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Using two-dimensional photon echo spectroscopy to probe the fine structure of the ground state biexciton of CdSe nanocrystals

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ABSTRACT

The origin of the fine structure of the ground state single- and biexciton of CdSe nanocrystals is reviewed, along with the theoretical framework used to describe these states. Calculations were performed to determine the transition dipole moments of optically allowed transitions from the single- to biexciton fine structure states. Two-dimensional photon echo spectroscopy measurements for a sample of CdSe nanocrystals are reported. The two-dimensional electronic spectrum at a population time of 0 fs is analyzed using a simulation based on k.p theory predictions of the exciton and biexciton manifolds of states. The analysis suggests that a particular excited state absorption transition from the single- to biexciton fine structure dominates the 2D spectra. These excited state absorptions are clearly resolved in 2D spectra and the method therefore has promise for gaining clearer insights into quantum dot spectroscopy.

1. Introduction

Semiconductor nanocrystals (NC) are unique materials characterized by their widely tunable absorption and emission spectra and their photostability. These properties have motivated a large body of work [1–5] on NCs based on their potential for applications such as photovoltaics [6], light emitting devices [7], spintronics [8] and as gain materials for lasers [9,10]. The most popular NC material studied to date has been CdSe, which is the material we will focus on here. One area of this field that is currently under intense scrutiny is multiple exciton generation [11–13], which suggests the possibility of using one photon to generate multiple exciton carriers. This involves excitation into high energy bands of the NC and the production of multiple excitons at lower energy levels. As a result, many recent studies have examined higher multiexcitonic states, their lifetimes, and relaxation mechanisms to lower lying excitonic states [1,4,14–17]. However, despite the great interest in this phenomena, very little is known about the electronic structure of these excitons, in particular the fine structure, since the inhomogeneous broadening of samples and the density of states [18] has proven to be prohibitive to experimental study of these states. In the following section we briefly review the origins of NC fine structure, and the theoretical and experimental work which has led to our current understanding of the fine structure of the ground state exciton and biexciton. Section 2 will explain the method used to theoretically describe the fine structure of these two states, and Section 3 will report two-dimensional photon echo (2DPE) spectroscopy, the results obtained using a CdSe NC sample, and a comparison to a simple simulation.

1.1. Origins of excitonic fine structure

Semiconductor NCs are composed of hundreds of unit cells, described by Bloch functions, and each cell has a HOMO and a LUMO. Taken together, these form valence and conduction bands, respectively. In the case of CdSe quantum dots, an sp^3 hybridized semiconductor, 4p orbitals in Se form the valence band, while the conduction band is comprised of 5s orbitals in Cd. A single electron excitation from the highest occupied valence band to the lowest unoccupied conduction band creates an s-type excited electron, and a p-type hole [19]. Due to the small size of the NCs, the electron and hole are confined together, and treatments of the electron and hole as a single exciton quasiparticle have been shown to be accurate and practical [20]. Changing the size of the NC affects the amount of exciton confinement, allowing for the tunability of the energy levels of the electronic states. This is observed in absorption and photoluminescence spectra. The first excitonic state produces the low energy feature seen in absorption spectra of semiconductor NCs, and the position of this feature is indicative of the size of the NC [21].

Semiconducting NCs are composed of heavy elements, leading to an increase in the effect of spin–orbit coupling compared to

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organic molecules. The splitting caused by spin–orbit coupling is so large that the two levels are commonly referred to as two separate bands, the $\Gamma_6 \times \Gamma_8$ band for the lower energy level and the $\Gamma_6 \times \Gamma_7$ or "split-off" band for the higher energy level [2]. In CdSe NCs, spin–orbit coupling results in a splitting of ~418 meV in the first excitonic state, as shown in Fig. 1. The first biexcitonic state, with two electrons excited from the HOMO to the LUMO, is also split by spin–orbit coupling, as shown. In the following work, we will consider an experiment where the laser pulse is resonant with the lower energy states of the single exciton fine structure, which allows for excited state absorption to the lowest fine structure states of the ground state biexciton.

Owing to this strong spin–orbit coupling in NCs, it is total angular momentum (instead of spin, as in molecules) which is a good quantum number. In other words, the states within the fine structure of NCs can be chosen to be eigenstates of the total angular momentum, and thus are conveniently labeled by their projected total angular momentum on the unique crystalline c-axis (F). An excited electron can have $F_{electron} = \pm 1/2$ since it is in an s-type conduction band orbital, while a hole can be $F_{hole} = \pm 3/2$ or $\times 1/2$ since it is in a p-type valence band orbital. Thus, an electron–hole pair can have $F = \pm 2, \pm 1$ or 0. The lowest excitonic state of CdSe NCs is comprised of eight fine structure states, two with $F = \pm 2$, four with $F = \pm 1$ and two with $F = 0$.

Owing to the confinement of the electron and hole, the exchange interaction becomes a significant contribution to the fine structure of NCs. In molecules, the exchange interaction causes the splitting of degenerate configuration states into singlet and triplet states. The exchange interaction produces a similar result in NCs, causing the splitting of degenerate states into bright and dark states, but the states are total angular momentum states instead of pure spin states. The states at higher energy have a total angular momentum of $\times 1$ (and thus $F = \pm 1$ or 0), while the lower energy states have a total angular momentum of $\times 2$ ($F = \pm 2, \pm 1$, or 0). The lower energy states are forbidden within the electric dipole approximation since a photon cannot carry an angular momentum of 2 [2,22]. Notice that states with projected total angular momentum of $\times 1$ and 0 can be either dark or bright. To distinguish between these states, they are referred in this work as upper ($F = \pm 1^U, 0^U$) or lower ($F = \pm 1^L, 0^L$). The right side of Fig. 1 illustrates the effect of the exchange interaction on each of the spin–orbit bands. Exchange is always a term which lowers the energy of spin aligned electrons relative to spin-paired electrons, since it lowers the amount of Coloumb repulsion between electrons by considering the effects of the Pauli exclusion principle: since two electrons with the same quantum numbers cannot exist in the same space, the Coloumbic repulsion will be lessened in a triplet state, where the unpaired electrons have the same spin. The exchange interaction does not cause splitting in the biexcitonic state, discussed in Appendix B.

The left side of Fig. 1 illustrates the effect of a wurtzite crystal field. This splitting would be absent in a cubic structure, where the

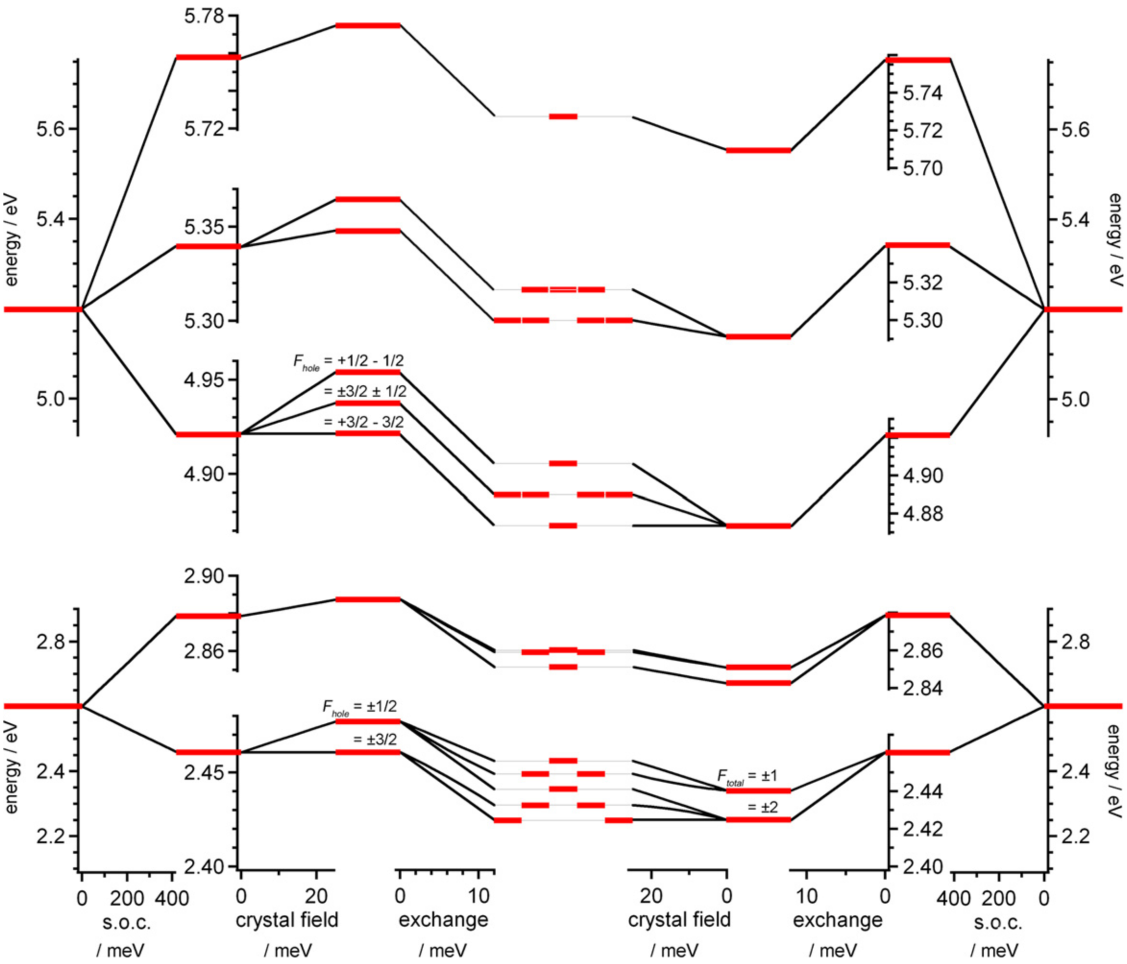

Fig. 1. Origins of the fine structure of the ground state single- and biexciton, in the lower and upper panels, respectively. Spin–orbit coupling (s.o.c.) causes the largest splitting, into two/three separate bands of states in the ground state single/biexciton. The right side shows splitting of each band due to the exchange interaction, the left side shows the effect of a wurtzite crystal field. The center shows the results when both exchange and crystal field are taken into account. The positioning of the states horizontally denotes the projection of total angular momentum of the state on the z-axis (F).