Supporting Information:

Photoluminescence Enhancement through Symmetry Breaking Induced by Defects in Nanocrystals

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In this study, the level structure of the exciton was considered as in the commonly used “standard model” of spherical NCs within a four-band model for the valence bands (referring to the quasi-cubic model, these are the $\Gamma_8$ bands) by incorporating the effects of the axial field and the electron-hole exchange interaction. To this “standard model”, considered as the unperturbed system, we add a Coulomb center within the context of quasi-degenerate perturbation theory. In this Supporting Information section we provide details of the standard model as well as the treatment of the charged impurity Coulomb potential through the multipole expansion.
Zeroth order description of electron and hole states in a spherical NC

In a spherical NC in the spherical approximation with no crystal field, the energy eigenstates are eigenstates of total angular momentum.\(^3-5\) The zeroth-order energies and wave functions of the ground electron state are

\[
E_e = \frac{\hbar^2 \pi^2}{2m_e a^2}
\]

\[
\psi_e^{\alpha}(r) = R_e(r) Y_{00}(\theta, \phi) v_{\alpha},
\]

where \(m_e\) is the electron effective mass, \(v_{\alpha}\) are the Bloch functions of the conduction band, \(S \uparrow\) and \(S \downarrow\), with the projection of the electron spin \(\alpha = \pm 1/2\).\(^1\) The radial function is given by

\[
R_e(r) = \frac{2^{1/2}}{a^{3/2}} j_0 \left( \frac{\pi r}{a} \right).
\]

The zeroth-order hole wave functions associated with the \(\Gamma_8\) band edge have the form of eigenstates of total angular momentum \(F, F_z\),\(^4\)

\[
|F, F_z\rangle = \sum_{L} R_{L,F}(r) |F, F_z; J, L\rangle.
\]

Here, the \(R_{L,F}\) are radial envelope functions and the angular basis functions \(|F, F_z; J, L\rangle\) are constructed using the familiar rules of addition of angular momentum as,

\[
|F, F_z; J, L\rangle = \sum_{J_z=-J}^{J} \sum_{L_z=-L}^{L} \langle J, J_z; L, L_z|F, F_z\rangle |J, J_z\rangle |L, L_z\rangle.
\]

The first term in the sum above is a Clebsch-Gordan coefficient, the states \(|J, J_z\rangle\) are the band edge Bloch functions with \(J = 3/2\), and \(|L, L_z\rangle\) are envelope functions which have
coordinate representations given by spherical harmonics.

Using this basis we express the effective mass Hamiltonian for flat band conditions in a free spherical wave basis of eigenstates of total angular momentum. The appropriate basis functions are the spherical waves which are regular at the origin:

\[ |k, F, F_z; J, L\rangle = \sqrt{\frac{2}{\pi}} i^L j_L(kr) |F, F_z; J, L\rangle \]  

\[ (S5) \]

where \( j_L(kr) \) is a spherical Bessel function with wavenumber \( k \). In this basis the Hamiltonian is block diagonal in \( F, F_z \) and parity.\(^4\) For each of the four possible values of \( F_z \) (\( \pm 3/2, \pm 1/2 \)) there are therefore four eigenvectors for each parity comprising a heavy hole and a light hole eigenvector with wavenumbers \( k_{hh} \) and \( k_{lh} \), respectively determined by the familiar dispersion relations \( E_{hh}(k) = E_v - (\gamma_1 - 2\gamma_2)(\hbar^2 k^2/2m_0) \), and \( E_{lh}(k) = E_v - (\gamma_1 + 2\gamma_2)(\hbar^2 k^2/2m_0) \), where \( \gamma_1 \) and \( \gamma \) are the Luttinger parameters\(^6\) and \( m_0 \) is the free electron mass.

We find the radial wave function inside the NC by mixing light- and heavy- hole waves as follows:

\[ \psi_E(r) = A\phi_E^{HH}(r) + B\phi_E^{LH}(r). \]  

\[ (S6) \]

The requirement that \( \psi \) vanish at \( r = a \) leads to the simple determinantal equation that determines the energy eigenstates of the ground hole state with even envelope parity:\(^1,4\)

\[ j_0(k_{hh}a)j_2(k_{lh}a) + j_0(k_{lh}a)j_2(k_{hh}a) = 0 \]  

\[ (S7) \]

The explicit form for the even parity energy eigenstates then is

\[ \psi_{3/2,F_z} = \sum_{L=0,2} R_L,3/2(r)|3/2, F_z; J, L\rangle \]  

\[ (S8) \]
where the radial wave functions are given by,

\[ R_{0,3/2}(r) = A \left( j_0(k_{hh}r) - \frac{j_0(k_{hh}a)}{j_0(k_{lh}a)} j_0(k_{lh}r) \right) \]

\[ R_{2,3/2}(r) = i^2 A \left( j_2(k_{hh}r) + \frac{j_0(k_{hh}a)}{j_0(k_{lh}a)} j_0(k_{lh}r) \right) . \]  

(S9)

Here, the constant \( A \) is determined by the normalization condition

\[ \int_0^a \left[ R_{0,3/2}^2(r) + R_{2,3/2}^2(r) \right] r^2 dr = 1 . \]  

(S10)

We label these states 1\( S_{3/2} \).

The next highest energy hole state corresponds to \( F=3/2 \) with odd envelope function parity (\( L = 1 \) and \( L = 3 \)). We will label these states as 1\( P_{3/2} \). The wave function of these states can be written as:

\[ \psi_{3/2,F_z} = \sum_{L=1,3} R_{L,3/2}(r) |3/2, F_z; J, L \rangle , \]  

(S11)

with the radial wave functions given by,

\[ R_{1,3/2}(r) = 3B \left( j_1(k_{hh}r) - \frac{j_1(k_{hh}a)}{j_1(k_{lh}a)} j_1(k_{lh}r) \right) \]

\[ R_{3,3/2}(r) = i^2 B \left( j_3(k_{hh}r) + 9 \frac{j_1(k_{hh}a)}{j_1(k_{lh}a)} j_3(k_{lh}r) \right) . \]  

(S12)

where the constant \( B \) is set by the normalization condition,

\[ \int_0^a \left[ R_{1,3/2}^2(r) + R_{3,3/2}^2(r) \right] r^2 dr = 1 . \]  

(S13)

The corresponding energies are given by the roots of the determinantal equation,\(^4\)

\[ 9j_1(k_{hh}a)j_3(k_{lh}a) + j_1(k_{lh}a)j_3(k_{hh}a) = 0 . \]  

(S14)
Exchange Hamiltonian

We begin the discussion of the exciton exchange interaction in small NCs by reviewing the short range component of the exchange interaction. In addition to the short-range component of exchange, it has been shown by Gupalov and Ivchenko to be critical to also include the effects of the long range exchange for the optically active $1S_{3/2}1S_e$ excitons. After developing the expressions for the short range exchange we will include a correction to account for the effect of the long range interaction, following Gupalov and Ivchenko.

The short-range electron-hole exchange interaction is given by

$$H_{\text{exch}}^{\text{SR}} = -\frac{2}{3} \epsilon_{\text{exch,SR}} V_{\text{cell}} (\sigma \cdot J) \delta(r_e - r_h) \quad (S15)$$

where $V_{\text{cell}}$ is the unit cell volume of hexagonal CdSe, $\epsilon_{\text{exch}}$ is the exchange constant, and $\sigma$ and $J$ are spin operators acting on the electron and hole Bloch functions respectively. Using the fact that the electron states included in our analysis possess $L_e = 0$, we can specify this expression further to the $1S_e$-derived excitons:

$$H_{\text{exch}}^{\text{SR}} = -\epsilon_{\text{exch,SR}} \frac{V_{\text{cell}}}{6\pi} (\sigma \cdot J) \delta(r_e - r_h) \quad (S16)$$

The exchange constant in the expression above can be found in terms of the singlet-triplet splitting, $\hbar\omega_{ST}$, of the bulk exciton of radius $a_{ex}$, by using the relationship

$$\epsilon_{\text{exch,SR}} = \frac{\pi}{2} \frac{a_{ex}^3}{V_{\text{cell}}} \hbar\omega_{ST} \quad (S17)$$

Using parameters $\hbar\omega_{ST} = 0.13 \text{ meV}$, $a_{ex} = 56 \text{ Å}$, and $V_{\text{cell}} = 112 \text{ Å}^3$ for hexagonal CdSe, we obtain $\epsilon_{\text{exch,SR}} = 320 \text{ meV}$.

The $1S_{3/2}$ and $1P_{3/2}$ lowest energy hole states lie very close in energy (See Figure 1 in the main text) with the splitting comparable to the exchange energy for smaller radius nanocrystals. In this study we consider mixing of these states due to perturbation by off-
center charged impurities, with coupling strength again comparable to the splitting between the $1S_{3/2}$ and $1P_{3/2}$ lowest energy hole states (see Fig. 2 in the main text). As a result, in order to model the exciton physics with reasonable fidelity we must treat the excitons formed from the ground $1S_e$ electron and the $F = 3/2$ holes of both parities within quasi-degenerate perturbation theory. Averaging of Eq. (S16) over the wave wave functions of $1S_{3/2}1S_e$ and $1P_{3/2}1S_e$ exciton manifold defined in Eqs. (S1) (S8) and (S11) we can write the exchange Hamiltonian as a 16x16 matrix in the following form:

$$\hat{H}_{ex} = \begin{pmatrix} \hat{H}_{1S_e,1S_{3/2}} & 0 \\ 0 & \hat{H}_{1S_e,1P_{3/2}} \end{pmatrix}. \quad (S18)$$

Each of the submatrices in the equation above is an 8x8 matrix. We now write the submatrix representations of $\hat{H}_{ex}$ in Eq.(S18) using the eight pair states ($F_e^z, F_h^z$) of a given parity, defined in the order, $(1/2, 3/2), (1/2, 1/2), (1/2, -1/2), \ldots, (-1/2, -3/2)$. The first submatrix takes the form,

$$\hat{H}_{1S_e,1S_{3/2}} = -\eta_{1S_{3/2}1S_e} \times \begin{pmatrix} \frac{3}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 & \sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & 0 & 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & -\frac{3}{2} & 0 & 0 & \sqrt{3} & 0 \\ 0 & \sqrt{3} & 0 & 0 & -\frac{3}{2} & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & 0 & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & \sqrt{3} & 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{3}{2} & 0 \end{pmatrix}, \quad (S19)$$

where the $\eta_{1S_{3/2}1S_e}$ prefactor is defined as follows:

$$\eta_{1S_{3/2}1S_e} = \hbar \omega_{ST} \left( \frac{a_{ex}}{a} \right)^3 \chi_{1S_{3/2}1S_e}. \quad (S20)$$
In this expression, $\chi_{1S_{3/2}1S_e}$ is a dimensionless overlap integral for the $1S_{3/2}1S_e$ excitons which depends on the hole effective mass parameters. It has the definition:

$$\chi_{1S_{3/2}1S_e} = \frac{a^3}{12} \left( I_{00,00}^{3/2,3/2} + \frac{I_{00,22}^{3/2,3/2}}{5} \right) \quad (S21)$$

Here, the terms $I_{00,00}^{3/2,3/2}$ and $I_{00,22}^{3/2,3/2}$ represent the excitonic radial overlap integrals of the form,

$$I_{00,lt}^{3/2,3/2} = \int_0^a dr r^2 R_{e,0}^2 (r) \left[ R_{l,3/2} (r) (r) \right]^2. \quad (S22)$$

The second submatrix, pertaining to the $1P_{3/2}1S_e$ pairs, takes the identical form, but with a different prefactor, $\eta_{1P_{3/2}1S_e}$:

$$\eta_{1P_{3/2}1S_e} = \hbar \omega_{ST} \left( \frac{a_{ex}}{a} \right)^3 \chi_{1P_{3/2}1S_e} \quad (S23)$$

$$\chi_{1P_{3/2}1S_e} = \frac{a^3}{12} \left( \frac{11I_{00,11}^{3/2,3/2} - 9I_{00,33}^{3/2,3/2}}{15} \right) \quad (S24)$$

In this expression, $\chi_{1P_{3/2}1S_e}$ is again a dimensionless integral which depends on effective mass parameters of the hole. Finally, the off-diagonal blocks $\hat{0}$ of Eq.S18 are represented by an eight-by-eight matrix of zeros, reflecting the fact that the exchange interaction does not mix the opposite parity states.

The expressions above are developed for the short-range exchange interaction affecting excitons in spherical CdSe NCs in the strong confinement regime. However, as noted above, it has been shown by Gupalov and Ivchenko to be critical to also include the effects of the long range exchange for the optically active $1S_{3/2}1S_e$ excitons.\textsuperscript{2,7} Inclusion of these terms results in a correction to the expression above for the $1S_{3/2}1S_e$ prefactor, $\eta_{1S_{3/2}1S_e}$. Neglecting the effects of the dielectric discontinuity at the NC surface, which would tend to increase the
correction, the parameter $\eta_{1S_{3/2}1S_e}$ is given by,$^2$

$$
\eta_{1S_{3/2}1S_e} = \hbar \omega_{ST} \left( \frac{a_{ex}}{a} \right)^3 \chi_{1S_{3/2}1S_e} \rightarrow \Delta_{ex} \left( \frac{a_{ex}}{a} \right)^3 \chi_{1S_{3/2}1S_e}
$$

(S25)

$$
\Delta_{ex} = \left( \hbar \omega_{ST} + \omega_{LT} \frac{\pi \zeta_{1S_{3/2}1S_e}}{9 \chi_{1S_{3/2}1S_e}} \right).
$$

(S26)

In this expression, $\hbar \omega_{LT}$ is the bulk longitudinal-transverse splitting, while $\zeta_{1S_{3/2}1S_e}$ is a dimensionless integral which depends on the hole effective mass parameters. The values of the various parameters used in our calculations are summarized in TableS1, as are the calculated values of the various overlap integrals using the given mass parameters. Using the mass and splitting parameters in the Table we find that inclusion of the long range exchange terms increases the energy prefactor for the $1S_{3/2}1S_e$ excitons from $\hbar \omega_{ST} = 0.13 \text{meV}$ to $\Delta_{ex} = 0.39 \text{meV}$, representing a factor of three increase over the exchange splitting obtained at any given nanocrystal radius found using the short-range term alone.

**Crystal field Hamiltonian**

In the quasi-cubic model, the wurtzite crystal field is expressed using an operator that acts on the $\Gamma_8$ Bloch functions to split the $J_z = \pm 3/2$ from the $J_z = \pm 1/2$ bands:$^9$

$$
\hat{H}_{cf} = \frac{\Delta}{2} \left( \frac{5}{4} - J_z^2 \right)
$$

(S27)

Averaging this operator over the hole wave functions of the $1S_{3/2}$ hole manifold defined in Eq. (S8) this operator can be represented by the matrix,

$$
H_{cf}^{S_{3/2}} = \left( I_{0,0}^{3/2,3/2} - \frac{3}{5} I_{2,2}^{3/2,3/2} \right) \left( \frac{\Delta}{2} \right) \begin{pmatrix}
-1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & -1
\end{pmatrix}.
$$

(S28)
where the radial envelope wave function overlaps are given by,

\[ I_{L_i,L_f}^{F_i,F_f} = \int_0^a drr^2 R_{L_i,F_i}^* (r) R_{L_f,F_f} (r). \]  

(S29)

It can be seen that operator \( H_{cf}^{S_{3/2}} \) splits the \( F_z = \pm 3/2 \) NC eigenstates from the \( F_z = \pm 1/2 \) states as expected. Averaging operator \( \hat{H}_{cf} \) over the hole wave functions of the \( 1P_{3/2} \) hole manifold defined in Eq. (S11) we find the matrix takes identical form but with a different prefactor:

\[ H_{cf}^{P_{3/2}} = (I_{1,1}^{3/2,3/2} + I_{3,3}^{3/2,3/2}) \left( \frac{\Delta}{2} \right) \left( \frac{1}{5} \right) \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}. \]  

(S30)

While the matrix has the same form as for the even parity states the magnitude of the splitting is different owing to the different structure of the envelope functions. Finally, to incorporate shape effects we have taken the parameter \( \Delta \sim \Delta_{ax} \) to be a phenomenological parameter in Eqs. S28-S30. With no shape distortion \( \Delta_{ax} \sim 25 \text{meV} \) while for “quasi-spherical” NC \( \Delta_{ax} \) is set to zero.

We incorporate these axial terms into the exciton problem by writing the crystal field Hamiltonian in the previously defined electron-hole pair basis with \( \Delta \sim \Delta_{ax} \), noting that the axial field does not split the \( 1S_e \) electron states:

\[ H_{ax} = \begin{pmatrix} H_{cf}^{S_{3/2}} & 0 & 0 & 0 \\ 0 & H_{cf}^{S_{3/2}} & 0 & 0 \\ 0 & 0 & H_{cf}^{P_{3/2}} & 0 \\ 0 & 0 & 0 & H_{cf}^{P_{3/2}} \end{pmatrix}. \]  

(S31)

In the last expression, \( 0 \) is a four-by-four matrix of zeros. The zeros in this matrix represent the fact that Eq. S27 does not mix states of opposite parity, not does it flip electron spins.
Off-center Coulomb impurity

We now consider the effect of a Coulomb impurity in the NC. We assume that there is an impurity of charge $q$ located within a NC at position vector $\mathbf{r}_0$ with polar coordinates $(r_0, \theta_0, \phi_0)$. Then the perturbation potential experienced by a carrier of charge $e$ at position $\mathbf{r}$ can be written using the standard multipole expansion,\textsuperscript{10}

$$V(\mathbf{r}) = \frac{qe}{\epsilon |\mathbf{r} - \mathbf{r}_0|} = \frac{qe}{\epsilon} \sum_{l,m} \frac{4\pi}{(2l + 1)} \frac{r_<^l}{r_>^{l+1}} Y_{lm}^*(\theta_0, \phi_0) Y_{lm}(\theta, \phi), \quad (S32)$$

where $r_> (r_<)$ is the greater (lesser) of $|\mathbf{r}|, |\mathbf{r}_o|$ and the $Y_{lm}$ are spherical harmonics. We note that the potential above acts on both the electrons and the holes so that the perturbation on an electron hole pair state can be written,

$$V_{ex} = V(\mathbf{r}_h) - V(\mathbf{r}_e) \quad (S33)$$

where the two terms represent the potential seen by the hole with charge $e$ at position $\mathbf{r}_h$ and the electron with charge $-e$ at position $\mathbf{r}_e$, respectively. We separate out the angular dependence of the operator $V$ and write the expansion as,

$$V(\mathbf{r}, \theta, \phi) = \frac{qe}{\epsilon a} \sum_{l,m} C_{lm}^m(r) Y_{lm}^*(\theta, \phi), \quad (S34)$$

where the expansion terms $C_{lm}^m(r)$ take the form,

$$C_{lm}^m(r) = \frac{4\pi}{(2l + 1)} \frac{ar_<^l}{r_>^{l+1}} Y_{lm}^*(\theta_0, \phi_0). \quad (S35)$$

Here we have introduced the nanocrystal radius $a$ into the common prefactor, $qe/(\epsilon a)$, which sets the Coulomb energy scale in the context of the NC problem. For convenience we separate
out the \( r \) dependence within each term and write,

\[
C_l^m(r) = c_l^m \times \frac{ar_l^i}{r^{l+1}},
\]

(S36)

with,

\[
c_l^m = \frac{4\pi}{(2l + 1)} Y_l^{m*}(\theta_0, \phi_0).
\]

(S37)

In these expressions we note that \( \epsilon \) is the low frequency dielectric constant of the NC. Since CdSe is anisotropic, we use the average dielectric constant in these expressions:

\[
\epsilon = \frac{\epsilon_\perp + 2\epsilon_\parallel}{3}
\]

(S38)

The dominant effects of the Coulomb center multipole expansion defined in Eq. S34 on the exciton level structure are due to the terms with \( l \leq 2 \). 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 \( l = 1 \) term mixes the even and odd parity hole states; while the \( l = 2 \) term mixes the hole spin sublevels for a given parity. While the \( l = 3 \) term also could couple levels within the \( F = 3/2 \) subspace, its effect is weaker than the \( l = 1 \) term by an order of magnitude so this term has been neglected.

We now develop the matrix representation of the perturbation Eq. S33 within the exciton space formed from the two-fold degenerate ground \( 1S_e \) electron states and the eight \( F = 3/2 \) hole states, reflecting the degeneracy of four for even and odd envelope parity, \( 1S_{3/2} \) and \( 1P_{3/2} \) respectively: As such the Coulomb center perturbation is represented by a 16 x16 matrix in this subspace. Averaging of Eq. (S33) over the wave functions of the \( 1S_{3/2}1S_e \) and \( 1P_{3/2}1S_e \) exciton manifolds defined in Eqs. (S1) (S8) and (S11) we can write the Coulomb
Hamiltonian in the following matrix form:

$$H_V = \begin{pmatrix}
H_{1S_3/2,1S_3/2} & 0 & H_{1S_3/2,1P_3/2} & 0 \\
0 & H_{1S_3/2,1S_3/2} & 0 & H_{1S_3/2,1P_3/2} \\
H^\dagger_{1S_3/2,1P_3/2} & 0 & H_{1P_3/2,1P_3/2} & 0 \\
0 & H^\dagger_{1S_3/2,1P_3/2} & 0 & H_{1P_3/2,1P_3/2}
\end{pmatrix} \quad \text{(S39)}$$

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 $1P_3/2$ $1S_e$ exciton subspace; these blocks only involve the even $l$ terms of the Coulomb multipole expansion, Eq. S34. The off-diagonal blocks couple between the two parity types and only involve the odd $l$ terms of Eq. S34. In the last expression, 0 is a four-by-four matrix of zeros which reflects the fact that the Coulomb perturbation does not flip the electron spin.

In Equation S39 the four-by-four block connected with the $1S_3/2$ $1S_e$ exciton manifold is given by,

$$H_{1S_3/2,1S_3/2} = H^{l=0}_{1S_3/2,1S_3/2} + H^{l=2}_{1S_3/2,1S_3/2}, \quad \text{(S40)}$$

while the four-by-four block connected with the $1P_3/2$ $1S_e$ exciton manifold is,

$$H_{1P_3/2,1P_3/2} = H^{l=0}_{1P_3/2,1P_3/2} + H^{l=2}_{1P_3/2,1P_3/2}, \quad \text{(S41)}$$

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

$$H^{l=0}_{1S_3/2,1S_3/2} = \frac{q_e}{\epsilon a} \left( M^h_{1S_3/2} - M^e_{1S_e} \right) \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1
\end{pmatrix}, \quad \text{(S42)}$$
where $M_{1S_e}^e$, $M_{1S_h}^h$, and $M_{1P_h}^h$ are the dimensionless radial Coulomb integrals for the electron and hole respectively:

\[
M_{1S_h}^h = a \int_0^a d\rho \rho^2 \frac{1}{\rho_{h,>}^2} (R_{0,3/2}^2 (r_h) + R_{2,3/2}^2 (r_h))
\]

\[
M_{1P_h}^h = a \int_0^a d\rho \rho^2 \frac{1}{\rho_{h,>}^2} (R_{3,3/2}^2 (r_h) + R_{3,3/2}^2 (r_h))
\]

\[
M_{1S_e}^e = a \int_0^a d\rho \rho^2 \frac{1}{\rho_{e,>}^2} (R_{0,1/2}^2 (r_e)).
\]

The $l = 2$ terms in the Coulomb expansion give rise to mixing within the even and odd parity exciton subspaces. For the exciton with even envelop parity it can be written as,

\[
H_{1S_h}^{l=0} = \frac{q e}{e a} \frac{M_{1P_h}^h - M_{1S_e}^e}{N_{1S_h}^e} \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1
\end{pmatrix},
\]

\[
H_{1P_h}^{l=2} \equiv \frac{q e}{e a} N_{1S_h}^{3/2,3/2} \tilde{H}_{L=2}
\]

In this equation, the term $N_{1S_h} = N_{02}^3$ is a radial dimensionless Coulomb overlap integral describing the coupling between the S component of one of the hole states with the D component of the other:

\[
N_{L_i,L_f}^{F_i,F_f} = a \int_0^a d\rho \rho^2 \frac{r_{L_i,F_i}^2}{r_{L_f,F_f}^3} R_{L_i,F_i}^* (r) R_{L_f,F_f} (r),
\]

where $a$ is the nanocrystal radius. The terms $\alpha$, $\beta$, and $\gamma$ can be written in terms of the components $c_L^M (\theta_0, \phi_0)$ for $l = 2$ associated with the Coulomb center. Using Eq. S37, for a
defect with angular coordinates \((\theta_0, \phi_0)\),

\[
\alpha = \frac{1}{\sqrt{4\pi}} \frac{4\pi}{5} (Y_0^0(\theta_0, \phi_0))^* = \frac{1}{\sqrt{20}} (3 \cos^2 \theta_0 - 1)
\]

\[
\beta = \frac{1}{\sqrt{4\pi}} \frac{4\pi}{5} (Y_2^2(\theta_0, \phi_0))^* = \sqrt{\frac{3}{2}} \frac{1}{\sqrt{20}} \sin^2 \theta_0 e^{-i\phi_0}
\]

\[
\gamma = \frac{1}{\sqrt{4\pi}} \frac{4\pi}{5} (Y_1^1(\theta_0, \phi_0))^* = -\sqrt{\frac{3}{2}} \frac{1}{\sqrt{20}} \sin 2\theta_0 e^{-i\phi_0}
\]  

(S49)

The Hamiltonian submatrix for the \(1P_{3/2}1S_e\) exciton manifold is 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:

\[
H_{1P_{3/2},1P_{3/2}} = \frac{q_e}{\epsilon a} N_{1P_{3/2}} \times \hat{H}_{L=2},
\]

where,

\[
N_{1P_{3/2}} = \left(2N_{11}^{3/2,3/2} + 3N_{13}^{3/2,3/2} - 2N_{33}^{3/2,3/2}\right) / 5
\]

(S50)

Finally, the \(L = 1\) components of the Coulomb potential couple the even and odd parity hole states. These are given by,

\[
H_{1S_{3/2},1P_{3/2}} = \frac{q_e}{\epsilon a} O_{1S_{3/2},1P_{3/2}} \begin{pmatrix}
\sqrt{\frac{3}{5}} b_z & \sqrt{\frac{2}{5}} b_- & 0 & 0 \\
\sqrt{\frac{2}{5}} b_+ & \frac{b_z}{\sqrt{15}} & 2\sqrt{\frac{2}{15}} b_- & 0 \\
0 & 2\sqrt{\frac{2}{15}} b_+ & -\frac{b_z}{\sqrt{15}} & \sqrt{\frac{2}{5}} b_- \\
0 & 0 & \sqrt{\frac{2}{5}} b_+ & -\sqrt{\frac{2}{5}} b_z
\end{pmatrix},
\]

(S52)

where the \(O\) term is given by

\[
O_{1S_{3/2},1P_{3/2}} = O_{01}^{3/2,3/2} + \frac{4}{5} O_{21}^{3/2,3/2} + \frac{3}{5} O_{23}^{3/2,3/2},
\]

(S53)

with the terms \(O_{L_i,L_f}^{3/2,3/2}\) representing dimensionless radial Coulomb integrals between the different \(L\) envelope function components of the \(F = 3/2\) even and odd parity hole states.
These are defined as,

\[ O_{L_i,F_i}^{F_i,F_f} = a \int_0^a dr r^2 r_2 R_{L_i,F_i}^\ast (r) R_{L_f,F_f} (r). \]  

(S54)

The terms within the matrix derive from Eq. S37,

\[ b_z = \frac{1}{\sqrt{4\pi}} c_1^0 = \frac{1}{\sqrt{4\pi}} \frac{4\pi}{3} Y_1^0(\theta_0, \phi_0) = \sqrt{\frac{1}{3}} \cos \theta_0, \]

\[ b_+ = \frac{1}{\sqrt{4\pi}} c_1^{-1} = \frac{1}{\sqrt{4\pi}} \frac{4\pi}{3} Y_1^{-1*}(\theta_0, \phi_0) = \sqrt{\frac{1}{3}} \frac{\sin \theta_0 e^{i\phi_0}}{\sqrt{2}}, \]

\[ b_- = -\frac{1}{\sqrt{4\pi}} c_1^1 = -\frac{1}{\sqrt{4\pi}} \frac{4\pi}{3} Y_1^{1*}(\theta_0, \phi_0) = \sqrt{\frac{1}{3}} \frac{\sin \theta_0 e^{-i\phi_0}}{\sqrt{2}}. \]  

(S55)

**Radiative lifetime calculation**

Above we showed how the exciton Hamiltonian is developed the 16 pair state basis spanning the space \(1S_{3/2}1S_e + 1P_{3/2}1S_e\). Each pair state is a product of one of the two ground electron \(1S_e\) states with one of the hole states with \(F = 3/2\). The pairs are denoted \(P_n\) and are taken in the following order: Using the notation \((F_{z,e}, F_{z,h})\), the first eight states are the \(1S_{3/2}1S_e\) pairs \((1/2, 3/2), (1/2, 1/2), (1/2, -1/2), (1/2, -3/2), (-1/2, 3/2), (-1/2, 1/2), (-1/2, -1/2), (-1/2, -3/2)\). Then pairs 9 through 16 are the \(1P_{3/2}1S_e\) pairs are taken in the same order. For radiative transitions only the first eight pairs contribute; the dipole matrix elements for the last eight pairs are zero due to the parity selection rule.

We represent each energy eigenstate in terms of the basis of pair states \(|P_n\rangle\), where \(n\) is an index that runs 1 through 16:

\[ |\psi_k\rangle = \sum_n \phi_k^n |P_n\rangle \]  

(S56)
where the pair states $P_n$ are products of the electron and hole single particle states:

$$|P_n⟩ = |e_n⟩|h_n⟩ \quad (S57)$$

The dipole matrix element connecting energy eigenstate $|ψ_k⟩$ to the vacuum state $|0⟩$. Using Eq. S56, this is given by

$$⟨ψ_k|\hat{p}|0⟩ = \sum_n (φ_n^k)\dagger⟨P_n|\hat{p}|0⟩ \quad (S58)$$

Further reduction requires us to determine the dipole matrix element connecting each pair state $|P_n⟩$ to the vacuum state $|0⟩$. This is given by

$$⟨P_n|\hat{p}|0⟩ = ⟨e_n|⟨h_n|\hat{p}|0⟩ = ⟨e_n|\hat{p}|T|h_n⟩ \quad (S59)$$

In this last equation, $\hat{T}$ is the time reversal operator, $T = -iσ_y\hat{K}$, where $σ_y$ is the Pauli spin matrix which flips the spin and $\hat{K}$ is the conjugation operator. We further reduce this expression by noting that the optical dipole matrix elements can be expressed in terms of the Kane matrix element, $P = -i⟨S|\hat{p}_z|Z⟩$. Finally, since the electron states $1S_e$ have envelope angular momentum zero the dipole matrix elements involving the $1P_{3/2}1S_e$ pair basis states vanish while the $1S_{3/2}1S_e$ terms can be written in terms of a common envelope radial overlap integral: $Q = \int_{a}^{b} r^2 dr R_e^e(r)R_h^h(r)$. For convenience we will write the matrix elements described by Eq. (S59) in the general form,

$$⟨P_n|\hat{p}|0⟩ = QPf_n \quad (S60)$$

where $f_n$ denotes the vector character of the dipole matrix element for each particular pair state. Finally, for a given exciton energy eigenstate $ψ_k$, we determine the square of the dipole
transition matrix element by squaring Eq. S58:

\[ |\langle \psi_k | \hat{p} | 0 \rangle|^2 = \left| \sum_n (\phi_n^k)^\dagger \langle P_n | \hat{p} | 0 \rangle \right|^2 = Q^2 P^2 \left| \sum_n (\phi_n^k)^\dagger f_n \right|^2 \]  

(S61)

Given an initial state \(|\psi_k\rangle\) and final state \(|0\rangle\) we can now calculate the lifetime of the state. Summing over polarizations we find the lifetime in Guassian units as\(^{11}\):

\[ \frac{1}{\tau_k} = \frac{4e^2 \omega n_r}{3m_0^2 c^3 \hbar} D^2 |\langle \psi_k | \hat{p} | 0 \rangle|^2. \]  

(S62)

In MKS units this is,

\[ \frac{1}{\tau_k} = \frac{e^2 \omega n_r}{3\pi \epsilon_0 m_0^2 c^3 \hbar} D^2 |\langle \psi_k | \hat{p} | 0 \rangle|^2 \]  

(S63)

In the expressions above the factor \(D\) represents the dielectric depolarization factor for a spherical nanocrystal of dielectric constant \(\epsilon_{NC}\) embedded in a dielectric medium of \(\epsilon_{med}\):\(^{10}\)

\[ D = \frac{3\epsilon_{med}}{2\epsilon_{med} + \epsilon_{NC}} \]  

(S64)

Because CdSe is not optically isotropic we take the high frequency dielectric constant as an average:

\[ \epsilon = \frac{\epsilon_\perp + 2\epsilon_\parallel}{3} \]  

(S65)

Using values from Madelung\(^{12}\) we calculate \(\epsilon_{NC} = 6.27\). In the experiments reported by Sahu et. al. doped CdSe NCs were suspended in hexanes.\(^{13}\) We therefore set the dielectric constant of the medium, \(\epsilon_{med}\) to that of the solvent, \(\epsilon_{med} = n_r^2\) with \(n_r = 1.38\) corresponding to hexane.\(^{14}\)

Using the Kane matrix element, \(P\), and the radial overlap integral, \(Q\):

\[ \frac{1}{\tau_k} = \frac{e^2 \omega n_r}{3\pi \epsilon_0 m_0^2 c^3 \hbar} \times D^2 \times Q^2 \times P^2 \times \left| \sum_n (\phi_n^k)^\dagger f_n \right|^2 \]  

(S66)
We now perform a re-arrangement to eliminate the Kane matrix element, using $2P^2/m_o = E_P = 17.5$ eV. The lifetime is now,

$$\frac{1}{\tau_k} = \frac{e^2\omega n_r}{6\pi\epsilon_0 m_0 c^3 \hbar} D^2 E_P |Q|^2 \times |\sum_n (\phi_n^*)^\dagger f_n |^2$$

(S67)

We group the prefactors as follows:

$$R \equiv \frac{e^2\omega n_r}{6\pi\epsilon_0 m_0 c^3 \hbar} E_P D^2 Q^2.$$  

(S68)

Putting it together then,

$$\frac{1}{\tau_k} = R \times |\sum_n (\phi_n^*)^\dagger f_n |^2.$$  

(S69)

For reference we note that for the bright exciton state of a spherical NC with $F = 1$ and $F_z = 0$, $|\sum_n (\phi_n^*)^\dagger f_n |^2 = 4/3$. Thus the radiative transition rate of the $|1,0\rangle$ exciton state is:

$$\frac{1}{\tau_{1,0}} = \frac{4}{3} R.$$  

(S70)

This expression gives the radiative decay time $\tau_{1,0} = 3.32$ ns, when we use the material parameters of CdSe and the dielectric constant of the media from Table S1.
Table S1: Material and model parameters for CdSe NCs and surrounding medium used in electronic structure and lifetime calculations

<table>
<thead>
<tr>
<th>Parameter (CdSe unless noted otherwise)</th>
<th>Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_e/m_0$</td>
<td>0.11</td>
<td>5</td>
</tr>
<tr>
<td>$\gamma_1$</td>
<td>2.04</td>
<td>15</td>
</tr>
<tr>
<td>$\gamma_2$</td>
<td>0.58</td>
<td>15</td>
</tr>
<tr>
<td>$\hbar\omega_{ST}$ (meV)</td>
<td>0.13</td>
<td>1</td>
</tr>
<tr>
<td>$\hbar\omega_{LT}$ (meV)</td>
<td>0.95</td>
<td>2</td>
</tr>
<tr>
<td>$\Delta_{ex}$ (meV)</td>
<td>0.39</td>
<td>Eq.S26</td>
</tr>
<tr>
<td>$\chi_{1S_{3/2}1S_e}$</td>
<td>0.782</td>
<td>Eq.S21</td>
</tr>
<tr>
<td>$\zeta_{1S_{3/2}1S_e}$</td>
<td>0.607</td>
<td>Eq.25 of Ref.[2]</td>
</tr>
<tr>
<td>$\chi_{1P_{3/2}1S_e}$</td>
<td>0.384</td>
<td>Eq.S24</td>
</tr>
<tr>
<td>$E_p$ (eV)</td>
<td>17.5</td>
<td>5</td>
</tr>
<tr>
<td>$\epsilon(\infty) = \frac{\epsilon_1(\infty)+2\epsilon_\parallel(\infty)}{3}$</td>
<td>6.27</td>
<td>12</td>
</tr>
<tr>
<td>$\epsilon(0) = \frac{\epsilon_1(0)+2\epsilon_\parallel(0)}{3}$</td>
<td>9.58</td>
<td>12</td>
</tr>
<tr>
<td>$Q^2$</td>
<td>0.925</td>
<td>Eq.S60</td>
</tr>
<tr>
<td>$n_r$</td>
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<td>14</td>
</tr>
<tr>
<td>$\epsilon = n_r^2$</td>
<td>1.90</td>
<td>14</td>
</tr>
</tbody>
</table>

Supporting References


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


