transition $|\mathbf{M}_{if}^{(\hat{\mathbf{e}})}(\chi)|^2$ and the recombination energy ω_{if}. Namely,

$$R_{if}(\chi^q) = \frac{4G}{3}\left(\frac{e^2}{m_0^2c^3\hbar^2}\right)n\omega_{if}(\chi^q)\sum_{\hat{\mathbf{e}}=\hat{x},\hat{y},\hat{z}}|\mathbf{M}_{if}^{(\hat{\mathbf{e}})}(\chi)|^2. \tag{8}$$

Here, e and m_0 are the charge and mass of the electron, respectively, and c is the velocity of light in vacuum; the refractive index n of the dot material accounts for the material's effects on the photon emission; and $G=G(\epsilon_{\text{in}},\epsilon_{\text{out}})$ accounts for the dielectric constant mismatch between the dot material (ϵ_{in}) and medium (ϵ_{out})—solid barrier in self-assembled dots and liquid solvent in colloidal.

Table I shows the calculated characteristic radiative recombination rates R_{i0} and R_{bi} $(i=b,\ b',\ d,\ d')$ for the monoexciton and biexciton, respectively, in a prototypical lens-shaped $In_{0.6}Ga_{0.4}As/GaAs$ self-assembled quantum dot with base diameter $b=252$ Å and height $h=35$ Å, and a colloidal CdSe quantum dot with diameter $D=38$ Å. We find that the rates for bright states indeed satisfy $R_{b0}\simeq R_{b'0}$ and that dark states obey $R_{d0}\sim R_{d'0}\sim 0$.

V. ANALYTIC SOLUTION TO THE MODEL RATE EQUATIONS FOR THE MONOEXCITON

The calculated radiative rates for the $In_{0.6}Ga_{0.4}As/GaAs$ self-assembled dot and the CdSe colloidal dot (Table I) show that it is a good approximation to consider $R_{D0}=0$. In this case, together with the assumptions that $R_{BD}=R_{DB}$ and[9] $n_B(0)=n_D(0)=1/2$, the solution of the model three-level system of rate equations [Eq. (6)] gives the following (the general framework for the analytic results is in the Appendix):

$$n_B(t) = F\exp(-\gamma_F t) + S\exp(-\gamma_S t) \tag{9}$$

with

$$\gamma_F = \frac{1}{2}(R_{B0}+4R_{BD}) + \frac{1}{2}\sqrt{R_{B0}^2+(4R_{BD})^2}, \tag{10}$$

$$\gamma_S = \frac{1}{2}(R_{B0}+4R_{DB}) - \frac{1}{2}\sqrt{R_{B0}^2+(4R_{BD})^2} \tag{11}$$

and

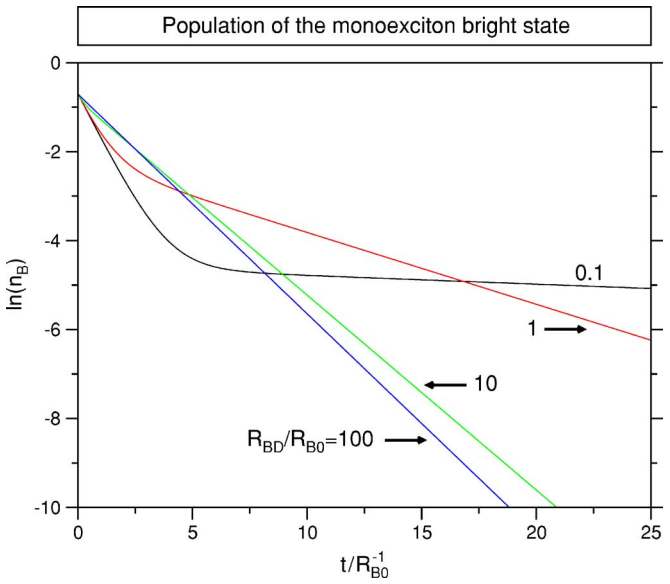

FIG. 2. (Color online) Population n_B [Eq. (9); logarithmic scale] of the model bright state of the monoexciton versus time (t; units of R_{B0}^{-1}) for different values of the spin-flip rate R_{BD}. R_{B0}=0.9 ns^{-1} for an $In_{0.6}Ga_{0.4}As/GaAs$ quantum dot with base diameter b=252 Å and height h=35 Å and R_{B0}=0.12 ns^{-1} for a CdSe dot with diameter D=38 Å (Table I).

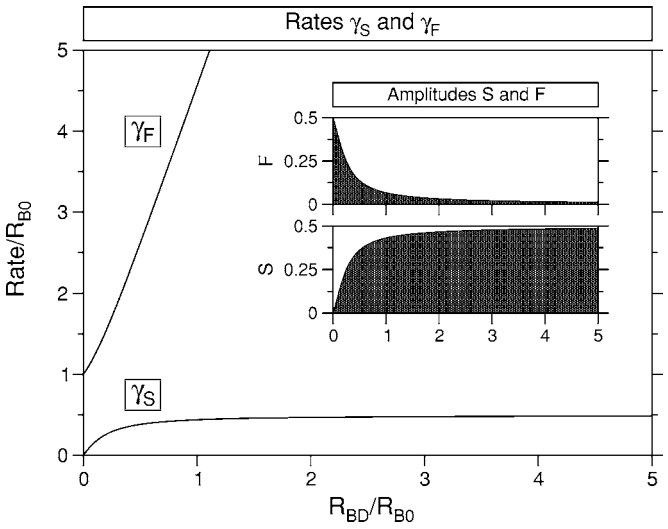

FIG. 3. Fast [γ_F; Eq. (10)] and slow [γ_S; Eq. (11)] components of the monoexciton population n_B in units of R_{B0}. Inset: Amplitudes F [Eq. (12)] and S [Eq. (13)] versus R_{BD}. The rates R_{B0} and R_{D0} that enter γ_F and γ_S are those of Table I.

$$F = \frac{1}{2}\left(\frac{R_{B0} - \gamma_S}{\gamma_F - \gamma_S}\right), \tag{12}$$

$$S = -\frac{1}{2}\left(\frac{R_{B0} - \gamma_F}{\gamma_F - \gamma_S}\right). \tag{13}$$

In time-resolved PL experiments the measured signal $I(t)$ is proportional to the number of photons per unit of time: dn_0/dt [Eq. (6)], which under the assumption of R_{D0}=0 results in $I(t)=R_{B0}\,n_B(t)$. Note that by being proportional to the occupation of the bright state the signal $I(t)$ carries information on both radiative and nonradiative (spin flip) processes. Figure 2 shows the logarithm of $n_B(t)$ as a function of time for different spin-flip rates R_{BD}, and Fig. 3 shows the slow (γ_S) and fast (γ_F) components of the decay of $n_B(t)$ versus R_{BD}. We find that in the limiting cases of (1) extremely *slow* ($R_{BD} \ll R_{B0}$) and (2) extremely *fast* ($R_{BD} \gg R_{B0}$) spin flip the decay of n_B is primarily determined by a single exponential. In case (1) we find $\gamma_F \simeq R_{B0}+2R_{BD}$ and $\gamma_S \simeq 2R_{BD}$, while $F \simeq 1/2$ and $S \simeq 0$ (Fig. 3, inset). Here, γ_F resembles the expected result for the decay rate of the PL in the presence of nonradiative recombination centers; the dark state of the monoexciton in this case.[10,11] The population of the bright state is

$$n_B(t) \simeq \frac{1}{2}\exp[-(R_{B0} + 2R_{BD})t]. \tag{14}$$

In this regime, $I(t)$ decays approximately with the characteristic lifetime of the bright states. In case (2), we find $\gamma_F \simeq R_{B0}/2+4R_{BD}$ and $\gamma_S \simeq R_{B0}/2$, and $S \sim 1/2$ and $F \sim 0$ (Fig. 3, inset); therefore,

$$n_B(t) \simeq \frac{1}{2}\exp\left(-\frac{R_{B0}}{2}t\right). \tag{15}$$

$I(t)$ thus decays with an approximate characteristic time of $\tau_R(X^0)=2R_{B0}^{-1}$; *twice* as large as the characteristic lifetime of the bright state.

VI. COMPARISON WITH EXISTING EXPERIMENTAL DATA

In the experimental literature, data on the bright-dark transition time are scarce. *(In,Ga)As/GaAs dots*. Dalgarno and co-workers[9,12] have studied recently the effect of the dark state in the decay of the monoexciton in a gated structure and have estimated $R_{BD}^{-1} > 20$ ns at a temperature of 5 K. In addition, they have found that this spin-flip rate varies strongly with the applied bias. From time-resolved PL experiments, Favero *et al.*[13] have extracted significantly disparate values for two different dots: $R_{BD} \sim 440$ and 30 ns.

InP/(In,Ga)P dots. In a two-photon absorption experiment, Snoke and co-workers[19] populated the dark states of the monoexciton and measured the subsequent luminescence as a function of time. From the data below 70 K, the authors found that the spin-flip, bright-dark transition time satisfies $R_{BD}^{-1} \geq 200$ ps.

CdSe dots. By performing fluorescence transient experiments at room temperature, Wang *et al.*[20] have concluded that the bright-dark, spin-flip relaxation times R_{BD}^{-1} =0.2–0.4 ps. Thus, the spin-flip process is orders of magnitude faster than the characteristic radiative recombination time.

These experiments reveal order-of-magnitude variations in the bright-dark spin-flip times, suggesting that the value of R_{BD} appropriate to interpret time-resolved photoluminescence experiments in quantum dots is controversial and further research is needed to understand the spin-flip mechanism.

In the slow spin flip regime, consistent with the findings of Dalgarno *et al.*[9] and Favero *et al.*,[13] our calculated value $\tau_R(X^0) \simeq R_{B0}^{-1} = 1.1$ ns for the $In_{0.6}Ga_{0.4}As/GaAs$ dot is in excellent agreement with the data of Bardot *et al.*,[14] who extracted 1.55 ns from time-resolved photoluminescence, and the value of 1 ns found by Buckle *et al.*[15] and Stevenson *et al.*[16] In the fast spin flip regime, for our prototypical CdSe dot (see Table I), we obtain $\tau_R(X^0) = 17$ ns, which is in excellent agreement with the values of 17 and 19 ns extracted, respectively, by Brokmann *et al.*[17] and Labeau *et al.*[18] from time-resolved photoluminescence in ZnS-passivated CdSe dots. In the regime of intermediate spin flip rates, measurements of the biexponential decay of $I(t)$—as those performed by Dalgarno *et al.*[9]—could be used to deduce the spin-flip rate.

VII. THE RATIO $\tau_R(X^0)/\tau_R(XX^0)$

To compare the biexciton decay rate with to the monoexciton decay rate in the limiting cases discussed above (Sec. V), we first note that atomistic pseudopotential-based calculations show (Table I) that the characteristic radiative rates for the biexciton ground state satisfy

$$R_{0B}(XX^0) \simeq R_{B0}(X^0),$$

$$R_{0D}(XX^0) \simeq R_{D0}(X^0). \tag{16}$$

Second, in contrast to X^0, we note that the solution of the rate equation for XX^0 [Eq. (7)] results in $n_B(XX^0) \sim \exp(-\gamma t)$; a single exponential that decays with rate

$$\gamma = 2(R_{0B} + R_{0D}) \simeq 2(R_{B0} + R_{D0}) \tag{17}$$

regardless of the value of the spin-flip rate R_{BD}. Similarly to X^0, the time-resolved PL signal is proportional to the population of the bright state of the biexciton. For slow spin flip [case (1), Sec. V] we find a decay-rate ratio between X^0 and XX^0 of

$$\gamma/\gamma_F \simeq \frac{2R_{0B}}{R_{B0} + 2R_{BD}} \simeq 2 \quad \text{(slow spin flip)}, \tag{18}$$

and for fast spin flip [case (2), Sec. V] we find

$$\gamma/\gamma_S \simeq \frac{2R_{0B}}{R_{B0}/2} \simeq 4 \quad \text{(fast spin flip)}. \tag{19}$$

We emphasize that depending on the magnitude of the spin-flip time the ratio $\tau_R(X^0)/\tau_R(XX^0)$ can change by a factor of 2, therefore the assumed spin-flip time is crucial when comparing results for $\tau_R(X^0)/\tau_R(XX^0)$. Recently, Wimmer *et al.*[7] have used a quantum Monte Carlo (QMC) approach with model single-band effective-mass electron and hole states to calculate

$$\tau_R(X^0)/\tau_R(XX^0) \simeq 2 \quad \text{(slow spin flip)}. \tag{20}$$

Those authors speculated that the disagreement with the pseudopotential and CI calculations of Ref. 8, which adopt the fast spin-flip regime and predict

$$\tau_R(X^0)/\tau_R(XX^0) \simeq 4 \quad \text{(fast spin flip)}, \tag{21}$$

originates from an inaccurate treatment of correlations in CI. However, as is obvious from Eqs. (18) and (19), the discrepancy can be directly attributed to the different assumptions for the spin flip rates. When the same spin-flip rates are assumed, our results for $\tau_R(X^0)/\tau_R(XX^0)$ are in agreement with the QMC results of Wimmer *et al.*,[7] suggesting that our treatment of correlations is adequate to predict the ratio of monoexciton and biexciton radiative lifetimes. On the other hand, the calculated values of the radiative recombination times depend not only on the treatment of correlation effects, but also on the accuracy of the electron and hole wavefunctions. Our atomistic results are in good agreement with experiment while the results of Wimmer *et al.*[7] based on the single-band effective mass approximation differ from experimental data by a factor of 2.

Finally, note that in our calculation of $\tau_R(X^0)/\tau_R(XX^0)$ we assume that the change in occupation of the monoexciton bright and dark states [Eq. (1)] is not affected by the decay of the biexciton state.

VIII. SUMMARY

We calculated the characteristic radiative recombination rates for the ground state of the monoexciton and biexciton in self-assembled (In,Ga)As/GaAs and colloidal CdSe quantum dots using atomistic wave functions. For the monoexciton we used these rates in a model three-level system of rate equations where we varied the spin-flip rate R_{BD}. The latter affects significantly the radiative decay time: Fast spin flip leads to an exciton radiative recombination rate twice as fast as the rate obtained from slow spin flip. The radiative decay times $\tau_R(X^0)$ calculated in the limit of slow spin flip are in excellent agreement with available data for self-assembled dots, while for colloidal dots the agreement is best for fast spin flip. The biexciton radiative decay is a single exponential with a relaxation time that is independent of the spin-flip rate. But the ratio between the radiative decay time of the biexciton $\tau_R(XX^0)$ and monoexciton does depend on R_{BD} and results, respectively, in $\tau_R X^0/\tau_R(XX^0) \simeq 4$ and 2 for fast and slow spin flip. This result resolved the apparent contradiction between the calculation of Wimmer *et al.*,[7] who predicted $\tau_R X^0/\tau_R(XX^0) \simeq 2$, and our previous atomistic calculation[8] in which we found $\tau_R(X^0)/\tau_R(XX^0) \simeq 4$.

ACKNOWLEDGMENTS

This work was funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Contract No. DE-AC36-99GO10337 to NREL.

APPENDIX: SOLUTION OF THE THREE-LEVEL MODEL RATE EQUATIONS FOR THE RADIATIVE DECAY OF X^0

We use the simplified model of Eq. (6) as shown in Fig. 1(b). To find $n_B(t)$ and $n_D(t)$, we propose

$$n_B(t) = F\exp(-\gamma_F t) + S\exp(-\gamma_S t), \tag{A1}$$

with $n_B(0)=F+S$ and $\gamma_F \neq \gamma_S$, and solve first for $n_D(t)$ with initial condition $n_D(0)$, where $n_B(0)+n_D(0)=1$. Then, to solve for S, F, γ_S, and γ_F, we substitute the solution of $n_D(t)$ in the rate equation for dn_B/dt [Eq. (6)], obtaining the following conditions:

$$\gamma_F^2 - (R_{B0} + 2R_{BD} + R_{D0} + 2R_{DB})\gamma_F + R_{B0}R_{D0} + 2R_{DB}R_{B0} + 2R_{BD}R_{D0} = 0, \tag{A2}$$

$$\gamma_S^2 - (R_{B0} + 2R_{BD} + R_{D0} + 2R_{DB})\gamma_S + R_{B0}R_{D0} + 2R_{DB}R_{B0} + 2R_{BD}R_{D0} = 0, \tag{A3}$$

$$2R_{DB}n_D(0) + (R_{D0} + 2R_{DB})n_B(0) - (R_{B0}R_{D0} + 2R_{DB}R_{B0} + 2R_{BD}R_{D0})\left(\frac{F}{\gamma_F} + \frac{S}{\gamma_S}\right) = 0. \tag{A4}$$

Thus, we find

$$\gamma_F = \frac{1}{2}[R_{B0} + R_{D0} + 2(R_{BD} + R_{DB})] + \frac{1}{2}\sqrt{(R_{B0} - R_{D0})^2 + 4(R_{B0} - R_{D0})(R_{BD} - R_{DB}) + 4(R_{BD} + R_{DB})^2}, \tag{A5}$$

$$\gamma_S = \frac{1}{2}[R_{B0} + R_{D0} + 2(R_{BD} + R_{DB})] - \frac{1}{2}\sqrt{(R_{B0} - R_{D0})^2 + 4(R_{B0} - R_{D0})(R_{BD} - R_{DB}) + 4(R_{BD} + R_{DB})^2}, \tag{A6}$$

and

$$F = \frac{R_{B0} + 2R_{BD} - \gamma_S}{\gamma_F - \gamma_S}n_B(0) - \frac{2R_{DB}}{\gamma_F - \gamma_S}n_D(0), \tag{A7}$$

$$S = -\frac{R_{B0} + 2R_{BD} - \gamma_F}{\gamma_F - \gamma_S}n_B(0) + \frac{2R_{DB}}{\gamma_F - \gamma_S}n_D(0). \tag{A8}$$

*Present address: Eclipse Energy Systems, Inc., St. Petersburg, Florida 33710, USA.
Electronic address: gnarvaez@eclipsethinfilms.com
†Electronic address: alex_zunger@nrel.gov

[1] M. Bayer, G. Ortner, O. Stern, A. Kuther, A. A. Gorbunov, A. Forchel, P. Hawrylak, S. Fafard, K. Hinzer, T. L. Reinecke, S. N. Walck, J. P. Reithmaier, F. Klopf, and F. Schäfer, Phys. Rev. B **65**, 195315 (2002); M. Bayer, A. Kuther, A. Forchel, A. Gorbunov, V. B. Timofeev, F. Schäfer, J. P. Reithmaier, T. L. Reinecke, and S. N. Walck, Phys. Rev. Lett. **82**, 1748 (1999).
[2] G. Bester, S. Nair, and A. Zunger, Phys. Rev. B **67**, 161306(R) (2003).
[3] A. Franceschetti, H. Fu, L. W. Wang, and A. Zunger, Phys. Rev. B **60**, 1819 (1999).
[4] M. Furis, H. Htoon, M. A. Petruska, V. I. Klimov, T. Barrick, and S. A. Crooker, Phys. Rev. B **73**, 241313(R) (2006).
[5] M. Nirmal, D. J. Norris, M. Kuno, M. G. Bawendi, Al. L. Efros, and M. Rosen, Phys. Rev. Lett. **75**, 3728 (1995).
[6] A. Zunger, Phys. Status Solidi B **224**, 727 (2001).
[7] M. Wimmer, S. V. Nair, and J. Shumway, Phys. Rev. B **73**, 165305 (2006).
[8] G. A. Narvaez, G. Bester, and A. Zunger, Phys. Rev. B **72**, 245318 (2005).
[9] P. A. Dalgarno, J. M. Smith, B. D. Gerardot, A. O. Govorov, K. Karrai, P. M. Petroff, and R. Warburton, Phys. Status Solidi A **202**, 2591 (2005).
[10] J. I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1975).
[11] M. Gurioli, A. Vinattieri, M. Zamfirescu, M. Colocci, S. Sanguinetti, and R. Nötzel, Phys. Rev. B **73**, 085302 (2006).
[12] J. M. Smith, P. A. Dalgarno, R. J. Warburton, A. O. Govorov, K. Karrai, B. D. Gerardot, and P. M. Petroff, Phys. Rev. Lett. **94**, 197402 (2005).
[13] I. Favero, G. Cassabois, C. Voisin, C. Delalande, Ph. Roussignol, R. Ferreira, C. Couteau, J. P. Poizat, and J. M. Gérard, Phys. Rev. B **71**, 233304 (2005).
[14] C. Bardot, M. Schwab, M. Bayer, S. Fafard, Z. Wasilewski, and P. Hawrylak, Phys. Rev. B **72**, 035314 (2005).
[15] P. D. Buckle, P. Dawson, S. A. Hall, X. Chen, M. J. Steer, D. J. Mowbray, M. S. Skolnick, and M. Hopkinson, J. Appl. Phys. **86**, 2555 (1999).
[16] R. M. Stevenson, R. J. Young, P. See, I. Ferrer, D. A. Ritchie, and A. J. Shields, Physica E (Amsterdam) **21**, 381 (2004).
[17] X. Brokmann, L. Coolen, M. Dahan, and J. P. Hermier, Phys. Rev. Lett. **93**, 107403 (2004).
[18] O. Labeau, P. Tamarat, and B. Lounis, Phys. Rev. Lett. **90**, 257404 (2003).
[19] D. W. Snoke, J. Hübner, W. W. Rühle, and M. Zundel, Phys. Rev. B **70**, 115329 (2004).
[20] H. Wang, C. de Mello Donegá, A. Meijerink, and M. Glasbeck, J. Phys. Chem. B **110**, 733 (2006).