Communication

Photoluminescence enhancement through symmetry breaking induced by defects in nanocrystals

Peter C Sercel, Andrew Shabaev, and Alexander Lev Efros

Nano Lett., **Just Accepted Manuscript** • DOI: 10.1021/acs.nanolett.7b01662 • Publication Date (Web): 17 Jul 2017Downloaded from <http://pubs.acs.org> on July 19, 2017**Just Accepted**

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

ACS Publications

Nano Letters is published by the American Chemical Society, 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Photoluminescence enhancement through symmetry breaking induced by defects in nanocrystals

Peter C. Sercel,^{*,†} A. Shabaev,^{*,‡} and Al. L. Efros^{*,¶}

[†]*T. J. Watson Laboratory of Applied Physics, California Institute of Technology,
Pasadena, California 91125, USA*

[‡]*George Mason University, Fairfax, VA 22030, USA*

[¶]*Naval Research Laboratory, Washington DC 20375, USA*

E-mail: psercel@caltech.edu; ashabaev@gmu.edu; efros@nrl.navy.mil

Abstract

We present a theoretical model for the effect of symmetry breaking introduced by the doping of semiconductor nanocrystals with Coulomb impurities. The presence of a Coulomb center breaks the nanocrystal symmetry and affects its optical properties through mixing of the hole spin and parity sublevels, breaking the selection rules responsible for the exciton dark state in undoped nanocrystals. After reviewing the effects on the exciton fine structure and optical selection rules using symmetry theory, we present a perturbative model to quantify the effects. We find that the symmetry breaking proceeds by two mechanisms: First, mixing by even parity terms in the Coulomb multipole expansion results in an exciton fine structure consisting of three optically active doublets which are polarized along x , y and z axes with a ground optically passive dark exciton state, and second, odd parity terms which break inversion symmetry significantly activate optical transitions which are optically forbidden in the

unperturbed nanocrystal due to both spin and parity selection rules. In the case of small sized “quasi-spherical” nanocrystals, introduction of a single positively charged Coulomb center is shown here to result in significant enhancement of the radiative decay rate at room temperatures by up to a factor of ten.

Introduction

Significant current interest in semiconductor nanocrystals (NCs) is connected with their potentially useful electronic and optical properties. The broad tunability of their absorption and photoluminescence, which is mainly controlled by just one synthetic parameter – the NC size,^{1,2} great optical stability and the opportunity to create super-crystals of NCs using bottom-up approach to assemblies,³ open exciting possibilities to create novel functional materials for multiple applications. The radiative decay time of photoluminescence (PL) in small size NCs is, however, quite long - it is on the order of 20 ns at room temperature even in the most heavily studied CdSe NCs,^{4,5} and is longer in the other studied NCs, made of A_3B_5 and A_2B_6 direct gap semiconductors.^{6,7} It is clear that the ability to reduce the radiative decay time by one order of magnitude would open a path to new potential applications or increase the efficiency of the others in areas such as lighting, display technology and nanophotonics by enabling enhanced emission efficiency and stronger exciton-photon coupling.

The relatively long radiative decay of CdSe and other semiconductor NCs as well as in various NC heterostructures is connected with the well-established fact that the ground exciton state in these nanostructures is an optically forbidden –dark– exciton. Indeed in a spherical shape NC made of direct gap semiconductors with cubic or zinc-blende lattice structures the ground exciton level is an optically forbidden state with total angular momentum 2, five-fold degenerate with respect to the total angular momentum projections ± 2 , ± 1 and 0. The upper, optically active, exciton level has total angular momentum 1, which is three-fold degenerate with respect to the total angular momentum projections ± 1 and 0, and is separated

from the ground exciton level by the electron-hole exchange energy 4η .^{8,9} The enhancement by spatial confinement of the exchange energy is inversely proportion to the NC volume^{9,10} $4\eta \sim 1/a^3$, where a is the NC radius, and in small nanocrystals, due to the effect of the long range exchange interaction, can be of the order of 100 meV.¹⁰ The typical radiative decay time of the upper bright excitons with angular momentum 1, τ_0 , is on the order of several nanoseconds. However, in small size spherical NCs these levels remain largely unpopulated even at room temperatures. At the same time, the radiative decay time of the dark exciton in CdSe NCs was measured to be on the order of 1 μ s at low temperatures at which only the dark exciton is populated.^{4,5,8} Its activation is connected with various phonon or dangling bond assisted mechanisms of the dark exciton recombination.¹¹

In wurtzite CdSe NCs, both the hexagonal crystal field and the NC shape asymmetry contribute to splitting the hole levels.^{9,12} The reduction of the NC symmetry associated with these effects leads to an exciton fine structure consisting of five sublevels, and also activates the lowest ± 1 exciton level.⁹ Even so, the presence of the dark exciton dominates the PL. The reduction of the spherical symmetry splits the four fold degenerate ground $1S_{3/2}$ hole levels in spherical NCs into two spin sublevels separated by energy Δ : The lower, $\pm 3/2$, and the upper $\pm 1/2$, hole sublevels. The activation is controlled by the ratio of Δ to the exchange energy η and leads to the following expression for the radiative decay rate of the $\pm 1^L$ exciton:⁹ $1/\tau_{\pm 1}^L = (1/\tau_0)(\sqrt{3}\Delta/16\eta)^2$ at $\Delta \ll \eta$. While the bright exciton $\pm 1^L$ is populated at room temperature because it is just $3\Delta/4$ above the ground dark exciton, its oscillator strength is a small fraction of that of the upper bright levels and does not appreciably affect the overall radiative decay rate except for the smallest NCs; for moderate sized NCs the radiative lifetime at room temperature is ~ 20 ns and is dominated by the thermal population distribution among the upper bright exciton levels and the dark and weakly emitting levels.

It is important to note that in wurtzite CdSe NCs, the axis of CdSe NC growth coincides with the NC wurtzite c-axis. As a result the contributions of the crystal field and the shape

1
2
3 asymmetry effects discussed above sum into a total axial splitting: $\Delta_{ax} = \Delta_{cf} + \Delta_{sh}$, where
4
5 Δ_{cf} describes the splitting caused by the crystal field¹³ and Δ_{sh} describes the splitting caused
6
7 by deviation of the NC shape from spherical.¹² In elongated CdSe NCs, Δ_{sh} is negative and
8
9 in small size NCs can lead to $\Delta_{ax} = 0$ even if the NCs do not have a spherical shape.⁹ These
10
11 “quasi-spherical” NCs possess the optical properties of pure spherical NCs, and can have
12
13 very long radiative decay time for the smallest NCs even at room temperatures.
14

15
16 Recently, Sahu et.al. reported an enhancement of the PL intensity of up to ten times
17
18 in CdSe NCs doped by a single Ag atom.¹⁴ Evidence was presented in that study that
19
20 at low doping levels the Ag atoms act as n-type donors which when ionized leave behind
21
22 a positive charge center within the NC; the extra electron was surmised to be trapped
23
24 outside the NC by virtue of the absence of any indication of trion emission and associated
25
26 nonradiative Auger recombination. Motivated by this result, in this paper we consider the
27
28 effect of symmetry breaking introduced by the doping of NCs with Coulomb impurities. The
29
30 level structure of the exciton is considered as in spherical NCs within a four-band model for
31
32 the Γ_8 valence bands by incorporating the effects of the axial field¹³ and the electron-hole
33
34 exchange interaction.^{8–10} This commonly used “standard model”, which is reviewed in the
35
36 Supporting Information, will be considered as the unperturbed system in our paper. The
37
38 presence of a Coulomb center breaks the NC symmetry and affects the PL through mixing
39
40 of the hole spin and parity sublevels, leading to a violation of the selection rules responsible
41
42 for the exciton dark state in undoped CdSe NCs. After reviewing the effects on the exciton
43
44 fine structure and optical selection rules using symmetry theory, we present a perturbative
45
46 model to quantify the effects. The magnitude of the Coulomb center perturbation depends
47
48 on the position of the impurity within the NC and inversely on the NC radius. As a result
49
50 the mixing is particularly strong in the smallest NCs. The symmetry breaking proceeds by
51
52 two mechanisms: First, mixing by even parity terms in the Coulomb multipole expansion
53
54 results in an exciton fine structure consisting of three optically active doublets which are
55
56 polarized along x , y and z axes with two optically passive exciton states, one of which is the
57
58
59
60

ground state, and second, the odd parity terms which break inversion symmetry significantly activate optical transitions which are optically forbidden in the unperturbed NC due to spin and parity selection rules. We show that in the case of “quasi-spherical” NCs, introduction of a single positively charged Coulomb center can result in significant enhancement of the radiative decay rate at room temperatures by up to a factor of ten in small sized NCs. This is a likely explanation for the ten-fold enhancement of the PL intensity observed in CdSe NCs doped by single Ag atoms.¹⁴

Symmetry analysis

CdSe and other wurtzite semiconductors are characterized by the crystallographic point symmetry group C_{6v} . This is the symmetry relevant to the band-edge states at the Γ point of the Brillouin zone. The electronic structure of this material is commonly modelled using the quasi-cubic approximation^{9,15,16} wherein the underlying valence band structure is taken to be described by the Luttinger-Kohn (LK) Hamiltonian¹⁷ in the spherical approximation, with the addition of a crystal field splitting which separates the $J_z = \pm 3/2$ and the $J_z = \pm 1/2$ valence band edge states. A good starting point for describing the electronic states is therefore the spherical NC with no crystal field, whose model symmetry is the full rotation group. As summarized in Table 1 the band-edge electron and hole states can then be labelled with their total angular momentum quantum numbers, where total angular momentum $\mathbf{F} = \mathbf{J} + \mathbf{L}$. Here $\mathbf{J}$ and $\mathbf{L}$ are the angular momenta of the Bloch function and envelope functions.^{9,18–20} The introduction of the hexagonal crystal field in principle breaks the symmetry of the model to C_{6v} . While in principle there can be odd-parity terms representing the lack of inversion symmetry in wurtzite crystals, these terms are small and are commonly neglected. Neglecting inversion asymmetry, the system Hamiltonian has symmetry D_{6h} rather than C_{6v} . Further neglecting warping terms in the band structure, the model symmetry is $D_{\infty h}$ in the absence of any other extrinsic perturbation such as a shape distortion from spherical symmetry or

the like. Because of the rotational invariance about the c-axis, the projection of total angular momentum about the c-axis (taken to lie along z) is a good quantum number. This descent in symmetry is illustrated in Fig.1. The symmetries of the band edge states as we follow this progression are shown in Fig.1 and Table 1 as are the relations of the angular momentum quantum numbers to the irreducible representations of the point groups; the selection rules and degeneracies shown follow the notation used in the KDWS tables.²¹ The electron and hole states are described by the double group (half-integer spin) irreducible representations for the relevant point group. The exciton quantum numbers/ irreducible representations (irreps) are then determined by decomposing the product representation $\Gamma_e \times \Gamma_h$ for the electron-hole pairs into irreducible representations. This decomposition reflects the further splitting of the band-edge exciton by the electron-hole exchange interaction.

Note that the selection rules and degeneracies are the same for C_{6v} and $D_{6h}/D_{\infty h}$ with the exception of the parity selection rule which is absent in the point group C_{6v} . For example in the case of point groups $D_{\infty h}$ or D_{6h} , the parity selection rule (not shown in Table 1) would prohibit optical dipole transitions involving the $1P_{3/2}1S_e$ exciton states. Here we have adopted the nomenclature $n_h L_{J_h} n_e L_e$ to denote an electron hole pair manifold formed from the n_e -th electron state with envelope angular momentum L_e and the n_h -th hole state with total angular momentum J_h formed by mixing envelope angular momentum L_h and $L_h + 2$.²² We now consider the effect of adding a charged impurity to a spherical NC. If the NC does not have a hexagonal crystal field, or if its Hamiltonian reflects quasi-spherical symmetry as discussed in the introduction, the covering group with the defect present is simply $C_{\infty v}$, where now, the axis of symmetry is defined by the orientation of the defect. Similarly, if a charged impurity is added to a wurtzite NC with the impurity oriented along the z-axis, defined parallel to the wurtzite crystal field axis, the symmetry group remains $C_{\infty v}/C_{6v}$ and the selection rules and degeneracies do not change. This is shown in Fig.1. The situation is different if the charged defect is located at an arbitrary orientation $\hat{u}$ relative to the crystal field axis. Unless the impurity is oriented along a special direction, there are then no longer

any C_2 axes but only a reflection plane containing the c-axis and the impurity axis $\hat{u}$; as such the covering group is C_s (See the far right drawing in Fig.1 (b)). For point group C_s , by symmetry, there can be no dark states. Table 1 illustrates this for the case where we have taken an impurity to lie in the x, z plane so that the covering group possesses only the mirror plane symmetry σ_{xy} perpendicular to the y axis. For this configuration, the X and Z exciton states of the parent $C_{\infty v}$ group are mixed, producing exciton states with linearly polarized dipole moments in the x, z plane, which are generally not mutually orthogonal, and the perturbation also mixes the Y polarized and dark exciton states of the $C_{\infty v}$ point group. Importantly, all exciton states are dipole allowed in C_s symmetry!

Only if the off-center impurity is aligned specially along the c-axis (giving point symmetry $C_{6v}/C_{\infty v}$) or if it lies within the x-y plane (giving point symmetry group C_{2v}) can there be dark states. This result suggests a mechanism by which introduction of charged Coulomb centers can increase the PL efficiency in systems such as that reported by Sahu et.al.¹⁴ Introduction of a Coulomb center lowers the symmetry so that the defining selection rules of the dark state are broken. Critically, the Coulomb center breaks the inversion symmetry, and when asymmetrically located, this causes all transitions involving the band-edge exciton fine structure sub-levels to be in principle dipole-allowed.

While these symmetry arguments are rigorous, the question remains how strong, quantitatively, is the perturbation which breaks the symmetry. If the perturbation is sufficiently weak, there will be approximate symmetries which will preserve the dark states' selection rules. For example, if the perturbation represented by a charged impurity is sufficiently weak, parity breaking mixing between even and odd states could be neglected giving an approximate symmetry C_{2h} for an arbitrary defect orientation. This is illustrated conceptually in Fig. 1 (d) by drawing two impurities oriented symmetrically along axis $\hat{u}$. If the Coulomb perturbation is very weak, although point group C_{2h} does not allow dark states, those states have a very small oscillator transition strength. In that case the exciton fine structure can be modeled approximately in degenerate perturbation theory within the subspace spanned

by the ground exciton $1S_{3/2}1S_e$ and the approximate model Hamiltonian can be shown to possess D_{2h} symmetry, even for an arbitrary impurity orientation in the presence of a crystal field, and even in the presence of multiple impurities.

Figure 1: Schematic illustration of the descent in symmetry from a spherical NC to a NC with axial crystal field along the z -axis with charged impurities located along an arbitrary axis $\hat{u}$ from the NC center. Defects are schematically shown as red balls. In (a) the covering group and the symmetry operations for each model shown in (b) are listed. By C_n^u we indicate an n -fold rotation about axis $\hat{u}$; σ_{mn} denotes the mirror plane containing axes m and n ; and i denotes inversion. For the C_{2h} and C_s models, the axis of the defects, $\hat{u}$, is taken to lie in the x - z plane. Panel (c) shows the quantum numbers or irreps for the exciton states derived principally from the $1S_{3/2}1S_e$ pair states under each covering group; the $1P_{3/2}1S_e$ derived excitons are not shown but can become optically allowed through mixing with the $1S_{3/2}1S_e$ excitons in the point groups lacking inversion symmetry. (d), Examples of possible approximate symmetries corresponding to the neglect of parity breaking terms in the Hamiltonian. For the C_{2h} model we show both the exact irreducible representations corresponding to the covering group as well as the approximate irreducible representations corresponding to the approximated Hamiltonian (symmetry D_{2h}) if coupling to excited states is neglected (see text).

As shown in Figure 1 and Table 1, with approximate symmetry D_{2h} the $1S_{3/2}1S_e$ exciton always has two dark sublevels, and the optically allowed sublevels would be mixed in such

Table 1: Point Groups, irreducible representations (irreps), and selection rules relevant to models of wurtzite nanocrystals. The table shows the descent in symmetry from the full rotation group of a spherical NC in the spherical approximation as we add the hexagonal crystal field and impurity potentials for different configurations. For the model point groups with inversion symmetry, the parity quantum numbers are not written as they are obvious. The axial crystal field associated with the underlying wurtzite lattice is denoted H_{cf} , referring to Eq. S26 of the SI; while terms associated with extrinsic perturbations such as impurity centers are denoted in terms of real p and d spherical harmonics. C_{p_u} or $C_{d_{u2}}$ denote perturbations associated with an impurity center oriented along direction $\hat{u}$. Specific directions are defined, e.g., as x or x' ; when directions are specified as u this indicates no special direction. In that case, selection rules are written taking $\hat{u}$ to lie in the $x - z$ plane for specificity. In all cases the hexagonal crystal field is taken to be oriented such that the c -axis lies along z . Irreducible representations and selection rules shown are for the $1S_{3/2}1S_e$ exciton sublevels.

Sym.	Full Rot	$D_{\infty,h}; D_{6h}$	$C_{\infty,v}; C_{6v}$	D_{2h}	$C_{2h}(C_2^y)$	$C_{2v}(C_2^x)$	$C_s(\sigma_{u,z})$
H	$H_o = H_{ex}$	$H =$ $H_o +$ H_{cf}	$H =$ $H_o +$ $H_{cf} +$ $C_{p_u} Y_{p_u}$	$H =$ $H_o +$ $H_{cf} +$ $C_{d_{x2}} Y_{d_{x2}}$	$H =$ $H_o +$ $H_{cf} +$ $C_{d_{u2}} Y_{d_{u2}}$	$H =$ $H_o +$ $H_{cf} +$ $C_{p_x} Y_{p_x} +$ $C_{d_{x2}} Y_{d_{x2}}$	$H =$ $H_o +$ $H_{cf} +$ $C_{p_u} Y_{p_u} +$ $C_{d_{u2}} Y_{d_{u2}}$
CB irrep	$F = 1/2$	$F_z = \pm 1/2$	$\Gamma_7(2)$	$\Gamma_5(2)$	$\Gamma_3(1), \Gamma_4(1)$	$\Gamma_5(2)$	$\Gamma_3(1), \Gamma_4(1)$
VB irrep	$F = 3/2$	$F_z = \pm 1/2$ $F_z = \pm 3/2$	$\Gamma_7(2)$ $\Gamma_9(2)$	$\Gamma_5(2)$ $\Gamma_5(2)$	$\Gamma_3(1), \Gamma_4(1)$ $\Gamma_3(1), \Gamma_4(1)$	$\Gamma_5(2)$ $\Gamma_5(2)$	$\Gamma_3(1), \Gamma_4(1)$ $\Gamma_3(1), \Gamma_4(1)$
Exciton irrep	$F = 1(3)$ σ_+, σ_-, z	$F_z = 0 z$	$\Gamma_1(1) z$	$\Gamma_3 z$	$\Gamma_2(1) x, z$	$\Gamma_4(1) z$	$\Gamma_1(1) x, z$
		$F_z = \pm 1 \sigma_+, \sigma_-$	$\Gamma_5(2) \sigma_+, \sigma_-$	$\Gamma_4 x$	$\Gamma_2(1) x, z$	$\Gamma_2(1) y$	$\Gamma_2(1) y$
		$F_z = 0 d$	$\Gamma_2(1) d$	$\Gamma_2 y$	$\Gamma_1(1) y$	$\Gamma_1(1) x$	$\Gamma_1(1) x, z$
				$\Gamma_1 d$	$\Gamma_1(1) y$	$\Gamma_3(1) d$	$\Gamma_2(1) y$
	$F = 2(5)$ d	$F_z = \pm 1 \sigma_+, \sigma_-$	$\Gamma_5(2) \sigma_+, \sigma_-$	$\Gamma_2 y$	$\Gamma_1(1) y$	$\Gamma_2(1) y$	$\Gamma_2(1) y$
		$F_z = \pm 2 d$	$\Gamma_6(2) d$	$\Gamma_4 x$	$\Gamma_2(1) x, z$	$\Gamma_1(1) x$	$\Gamma_1(1) x, z$
				$\Gamma_3 z$	$\Gamma_2(1) x, z$	$\Gamma_4(1) z$	$\Gamma_1(1) x, z$
				$\Gamma_1 d$	$\Gamma_1(1) y$	$\Gamma_3(1) d$	$\Gamma_2(1) y$

a way as to produce excitons with two sets of three linearly polarized mutually orthogonal transition dipoles. This is the same pattern as seen with the previously discussed point symmetry C_{2v} because the two point groups, C_{2v} and D_{2h} , are isomorphic. To make further progress we must develop a quantitative model in order to determine what constitutes an acceptable approximate symmetry for a given defect configuration.

We turn in the next section to a description of the model developed to quantify these questions.

Electronic structure in doped spherical nanocrystals

In CdSe nanocrystals (NC) of spherical shape, the band-edge states are well described in the effective mass approximation within the framework of the standard quasi-cubic model.^{8–10} In this description, the zeroth order single particle states are expressed as eigenstates of the total angular momentum $\mathbf{F} = \mathbf{J} + \mathbf{L}$ where $\mathbf{J}$ and $\mathbf{L}$ are the angular momenta of the Bloch function and envelope functions. The electron-hole exchange interaction and the anisotropy associated with the axial crystal field and shape distortion are treated perturbatively.^{8–10} To this “standard model” of the CdSe NC, which is reviewed in the Supporting Information, we add a perturbative treatment of the Coulomb center potential associated with a charged defect inside a NC or at the NC surface.

Before proceeding we must establish the energy scale of the problem, which determines which basis states must be included to make an adequate description of the physics. The presence of a Coulomb center at $\mathbf{r}_0$ with spherical coordinates (r_0, θ_0, ϕ_0) creates a potential within the NC that can be written in terms of a multipole expansion:²⁴

$$V(\mathbf{r}) = \frac{qe}{\epsilon|\mathbf{r} - \mathbf{r}_0|} = \frac{qe}{\epsilon a} \sum_{l,m} \frac{4\pi}{(2l+1)} \frac{ar_{<}^l}{r_{>}^{l+1}} Y_l^{m*}(\theta_0, \phi_0) Y_l^m(\theta, \phi), \quad (1)$$

The prefactor $qe/\epsilon a$ parameterizes the strength of the Coulomb center perturbation and sets the relevant energy scale. Here, q is the charge of the center; ϵ is the average low-frequency

dielectric constant of the NC, and a is the NC radius. Note that in Eq. 1, for simplicity, we have neglected corrections due to the dielectric constant discontinuity at the NC surface, which tend to strengthen the Coulomb perturbation. We evaluate the energy spacings of the zero-order electron and hole states relative to this scale as a function of NC radius a , using Eqs. S7 and S14 of the SI, as shown in Fig.2. For reference, the wurtzite crystal field, Δ_{cf} , is also shown in Fig.2, as are the exchange energies for the $1S_{3/2}1S_e$ and the $1P_{3/2}1S_e$ excitons, $\eta_{1S_{3/2}1S_e}$ and $\eta_{1P_{3/2}1S_e}$, defined in Eqs. (S25) and (S23) of the SI, respectively. Inspection of the figure shows that the exchange energies for the $1S_{3/2}1S_e$ excitons have values of tens of meV for the smallest NCs and are significantly larger at any given radius than the $1P_{3/2}1S_e$ values; this reflects the effect of the long-range exchange interaction which affects the optically active $1S_{3/2}1S_e$ states but not the dipole inactive $1P_{3/2}1S_e$ excitons. The parameters used for all these calculations are summarized in Table S1 of the SI. Panel (a) in the figure shows that the first excited electron state, $1P_e$ can be safely neglected in our model since its energy separation from the ground electron state, $1S_e$, is more than an order of magnitude larger than the Coulomb energy for all NC radii considered – mixing involving the excited electron state will be negligible. On the other hand, the first excited hole state, $1P_{3/2}$ lies very close in energy to the ground $1S_{3/2}$ hole state relative to the Coulomb energy, so this state must be included in the model in order to capture the physics correctly. This can be seen most clearly in Fig.2(b) which shows the hole states on a linear energy scale. Also shown in both panels are the next two excited hole states, $1P_{5/2}$ and $1D_{5/2}$, the two parity states of total angular momentum $F = 5/2$. These states are very close in energy but both are separated in energy from the ground $1S_{3/2}$ hole state by an amount significantly larger than the Coulomb energy scale. Other excited hole states such as those corresponding to $F = 1/2$ are substantially higher in energy. As a result, coupling to these higher lying hole states is negligible in comparison to coupling between $1S_{3/2}$ and $1P_{3/2}$ so we neglect them in the analysis to follow. This approximation does impact the symmetry of calculated levels. For the doped NCs whose covering group is strictly C_{2h} , neglecting the coupling to the higher

lying $F = 5/2$ hole manifold results an approximate Hamiltonian with symmetry D_{2h} , which gives a ground dark exciton state (see the C_{2h} configuration and the level symmetry in Fig. 1(d)).

Figure 2: Key energy scales plotted versus NC radius, a . The level spacing between the ground- and first-excited electron and hole states, $\epsilon_e = E_{1P_e} - E_{1S_e}$ and $\epsilon_{P_{3/2}} = E_{1P_{3/2}} - E_{1S_{3/2}}$, respectively, are shown along with the Coulomb energy $\epsilon_c = qe/\epsilon a$. Here, E_{1P_e} and E_{1S_e} are the energies of the ground $1S_e$ and excited $1P_e$ electron levels. The exchange energy for the $1S_{3/2}1S_e$ and $1P_{3/2}1S_e$ excitons, $\eta_{1S_{3/2}1S_e}$ and $\eta_{1P_{3/2}1S_e}$, respectively defined in Eqs. (S25) and (S23) of the SI, and the wurtzite crystal field, Δ_{cf} , are shown for reference. Also shown are the level spacing between the ground- and second-excited hole states, $\epsilon_{P_{5/2}} = E_{1P_{5/2}} - E_{1S_{3/2}}$ and $\epsilon_{D_{5/2}} = E_{1D_{5/2}} - E_{1S_{3/2}}$, where $E_{1P_{5/2}}$ and $E_{1D_{5/2}}$ are the energy of $1P_{5/2}$ and $1D_{5/2}$ hole levels. Panel(a) displays the energies on a logarithmic scale while panel (b) shows a linear scale to more clearly show the hole energies. The plot shows that a realistic model of the exciton fine structure must include both the $1S_{3/2}$ and $1P_{3/2}$ hole states, while the first excited electron state, $1P_e$, and the more highly excited hole states corresponding to $F = 5/2$, only weakly contribute to the band edge states and can be neglected. The energies of electron states are calculated in the single-band approximation while the hole energies are determined in the four-band model associated with the Γ_8 band edge. Parameters used in these calculations are given in Table S1 of the SI.

As a result, in order to model the exciton physics with reasonable fidelity we must treat the excitons formed from the two-fold degenerate ground $1S_e$ electron and the four-fold degenerate $F = 3/2$ holes of both parities within quasi-degenerate perturbation theory. As such the Coulomb center perturbation is represented by a 16x16 matrix in this subspace. The dominant effects of the Coulomb center potential, Eq. (1) are due to the terms up to

$l = 2$; indeed, terms with $l \geq 4$ do not couple states within the $F = 3/2$ subspace. The $l = 0$ term creates an overall shift in the electron and hole energy levels; the $l = 1$ terms mix the even and odd parity hole states; while the $l = 2$ terms mix the hole spin sublevels for a given parity. While the $l = 3$ terms, like the $l = 1$ terms, also couple between the even and odd parity hole states $1S_{3/2}$ and $1P_{3/2}$, their effect, as quantified by the average radial Coulomb integral for these terms (described in the SI), is weaker than that of the $l = 1$ terms by roughly an order of magnitude so this term is neglected.

It is straightforward to evaluate the effect of the Coulomb potential, Eq. 1; we defer the details of the calculation to the Supporting Information and state the results. Using a basis of electron-hole pair states $1S_{3/2}1S_e$ denoted (F_z^e, F_z^h) taken in the order, $(1/2, 3/2), (1/2, 1/2), (1/2, -1/2), \dots, (-1/2, -3/2)$, followed by the $1P_{3/2}1S_e$ pairs are taken in the same order, the Coulomb perturbation takes the form of a 16x16 matrix,

$$H_V = \begin{pmatrix} H_{1S_{3/2},1S_{3/2}} & \tilde{0} & H_{1S_{3/2},1P_{3/2}} & \tilde{0} \\ \tilde{0} & H_{1S_{3/2},1S_{3/2}} & \tilde{0} & H_{1S_{3/2},1P_{3/2}} \\ H_{1S_{3/2},1P_{3/2}}^\dagger & \tilde{0} & H_{1P_{3/2},1P_{3/2}} & \tilde{0} \\ \tilde{0} & H_{1S_{3/2},1P_{3/2}}^\dagger & \tilde{0} & H_{1P_{3/2},1P_{3/2}} \end{pmatrix}. \quad (2)$$

The upper left 8x8 block governs coupling within the $1S_{3/2}1S_e$ exciton subspace; the lower right 8x8 block governs coupling within the opposite parity $1P_{3/2}1S_e$ exciton subspace; and the off-diagonal blocks describe the coupling between them. In the matrix above, $\tilde{0}$ is a four-by-four matrix of zeros which reflects the fact that the Coulomb perturbation does not flip the electron spin. For the $1S_{3/2}1S_e$ excitons, the 4x4 block is given by,

$$H_{1S_{3/2},1S_{3/2}} = H_{1S_{3/2},1S_{3/2}}^{l=0} + H_{1S_{3/2},1S_{3/2}}^{l=2}, \quad (3)$$

and, for the $1P_{3/2}1S_e$ excitons,

$$H_{1P_{3/2},1P_{3/2}} = H_{1P_{3/2},1P_{3/2}}^{l=0} + H_{1P_{3/2},1P_{3/2}}^{l=2} . \quad (4)$$

We first give the $l = 0$ Coulomb terms for both parities:

$$\begin{aligned} H_{1S_{3/2},1S_{3/2}}^{l=0} &= \frac{qe}{\epsilon a} \left(M_{1S_{3/2}}^h - M_{1S_e}^e \right) \hat{\mathbb{I}} , \\ H_{1P_{3/2},1P_{3/2}}^{l=0} &= \frac{qe}{\epsilon a} \left(M_{1P_{3/2}}^h - M_{1S_e}^e \right) \hat{\mathbb{I}} . \end{aligned} \quad (5)$$

In these equations, $\hat{\mathbb{I}}$ is the 4x4 identity matrix, $M_{1S_{3/2}}^h$, $M_{1P_{3/2}}^h$ and $M_{1S_e}^e$ are the dimensionless radial Coulomb integrals for the hole and electron respectively, which are associated with the monopole ($l = 0$) term in the Coulomb potential expansion. The explicit form of these integrals, which are plotted in Fig. 3(a), is given in the SI. Notably, $M_{1S_{3/2}}^h$ and $M_{1P_{3/2}}^h$ integrals give rise to shifts of opposite sign for the even and odd envelope parity exciton sublevels owing to the different structure of the radial wave functions of the hole for the two parities effecting charge density cancellation between the hole and the electron.

The $l > 0$ terms do not affect the $1S_e$ electron state. Importantly, however, they lead to mixing between the hole states. We consider the quadrupole ($l = 2$) terms first. Since the quadrupole terms have even parity they do not couple between the even and odd parity hole states and therefore, between the even and odd parity exciton states. At the same time, the angular dependence of these terms will be the same for the even and odd parity exciton manifolds, $1S_{3/2}1S_e$ and $1P_{3/2}1S_e$, respectively, because the hole states within each of these manifolds both have the same angular momentum, $F = 3/2$. As a result, corresponding matrix elements of each of the quadrupole terms for the two parities will be proportional, as a consequence of the Wigner-Eckart theorem. For the $1S_{3/2}1S_e$ excitons this matrix is given by,

$$H_{1S_{3/2},1S_{3/2}}^{l=2} = \frac{qe}{\epsilon a} N_{1S_{3/2}} \tilde{H}_{l=2} , \quad (6)$$

where $N_{1S_{3/2}}$ is a dimensionless radial Coulomb integral for the $1S_{3/2}$ states created by the quadrupole $l = 2$ expansion of Coulomb potential (see Eq. (1)) given explicitly in the SI and plotted in Fig. 3(b) as a function of the Coulomb center distance from the NC center d . Using the Wigner-Eckart theorem it is straightforward to show that the matrix $\tilde{H}_{l=2}$ has the form,

$$\tilde{H}_{l=2} = \begin{pmatrix} \frac{2\alpha}{\sqrt{5}} & -2\sqrt{\frac{2}{5}}\gamma & 2\sqrt{\frac{2}{5}}\beta & 0 \\ -2\sqrt{\frac{2}{5}}\gamma^* & -\frac{2\alpha}{\sqrt{5}} & 0 & 2\sqrt{\frac{2}{5}}\beta \\ 2\sqrt{\frac{2}{5}}\beta^* & 0 & -\frac{2\alpha}{\sqrt{5}} & 2\sqrt{\frac{2}{5}}\gamma \\ 0 & 2\sqrt{\frac{2}{5}}\beta^* & 2\sqrt{\frac{2}{5}}\gamma^* & \frac{2\alpha}{\sqrt{5}} \end{pmatrix}. \quad (7)$$

The terms α , β , and γ above are quadrupole functions of the angular coordinates, (θ_0, ϕ_0) , of the Coulomb center. They originate from the various Y_l^m terms in Eq. 1 for $l=2$. Using Eq. (S37) of the SI,

$$\begin{aligned} \alpha &= \frac{1}{\sqrt{4\pi}} \frac{4\pi}{5} (Y_2^0(\theta_0, \phi_0))^* = \frac{1}{\sqrt{20}} (3 \cos^2 \theta_0 - 1), \\ \beta &= \frac{1}{\sqrt{4\pi}} \frac{4\pi}{5} (Y_2^2(\theta_0, \phi_0))^* = \sqrt{\frac{3}{2}} \frac{1}{\sqrt{20}} \sin^2 \theta_0 e^{-2i\phi_0}, \\ \gamma &= \frac{1}{\sqrt{4\pi}} \frac{4\pi}{5} (Y_2^1(\theta_0, \phi_0))^* = -\sqrt{\frac{3}{2}} \frac{1}{\sqrt{20}} \sin 2\theta_0 e^{-i\phi_0}. \end{aligned} \quad (8)$$

The Hamiltonian submatrix for the $1P_{3/2}1S_e$ excitons is simply proportional to the submatrix for the $1S_{3/2}1S_e$ excitons as required by the Wigner-Eckart theorem, but it has a different pre-factor reflecting a different reduced matrix element for the $1P_{3/2}1S_e$ states:

$$H_{1P_{3/2}, 1P_{3/2}} = \frac{qe}{\epsilon a} N_{1P_{3/2}} \tilde{H}_{l=2}. \quad (9)$$

The governing $l = 2$ Coulomb integral for these states, $N_{1P_{3/2}}$ is also plotted in Fig. 3(b); it is appreciably smaller and opposite in sign from the corresponding Coulomb overlap integral for the $1S_{3/2}1S_e$ even parity exciton states.

Finally, the dipole terms due to the $l = 1$ components of the Coulomb potential cross

couple the even and odd parity hole states as required since this term breaks the inversion symmetry. Again using the Wigner-Eckart theorem these terms can be shown to have the form,

$$H_{1S_{3/2},1P_{3/2}} = \frac{qe}{\epsilon a} O_{1S_{3/2},1P_{3/2}} \begin{pmatrix} \sqrt{\frac{3}{5}}b_z & \sqrt{\frac{2}{5}}b_- & 0 & 0 \\ \sqrt{\frac{2}{5}}b_+ & \frac{b_z}{\sqrt{15}} & 2\sqrt{\frac{2}{15}}b_- & 0 \\ 0 & 2\sqrt{\frac{2}{15}}b_+ & -\frac{b_z}{\sqrt{15}} & \sqrt{\frac{2}{5}}b_- \\ 0 & 0 & \sqrt{\frac{2}{5}}b_+ & -\sqrt{\frac{3}{5}}b_z \end{pmatrix}, \quad (10)$$

where $O_{1S_{3/2},1P_{3/2}}$ is a dimensionless radial Coulomb integral caused by the $l = 1$ components of the Coulomb potential expansion, given explicitly in the SI and plotted in Fig. 3(b) as a function of the distance, d , of the Coulomb center from the NC center. The terms within the matrix derive from the various Y_l^m spherical harmonics in Eq. 1 for $l = 1$. Using Eq.(S37) of the SI, these are seen again to depend on the angular coordinates (θ_0, ϕ_0) of the defect:

$$\begin{aligned} b_z &= \frac{1}{\sqrt{4\pi}} \frac{4\pi}{3} Y_1^0(\theta_0, \phi_0) = \sqrt{\frac{1}{3}} \cos \theta_0, \\ b_+ &= \frac{1}{\sqrt{4\pi}} \frac{4\pi}{3} Y_1^{-1*}(\theta_0, \phi_0) = \sqrt{\frac{1}{3}} \frac{\sin \theta_0 e^{i\phi_0}}{\sqrt{2}}, \\ b_- &= -\frac{1}{\sqrt{4\pi}} \frac{4\pi}{3} Y_1^{1*}(\theta_0, \phi_0) = \sqrt{\frac{1}{3}} \frac{\sin \theta_0 e^{-i\phi_0}}{\sqrt{2}}. \end{aligned} \quad (11)$$

The $l = 1$ dipole terms mix the opposite parity $1S_{3/2}$ and $1P_{3/2}$ hole states. This mixing is quite appreciable as can be seen from the relative magnitude of the integral $O_{1S_{3/2},1P_{3/2}}$ in the plot. As required by symmetry, if $d = 0$ the radial integrals for both $l = 1, 2$ vanish.

Figure 3: Radial dimensionless Coulomb multipole integrals plotted versus the radial coordinate of the defect d relative to NC radius a . (a): The $l=0$ radial Coulomb integrals for the $1S_{3/2}1S_e$ and $1P_{3/2}1S_e$ excitons, respectively. (b): The $l=1$ and $l=2$ radial Coulomb integrals for the $1S_{3/2}1S_e$ and $1P_{3/2}1S_e$ excitons. The $l=2$ components cause mixing within the $1S_{3/2}$ and $1P_{3/2}$ hole sublevels but do not couple between opposite parity hole states (lines labeled N). The $l=1$ multipole term mixes the opposite parity $1S_{3/2}$ and $1P_{3/2}$ hole states.

The effect of the different multipole terms can be visualized by plotting the exciton level structure and the radiative transition rates for various NC configurations. The level structure was determined for each case by diagonalization of the exciton Hamiltonian including the electron-hole exchange and the wurtzite axial field in addition to the Coulomb perturbation, Eq. 1 (see the Supporting Information for details). The radiative transition rates for each state are then computed in terms of the matrix elements of the dipole operator $\hat{\mathbf{p}}$ using²³

$$\Gamma_k = \frac{1}{\tau_k} = \frac{4e^2\omega n_r}{3m_o^2c^3\hbar} D^2 |\langle \psi_k | \hat{\mathbf{p}} | o \rangle|^2 \quad (12)$$

The factor D above represents the dielectric depolarization for a spherical nanocrystal of dielectric constant ϵ_{NC} embedded in a dielectric medium of ϵ_{med} :²⁴

$$D = \frac{3\epsilon_{med}}{2\epsilon_{med} + \epsilon_{NC}} \quad (13)$$

The other factors in the expression are n_r , the refractive index of the medium surrounding the NC, taken here to be that of hexane; the angular frequency, ω , here taken to correspond to 570 nm emission and set constant in the calculations to facilitate visualizing the relative effects due to state mixing; m_0 is the free electron mass and ϵ_0 is the permittivity of free space. For reference and as shown in the Supporting Information, we note that these expressions lead to a radiative lifetime of 3.32 ns for the bright exciton state of a spherical CdSe NC in hexane, using the material and band parameters in Table S1 of the SI. In our calculations we purposely ignore the size dependence of the total exciton oscillator strength and the frequency dependence of the radiative decay time in order to focus on the effect and the role of the Coulombic potential.

It is well known that the crystal field Δ_{ax} destroys the full rotational invariance in spherical CdSe NCs leaving rotational symmetry about the c -axis, taken to be the z axis. This leads to the splitting of the $F = 1$ and $F = 2$ levels and their mixing but F_z remains a good quantum number. In the $1S_{3/2}1S_e$ exciton manifold, mixing leads to the optical activation of the lower $\pm 1^L$ levels, which pick up oscillator transition strength. The same type of splitting and mixing occurs in the $1P_{3/2}1S_e$ exciton manifold, however, all exciton sub-levels from this manifold remain optically passive. In Fig.4 we show the effect of a singly charged Coulomb impurity on the band edge exciton fine structure. In these calculations we neglect the odd multipole terms, retaining inversion symmetry for illustration purposes. At this level of approximation the system has symmetry D_{2h} even for arbitrary orientation of the defect; reference to Table 1 shows that this symmetry always gives rise to three optically active doublets which are orthogonally polarized along the principle axes of the D_{2h} Hamiltonian, labelled as x , y , and z , and two optically passive exciton states, one of which is always the ground state. Analytic expressions for the energy fine structure and the sublevels' transition dipole moments have been derived and will be published elsewhere.

The results for this case are plotted in Fig. 4 for a NC of radius $a = 1.2$ nm with $\Delta_{ax} = 25$ meV as a function of the radial position d/a of a defect aligned along an axis $\pi/4$ from the

c-axis. Panels (a) and (b) show the exciton sublevel energies and their radiative transition rates for a negative charge center while corresponding results for a positive charge are shown in Fig.4 (c) and (d), respectively. The main effect of the Coulomb mixing is creation of two sets of three dipoles that are orthogonally polarized along the principle symmetry axes of the system, and to pull down oscillator strength from the upper $0^U, \pm 1^U$ levels into the lower exciton states. This is reflected in the increased transition rates for the lower x, y, z exciton states shown in Fig.4 (b) and (d). Apart from other effects, this tends to accelerate the average radiative decay rates at a given temperature since the lower lying states, which have higher thermal occupancy at finite temperature, have gained oscillator strength. However the situation is more complex since the presence of the defect causes quite appreciable state shifting due to the $l = 0$ multipole term. This can be seen most clearly when the defect is located at the center of the NC ($d/a = 0$) since both the $l = 1$ and $l = 2$ multipole terms vanish by symmetry at this point (see Fig. 3(b)). For a negative charge $q < 0$, the effect is to pull the $1S_{3/2}1S_e$ derived excitons downwards in energy (by 32meV) and pull the dark $1P_{3/2}1S_e$ derived states upwards (by 66meV), separating the two by a huge amount. This is because the $1S_{3/2}1S_e$ ($1P_{3/2}1S_e$) exciton states have a net positive (negative) charge density at the origin. As a result, for this situation, the average population of the emitting states at a finite temperature will be relatively higher with a negative charge center in comparison with an undoped NC and therefore favoring a faster radiative decay rate. This situation is reversed for a positive charge center $q > 0$ where the $1S_{3/2}1S_e$ and the dark $1P_{3/2}1S_e$ derived states are pulled closer together: Other factors being equal, this effect favors lower population of the bright $1S_{3/2}1S_e$ states because thermal occupation of the dark $1P_{3/2}1S_e$ is enhanced relative to an undoped NC. The main point is that positive and negative charge centers affect the problem *differently* through their effect on the population balance due to the level shifting $l = 0$ component. Compounding the complexity of the problem, if the defect is located away from the NC center, level mixing effects come into play which pull down oscillator strength from higher energy to lower energy states. The net effect represents

a trade-off that is hard to predict; which effect dominates will depend on the parameters of the model, most notably the NC radius.

Figure 4: Exciton level structure and dipole transition rates for a CdSe NC with charged impurity, approximate symmetry D_{2h} , calculated for radius $a = 1.2$ nm with $\Delta_{ax} = 25$ meV. Level structure and transition rates plotted versus the radial position d/a for a defect aligned along an axis $\pi/4$ from the c -axis, for a negative charge (a) and (b), and positive charge (c) and (d), respectively. Red and black lines correspond to $(1S_{3/2}1S_e)$ exciton state manifold while blue lines correspond to $(1P_{3/2}1S_e)$ exciton state manifold. Symbols indicate the exciton states described by the following irreducible representations: $\circ$ – (Γ_3, z) , $\times$ – (Γ_2, y) , $+$ – (Γ_4, x) , and $\square$ – (Γ_1, d) .

Including the inversion-breaking $l = 1$ Coulombic terms in the calculations further complicates the picture since this term will couple the even and odd parity excitons as seen in

Figure 5. There we show the level structure and dipole transition rates for $\Delta_{ax}=25\text{meV}$ as a function of the radial defect position d/a for a positively charged defect oriented at angle $\phi_0 = 0$, $\theta_0 = \pi/4$ from the c-axis in a NC of radius $a = 1.2\text{ nm}$ in panels (a,b); versus angle θ_0 in a NC of radius $a = 1.2\text{ nm}$ in panels (c, d), with the defect positioned one half radius from the NC center ($d/a = 0.5$); and versus NC radius a in panels (e,f) for defect coordinates $\phi_0 = 0$, $\theta_0 = \pi/4$ and $d/a = 0.5$. The breaking of inversion symmetry allows the $1S_{3/2}1S_e$ and $1P_{3/2}1S_e$ pair states to mix, resulting in a complex, nearly continuous level structure which is sensitively dependent on the angular and radial position of the defect, as inspection of the figure will show. For these cases, all the exciton sublevels become dipole allowed: The only exceptions are for those configurations in which the defect lies along special symmetry directions such as the c-axis (giving a configuration with symmetry $C_{\infty v}$) or in the plane perpendicular to it (giving symmetry (C_{2v})). In the figure, lines that correspond to states predominantly formed from $1S_{3/2}1S_e$ versus $1P_{3/2}1S_e$ pairs at small d/a are labelled with different symbols (see figure caption). The key point is that for the general case of arbitrary θ_0 the exciton fine structure does not have dark exciton states.

Figure 5: Exciton level structure and dipole transition rates for a CdSe NC with a positively charged impurity, retaining Coulomb dipolar terms (symmetry C_s). Dependence of the level structure (a) and transition rates (b) on the radial position of the defect, d/a , for $\phi_0 = 0$, $\theta_0 = \pi/4$ calculated at a NC radius $a = 1.2$ nm with $\Delta_{ax} = 25$ meV. Dependence of the energy level structure (c) and the dipole transition rates (d) on the defect angular orientation θ_0 calculated for fixed $d/a = 0.5$ and $\phi_0 = 0$ calculated in NC with radius $a = 1.2$ nm. Note that the transition rates of certain states go to zero at special angles such as $\theta_0 = 0, \pi/2$ reflecting the special symmetries of these configurations. Dependence of the energy level structure (e) and their transition rates (f) on the NC radius a calculated for defect coordinates $\phi_0 = 0$, $\theta_0 = \pi/4$ and $d/a = 0.5$. Symbols indicate the irreducible representation: $\circ$ and $\diamond$ – (Γ_1, x, z) ; $\square$ and $\triangle$ – (Γ_2, y) . Lines with symbols $\circ$ and $\square$ correspond to states predominantly formed from the $1S_{3/2}1S_e$ exciton state manifold at small d/a and lines with symbols $\diamond$ and $\triangle$ correspond to states primarily formed from $1P_{3/2}1S_e$ exciton state manifold at small d/a . For the general case of arbitrary θ_0 there are no dark states.

Consideration of the level structure depicted in Fig.5 makes it very clear that in order to assess the overall effect of the charged center on the PL efficiency we must consider that NC radiative emission can occur from multiple states whose populations are coupled through fast inter-level scattering. At room temperature it is known that transitions between the fine structure levels in CdSe NCs occurs on a ps timescale,²⁵ much faster than the radiative lifetimes of the individual fine structure levels. In this case the NC radiative decay rate is the thermally weighted average of the decay rates of all exciton sublevels, which are populated according to a thermal equilibrium distribution. Assuming that all exciton states, k , with energy E_k are populated according to a Boltzmann distribution, the effective lifetime of the thermalized nanocrystal at temperature T can be written

$$\tau = \frac{\sum_k e^{-E_k/k_B T}}{\sum_k (\Gamma_k e^{-E_k/k_B T})} \quad (14)$$

where $\Gamma_k = 1/\tau_k$ is the radiative decay rate of the k exciton state defined in Eq.12 and k_B is Boltzmann's constant. In Fig. 6 we show the effective lifetimes at room temperature as a function of NC radius a for the case of no impurity, and for both positive and negative charge centers. All the calculations shown assume that the defect is located in the x-z plane at angle $\theta_0 = \pi/4$ from the c -axis and at the mid-radius point $d/a = 0.5$. Panel (a) was calculated for a NC with $\Delta_{ax} = 25$ meV while panel (c) shows calculations for a "quasi-spherical" NC with $\Delta_{ax} = 0$ meV.

The right hand side panels (b) and (d) show the ratio of the lifetime for the doped NC relative to an undoped NC of the same size. The plots show that at large radii a positive charge center causes a slight increase of the radiative lifetime by about 15% which is due primarily to the Coulomb level shifting effect discussed above. For negative charge centers this effect is opposite and there is a slight reduction in the radiative lifetime. However at small NC radii $a \leq 1.5$ nm the situation is different. As the NC radius a decreases, the exchange energy increases ($\eta_{ex} \sim 1/a^3$ in this model) causing the upper, strongly emitting,

1
2
3
4 levels of an undoped NC to shift upwards and become depopulated at finite temperature.
5
6 This leads to a dramatic increase of the radiative lifetime for radii $a \leq 1.5$ nm in Fig. 6.
7
8 This effect is counteracted by level mixing in NCs with an off-center Coulomb impurity:
9
10 Level mixing induced by the center transfers oscillator strength to lower sub-levels that are
11
12 thermally populated, reducing the effective lifetime at any given temperature. The effect
13
14 becomes significant, however, only if the $1S_{3/2}1S_e$ exchange energy is larger than $k_B T$. An
15
16 accurate picture requires taking into account the long-range contribution to the electron hole
17
18 exchange¹⁰ which we find is approximately twice as large as the short-range contribution to
19
20 the total exchange splitting $4\eta_{1S_{3/2}1S_e}$ as discussed in the SI. Without the long-range exchange
21
22 interaction the upper bright level depopulation is much less pronounced at room temperature
23
24 and the relative change in the effective lifetime due to the Coulomb center is reduced.

25
26 In NCs with a *positive* charge center the effective radiative lifetime is shortened typically
27
28 by a factor two at small radii relative to that of an undoped NC of the same radius (see
29
30 panel (b)). For this case the $l = 0$ term in the Coulomb expansion brings the $1S_{3/2}1S_e$
31
32 and $1P_{3/2}1S_e$ states closer to resonance so that mixing by the $l = 1, 2$ terms is accentuated,
33
34 causing a dramatic shift of the oscillator strength from higher to lower sublevels. Strikingly,
35
36 a *positive* charge center gives rise to a factor of ten decrease of the radiative lifetime for
37
38 “quasi-spherical” NCs at the smallest NC radius (panel (d)). These results are qualitatively
39
40 consistent with the increase in PL efficiency of up to ten-fold which was observed by Sahu
41
42 et.al.¹⁴ for NCs doped with positive Ag charge centers. The measured PL quantum yield
43
44 of one of the samples in the Sahu study was reportedly 14% before doping and increased
45
46 to 27% after doping with 1.2 Ag per nanocrystal;¹⁴ this would correspond to a radiative
47
48 lifetime reduction of ~ 2.3 assuming that the change in the radiative lifetime is the domi-
49
50 nant factor responsible for the PL increase in that study. Another feature of the Sahu study
51
52 is the remarkable stability of the measured optical transition energies to doping. However,
53
54 the mixing between the various states which occurs in our model due to the Coulomb per-
55
56 turbation would be obscured by the rather large inhomogeneous broadening (~ 30 nm or
57
58
59
60

~ 115 meV) in the ensemble measurements which have been reported.¹⁴

Figure 6: Effective room-temperature lifetimes for CdSe NCs versus NC radius a calculated using Eq. 14 without defect ($q = 0$); with positively charged defect ($q > 0$), and with negatively charged defect ($q < 0$). Defects are positioned in the x, z plane at angle $\theta = \pi/4$ from the c -axis. Panels (a) and (c) show τ versus radius a for NCs with starting symmetry D_{6h} in (a), with axial field $\Delta_{ax}=25$ meV; (c) “quasi-spherical” NC with $\Delta_{ax} = 0$. Panels (b) and (d) respectively show the ratio of the effective lifetime τ for positive and negative charge centers relative to the corresponding NC with no charge center.

The model does have quantitative limitations. As previously discussed, we have neglected the size dependence of the total exciton oscillator strength and the frequency dependence of the radiative decay time, and have neglected the effects of the dielectric discontinuity at the NC surface on the Coulomb multipole expansion and on the long range exchange,

which tend to strengthen the Coulomb perturbation as well as the long range exchange corrections. Also, the basis states are written using the four-band model for the valence band and assumes infinite barriers at the NC surface. This causes an overestimation of the size dependence to the energy of the quantum size levels^{20,26} and the exchange splitting;²⁷ as such, details such as the specific size dependence of the effective lifetime computed here should not be considered quantitatively predictive. Nevertheless the qualitative feature that charged centers mix the upper bright and lower weakly or non-emitting sublevels, transferring oscillator strength to lower energy levels that are thermally accessible at finite temperature, is robust. Generally, the presence of a charged center breaks the symmetries responsible for the dark ground state angular momentum and parity selection rules (with exceptions for cases wherein the center is positioned along special directions or positions such as NC center that have high symmetry). The effects described here are particularly strong for positive charge centers because these cause a narrowing of the spacing between the emitting $1S_{3/2}1S_e$ and the dark $1P_{3/2}1S_e$ exciton states, accentuating the level mixing effects; the calculation shows substantially less effect for negative charge centers.

It is important to note that Ag donors in CdSe NC occupy an interstitial position in the CdSe lattice and are quite mobile at room temperature. The barrier height for Ag hopping is ~ 0.2 eV.²⁸ This means that at room temperature Ag moves from one interstitial position to another every 45 ns on average, a timescale comparable to the radiative decay time. This obviously would result in the broadening of optical emission spectra and band edge absorption. At low temperatures interaction of positive Ag donors with the exciton could bring them to the $d/a \sim 0.5$ region of NC where the low lying exciton fine structure levels have smallest energy (see Fig5 (a)).

In summary, we have shown that the descent of the NC symmetry from spherical to C_s , which is characterized by just one mirror plane symmetry element, leads step by step to activation of all five $F_z = \pm 2, \pm 1, 0$ excitons. Even the ground exciton becomes optically active, which should be seen in low-temperature photoluminescence measurements. For

several intermediate symmetries the band edge exciton fine structure consists of sets of three linearly polarized mutually orthogonal dipoles and a dark exciton, one of which is always the ground state. We quantify the effect of symmetry descent on the exciton fine structure by introducing a charged Coulomb impurity in the NC. The calculations show that the NC symmetry breaking by a Coulomb impurity, particularly a positively charged center, shortens the radiative decay of NCs even at room temperatures in qualitative agreement with the increase in PL efficiency observed by Sahu et.al.¹⁴ for NCs doped with positive Ag charge centers.

Supporting Information Available: Details on electronic structure calculation including: Description of electron and hole states in a spherical NC; the exchange Hamiltonian, the crystal field Hamiltonian and the treatment of the off-center Coulomb impurity; radiative lifetime calculation.

Acknowledgments. A.S. acknowledges support from the Center for Advanced Solar Photophysics (CASP), an Energy Frontier Research Center (EFRC) funded by BES, OS, U.S. DOE. A.L.E. acknowledges support from the U.S. Office of Naval Research (ONR) through the core funding of the Naval Research Laboratory. The authors declare no competing financial interests.

References

- (1) Ekimov, A. I.; Efros, Al. L.; Onushchenko, A. A. Solid State Commun. **1985**, 56, 921–924.
- (2) Murray, C. B.; Norris, D. J.; Bawendi, M. G. J. Am. Chem. Soc. **1993**, 115, 8706–8715.
- (3) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. Science **1998**, 270, 1335–1339.
- (4) Crooker, S. A.; Barrick, T.; Hollingsworth, J. A.; and Klimov, V. I. Appl. Phys. Lett. **2003**, 82, 2793–2795.

- (5) Labeau, O.; Tamarat, P.; and Lounis, B. Phys. Rev. Lett. **2003**, 90, 257404.
- (6) Du, H.; Chen, C.; Krishnan, R.; Krauss, T. D.; Harbold, J. M.; Wise, F. W.; Thomas, M. G.; Silcox, J. Nano Lett. **2002**, 2, 1321–1324.
- (7) Bischof, T. S., Correa, R. E., Rosenberg, D., Dauler, E. A. and Bawendi, M. G. Nano Lett. **2014**, 14, 6787–6791.
- (8) Nirmal, M.; Norris, D. J.; Kuno, M.; Bawendi, M. G.; Efros, Al. L.; Rosen, M. Phys. Rev. Lett. **1995**, 75, 3728–3731.
- (9) Efros, Al. L.; Rosen, M.; Kuno, M.; Nirmal, M.; Norris, D. J.; Bawendi, M. G. Phys. Rev. B **1996**, 54, 4843–4856.
- (10) Gupalov, S. V.; Ivchenko, E.L. Phys. Solid State **2000**, 42, 2030–2038.
- (11) Rodina A. V.; Efros, Al. L. Phys. Rev. B **2016**, 93, 155427.
- (12) Efros, Al. L.; Rodina A. V. Phys. Rev. B **1993**, 47, 10005–10007.
- (13) Efros, Al. L. Phys. Rev. B **1992**, 46, 7448–7458.
- (14) Sahu, A.; Kang, M. S.; Kompch, A.; Notthoff, C.; Wills, A.; Deng, D.; Winterer, M.; Frisbie, C.; Norris, D. J. Nano Lett. **2012**, 12, 2587–2594.
- (15) Hopfield, J. J. J. Phys. Chem. Solids **1960**, 15, 97–107.
- (16) Bir, G. L.; Pikus, G. E. Symmetry and Strain-Induced Effects in Semiconductors; John Wiley and Sons: New York, 1974.
- (17) Luttinger, J. M. Phys. Rev. **1956**, 102, 1030–1041.
- (18) Efros, Al. L.; Efros, A.L. Sov. Phys. Semicond. **1982**, 16, 772–775.
- (19) Sercel, P. C.; Vahala, K. J. Phys. Rev. B **1990**, 42, 3690–3710.

(20) Ekimov, A. I.; Hache, F.; Schanne-Klein, M. C.; Ricard, D.; Flyzannis, C.; Kudryavtsev, I. A.; Yazeva, T. V.; Rodina, A. V.; Efros, Al.L. J. Opt. Soc. Am. B **1993**, 10, 100–107.

(21) Koster, G. F.; Dimmock, J. O.; Wheeler, R. G.; Statz, H. Properties of the thirty-two point groups; MIT Press: Cambridge, 1963.

(22) Norris, D. J.; Sacra, A.; Murray, C. B.; Bawendi, M. G. Phys. Rev. Lett. **1994**, 72, 2612–2615.

(23) Landau, L. D.; Lifshitz, E. M. Electrodynamics of Continuous Media; Pergamon Press: Oxford, 1960.

(24) Jackson, J. D. Classical Electrodynamics; John Wiley and Sons: New York, 1999

(25) Wong, C. Y.; Kim, J.; Nair, P. S.; Nagy, M. C.; Scholes, G. D. J. Phys. Chem. C **2009**, 113, 795–811.

(26) Norris, D. J.; Bawendi, M. G. Phys. Rev. B **1996**, 53, 16338–16346.

(27) Franceschetti, A.; Fu, H.; Wang, L. W.; Zunger, A. Phys. Rev. B **1999**, 60, 1819–1829.

(28) Ott, F. D.; Spiegel, L.; Norris, D.J.; Erwin, S.C. Phys. Rev. Lett. **2014**, 113, 156803

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27

ACS Paragon Plus Environment

$1S_{3/2} \times 1S_e$