The Excitonic Exchange Splitting and Radiative Lifetime in PbSe Quantum

(ii) Spherical dots made of a direct-gap, ¡-to-¡ *wurtzite material* (e.g., CdSe[4,6,8,9]). Here the h_1 and h_2 single-particle levels (which are degenerate in the zinc-blende structure) are split by crystal-field effects. The $(h_1) \otimes (e_1)$ and the $(h_2) \otimes (e_1)$ manifolds are each 4-fold degenerate at the single-particle level. Electron−hole exchange interactions split the 4-fold $(h_1) \otimes (e_1)$ excitonic manifold into a lower-energy, dark doublet, and a higher-energy, bright doublet, separated by the exchange splitting ¢$_x$. The higher-energy $(h_2) \otimes (e_1)$ excitonic manifold splits into a lower-energy dark state and two higher-energy bright states (Figure 1b).

(iii) Spherical dots made of an indirect-gap ¡-to-X diamond-like material (e.g., Si[5,10]). These dots have the diamond point-group symmetry O_h, so the VBM is orbitally doubly degenerate $(h_1 + h_2)$. Unlike case (i) above, however, the CBM states derive from the X valleys of the bulk Brillouin zone, which are spatially 3-fold degenerate. This degeneracy is split by quantum confinement effects, which lead to three nondegenerate CBM levels (e_1, e_2, e_3) belonging to different irreducible representations. The exciton manifold, which has 24 dimensions (including spin), exhibits a complex excitonic fine structure, with dark spin-triplet states located below bright spin-singlet states, as shown in Figure 1c (spin−orbit interaction is not included in Figure 1c).

(iv) Spherical dots made of an indirect-gap, ¡-to-L diamond-like material (e.g., Ge[11]). These dots have the diamond point-group symmetry, so the VBM is orbitally doubly degenerate $(h_1 + h_2)$. The CBM states derive from the four L points of the bulk Brillouin zone. The degeneracy of the L points is split by quantum confinement effects, leading to four orbitally nondegenerate CBM levels (e_1, e_2, e_3, e_4). The excitonic manifold $(h_1 + h_2) \otimes (e_1 + e_2 + e_3 + e_4)$, which has dimension 32 (including spin), is further split by electron−hole Coulomb and exchange interactions, as shown in Figure 1d.

In this work, we consider the excitonic manifold of nearly spherical, rock salt PbSe quantum dots. This material defines a new excitonic prototype, in that both the VBM states and the CBM states originate from the L valleys of the bulk fcc Brillouin zone. Because the L valley is 4-fold degenerate, the dimension of the excitonic manifold is 64 (including spin). However, quantum-confined electronic states derived from the bulk L valleys are split by intervalley coupling, interband coupling, effective mass anisotropy, and finite barrier confinement.[12,13] Electron−hole Coulomb and exchange interactions induce additional splittings of the excitonic energy levels. To clarify these effects, we have calculated the excitonic fine structure of PbSe quantum dots of radius $R = 15.3$ Å and $R = 30.6$ Å using a configuration-interaction approach.[8,9] We identify two main energy splittings, both of which are accessible to experimental probe: (i) The intervalley splitting is the energy difference between the two near-edge peaks of the absorption spectrum. We find $= 80$ meV for the 15.3 Å radius dot, and $= 18$ meV for the 30.6 Å d radius dot. (ii) The exchange splitting ¢$_x$ is the energy difference between the lowest-energy optically *dark* exciton state and the lowest-energy optically *bright* exciton state. We find that ¢$_x$ decreases from 17 meV for $R =$ 15.3 Å to 2 meV for $R = 30.6$ Å. (iii) Interestingly, while in CdSe dots, the exciton splits into a lower-energy dark doublet and a higher-energy bright doublet, in PbSe dots the lowest-energy exciton state is a nondegenerate dark state, followed by a triply degenerate bright state. (iv) Our calculated exciton fine structure gives the temperature dependence of the radiative lifetime $_R$. At room temperature, $_R$ is $\sim 10^2-10^3$ ns, considerably longer than ~ 10 ns in CdSe dots, in quantitative agreement with experiment.[14,15] We discuss our calculated results in view of recent experimental measurements of Stokes shift and radiative lifetime of PbSe colloidal quantum dots.

Method of Calculation. We use the following three steps to calculate the fine structure of low-energy exciton states.[8,12,13,16]

In step 1, we calculate the single-particle eigenstates of a quantum dot by solving the effective Schrödinger equation:

where the wave functions $\psi_i(\mathbf{r},\ )$ are expanded in a plane wave basis set. The spin−orbit coupling operator $\hat{V}_{SO}$ is given by

where $\langle l_{\mathbf{R}_{n,\alpha}}$ is a projection operator of orbital angular momentum l centered at $\mathbf{R}_{n,\alpha}$, and $V^{SO}_{l,\alpha}$ is a Gaussian p-like potential. The case $_{SO}$

The effective radius R is calculated using the formula $R = a_0(\ N_{\mathrm{dot}})^{1/3}$, where $\ = 3/32\ $ and N_{dot} is the total number of real atoms in the dot. The dangling bonds at the surface of the quantum dots are passivated by "ligand potentials", in order to remove all surface states[16] from the dot band gap to $\sim$1 eV away from the band edges.

In step 2, we calculate electron−hole Coulomb (

Excitonic Spectrum and its Deconvolution into Distinct Contributions: Excitonic Exchange-Splitting. In PbSe quantum dots, the lowest-energy excitonic manifold originates from the electron−hole configurations ($h_1 - h_4$) ⊗ ($e_1 - e_4$). Since each single-particle state is doubly degenerate (because of Kramer's degeneracy), the dimension of the full ground-state excitonic manifold is 64. These 64 excitonic states are split by intervalley and interband couplings as well as electron−hole Coulomb and exchange interactions. To identify the physical factors leading to the fine-structure splittings, we show in Figure 2 the evolution of the excitonic states originating from the configurations (h_1) ⊗ (e_1) and (h_2) ⊗ (e_2) as a function of the level of approximation used in

(no spin−orbit coupling), the $(h_1) \otimes (e_1)$ exciton splits into a lower-energy spin triplet (dark) and a higher-energy spin singlet (bright). This type of exchange splitting was found for example in calculations of the excitonic fine structure of Si quantum dots,[5,10] where the spin−orbit coupling was neglected (see Figure 1c). As $_{SO}$ is gradually increased (Figure 3), the lowest excitonic level becomes a nondegenerate dark state, while the higher excitonic level becomes a 3-fold degenerate bright state. This result indicates that spin−orbit coupling dramatically alters the excitonic fine structure of PbSe quantum dots and that the spin-singlet and spin-triplet characters are heavily intermixed in the presence of spin−orbit coupling. Because the orbital character of the band-edge single-particle wave functions is the same for other PbSe quantum dots in this size range, we expect that the fine-structure splitting shown in Figure 3 is a characteristic feature of PbSe quantum dots.

distribution effects and line-broadening in the procedure used by Schaller et al.[25]

Radiative Lifetime. Figure 6 shows the radiative lifetime $_R$ of PbSe quantum dots as a function of temperature T, calculated from eq 12. The effective dielectric constants ϵ_{dot} of the dot is obtained using a modified Penn model[8] ($\epsilon_{dot} =$ 10.77 for $R = 15.3$ Å, and $\epsilon_{dot} = 15.69$ for $R = 30.6$ Å). The dielectric constant of the surrounding matrix ($\epsilon_{out} = 2.1$, corresponding to chloroform) is chosen to be consistent with the experimental setup of Wehrenberg et al.[14] The computed room-temperature radiative lifetimes of PbSe dots of radius $R =$

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