Symmetry breaking induced activation of the nanocrystal photoluminescence*

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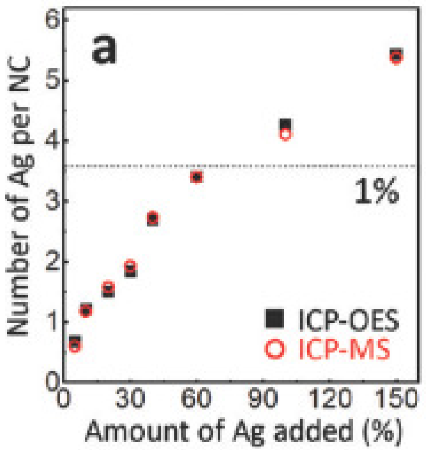
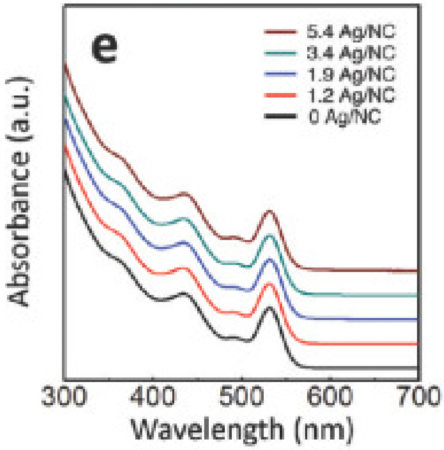
Photoluminescence of Ag Doped CdSe Nanocrystals

Sahu et al. Nano Lett. 2012, 12, 2587−2594

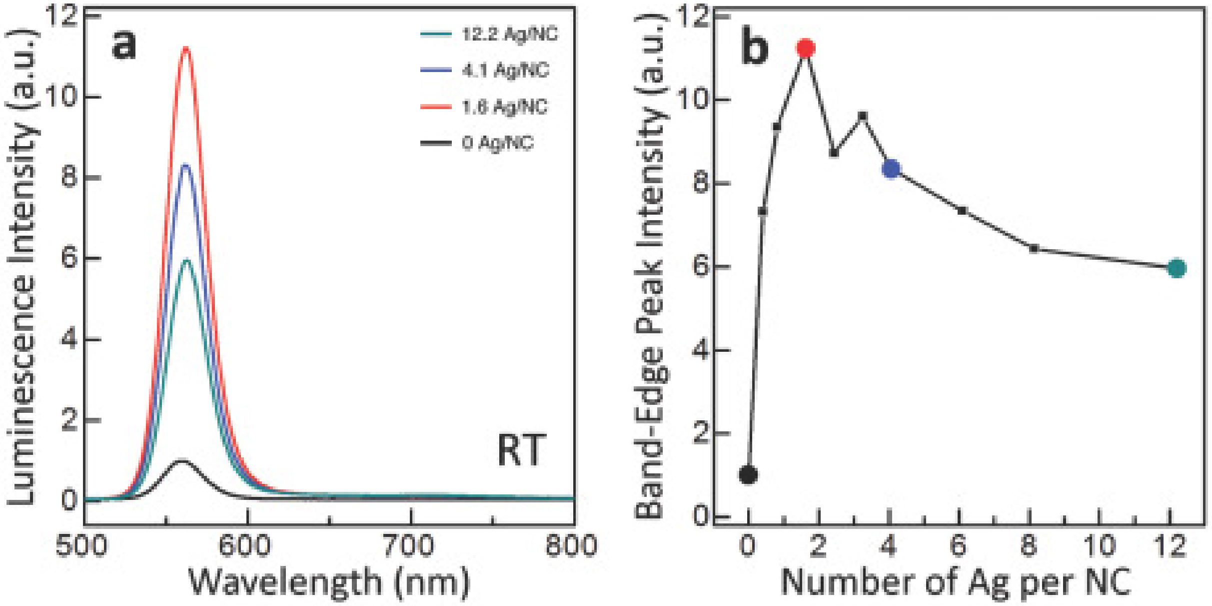
Cation-exchange doping

2.7 nm diameter NCs





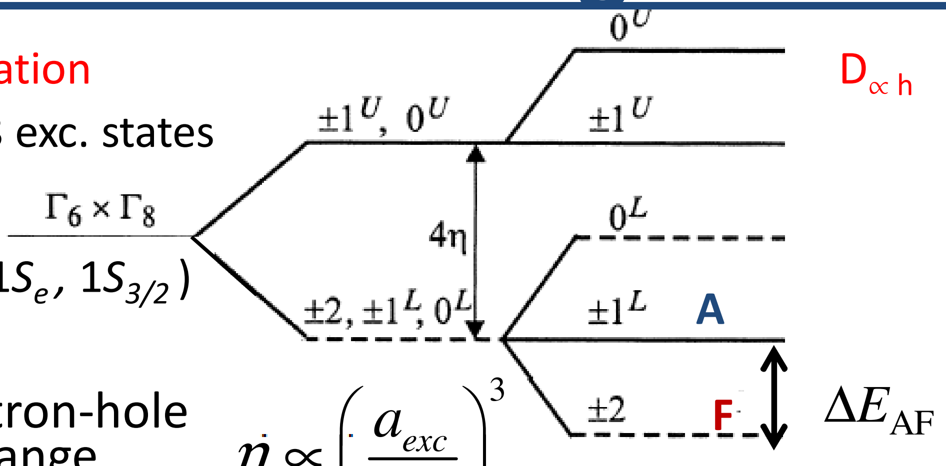
3.1 nm diameter nanocrystals in hexanes



Basic Band Edge Exciton Model

All rotation

2x4=8 exc. states



A- bright (active) exciton

F- dark (forbidden) exciton

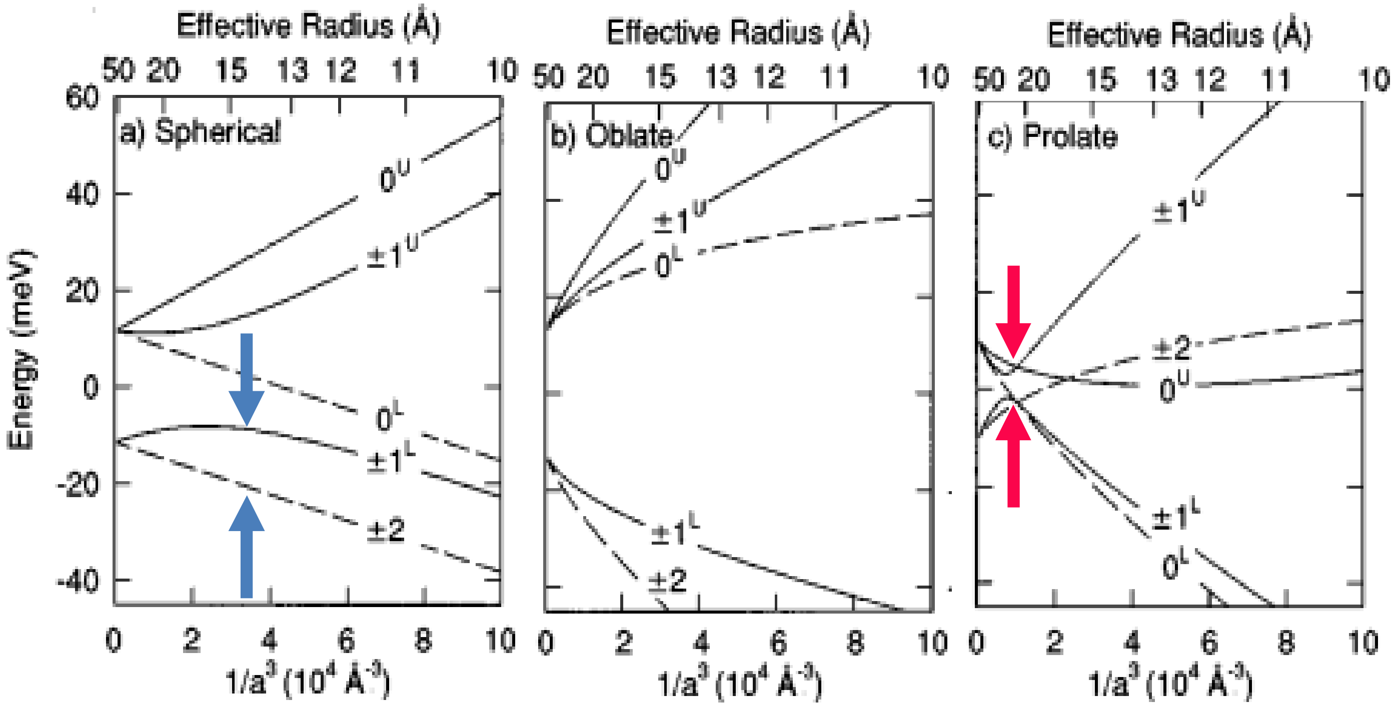
$$1/\tau^L_{\pm1} = (1/\tau_0)(\sqrt{3}\Delta/16\eta)^2$$

electron-hole exchange interaction

$$\eta \propto \left(\frac{a_{exc}}{a}\right)^3$$

Δ= crystal field + shape

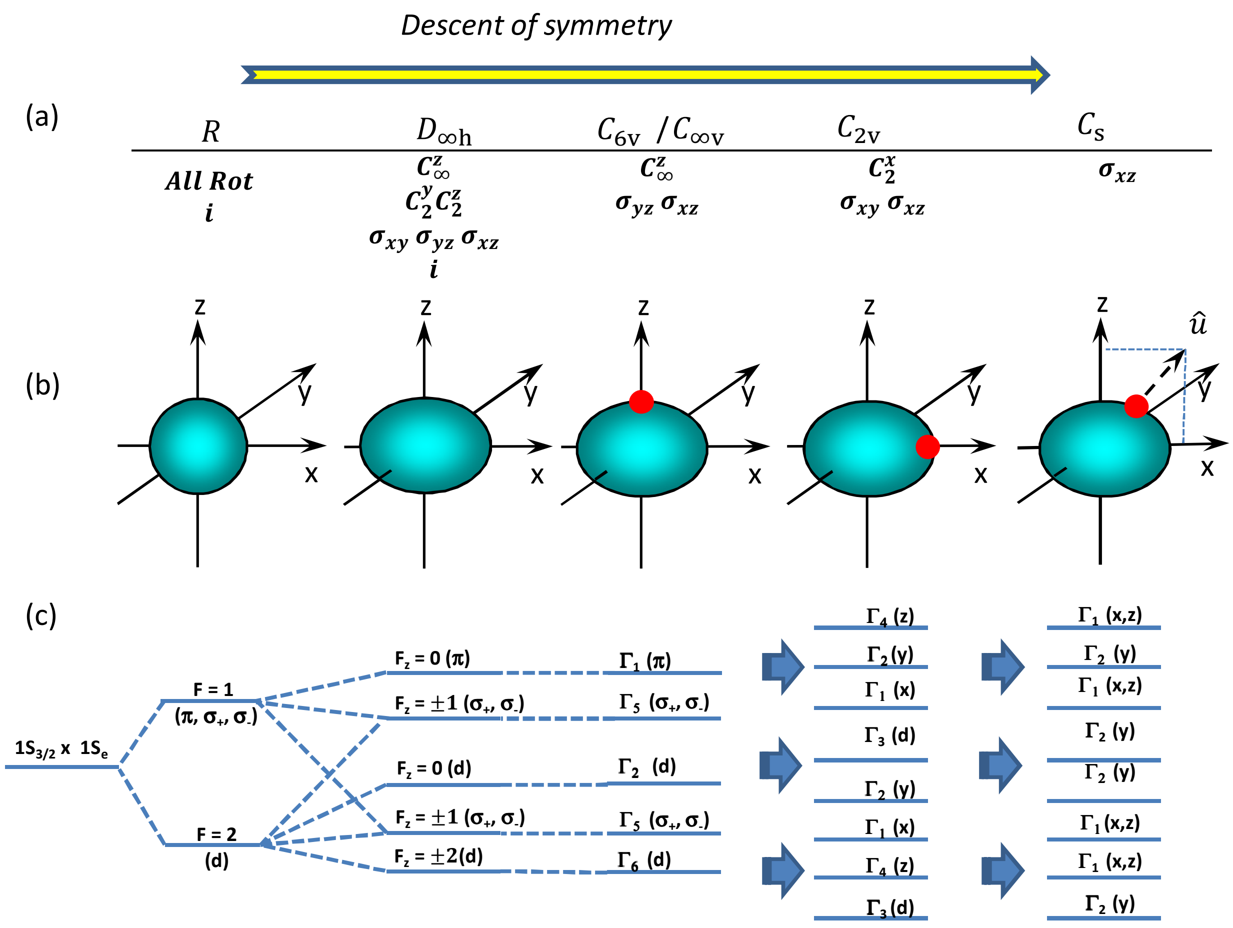
CdSe:



Al. Efros, *et al.*,
Phys. Rev. B
54, 4843 (1996)

Band Edge Exciton Fine Structure

The exciton quantum numbers (irreducible representations) are determined by decomposing the product representation $\Gamma_e \times \Gamma_h$ for the electron-hole pairs into irreducible representations. This decomposition describes the further splitting and polarization properties of excitons



R	$D_{\infty h}$	C_{6v} / $C_{\infty v}$	C_{2v}	C_s
All Rot $\boldsymbol{i}$	C_∞^z $C_2^y C_2^z$ $\sigma_{xy}\ \sigma_{yz}\ \sigma_{xz}$ $\boldsymbol{i}$	C_∞^z $\sigma_{yz}\ \sigma_{xz}$	C_2^x $\sigma_{xy}\ \sigma_{xz}$	σ_{xz}

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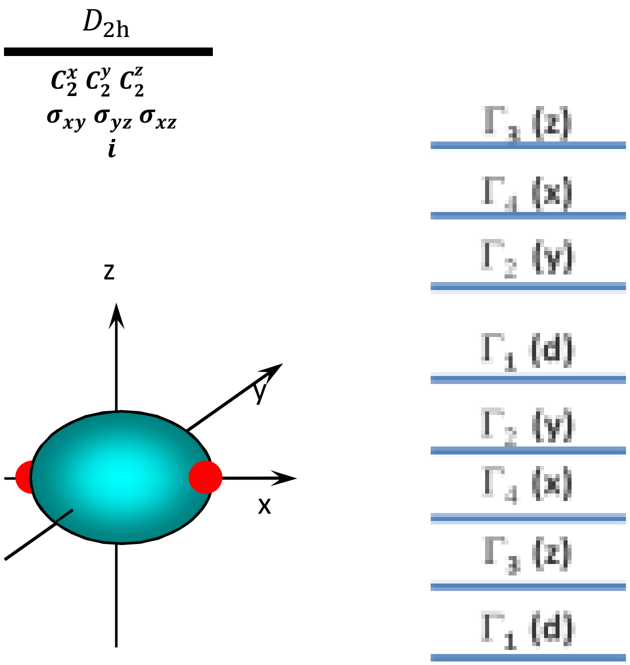
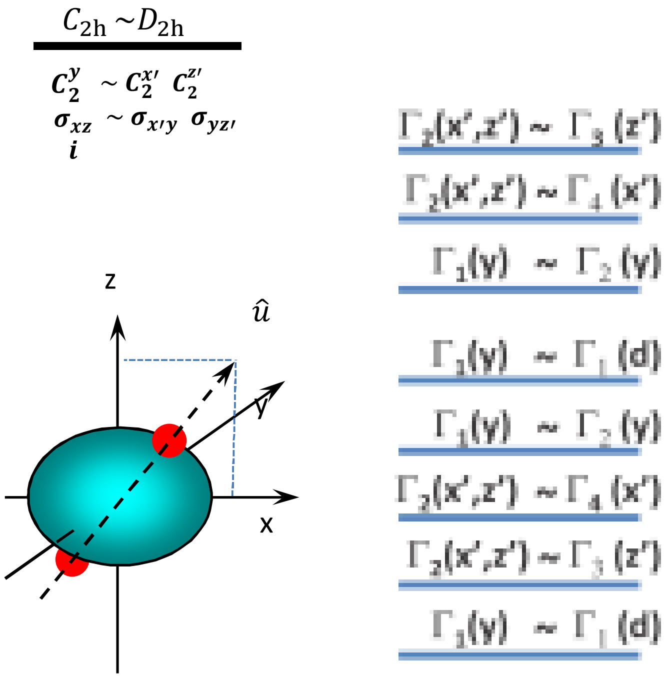
Approximate Symmetries

How rigorous are the symmetry arguments?





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

Model Hamiltonian possess D $_{2h}$ symmetry if we neglect $1P_{3/2}\ 1S_e$ excitons

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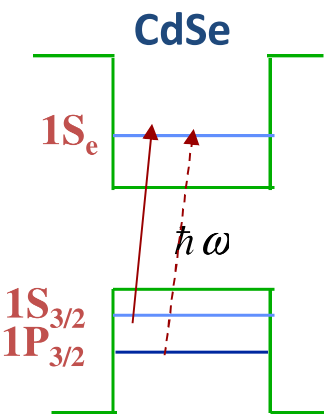
Electronic Structure in Doped Nanocrystals



The band edge absorption and PL in spherical NCs are controlled by transitions between ground $1S_e$ electron and $1S_{3/2}$ hole levels.

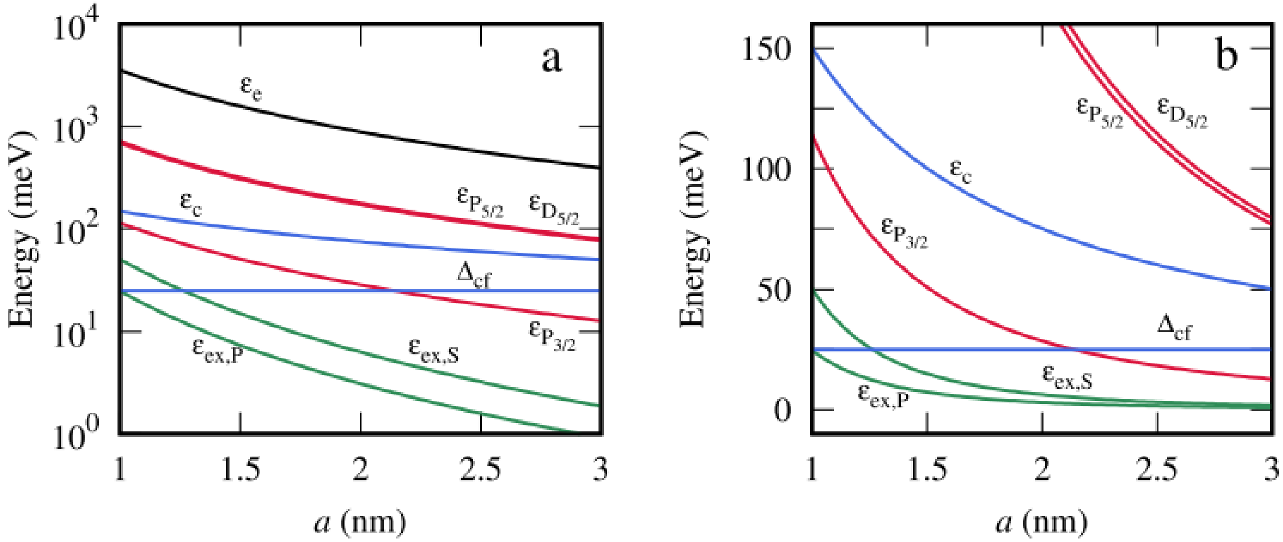
The second hole level $1P_{3/2}$ does not participate in optical transitions

Coulomb center creates a potential acting on electrons and holes

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

Off center Coulomb defect $\boldsymbol{r}_0\neq 0$ mixes up $1S_{3/2}$ and $1P_{3/2}$ states and allows $1S_e$ $1P_{3/2}$ transitions

Size dependence of critical parameters that control band edge exciton fine structure



Level spacing:

$$\varepsilon_e = E_{1P_e} - E_{1S_e}$$
$$\varepsilon_{P_{3/2}} = E_{1P_{3/2}} - E_{1S_{3/2}}$$
$$\varepsilon_{P_{5/2}} = E_{1P_{5/2}} - E_{1S_{3/2}}$$
$$\varepsilon_{D_{5/2}} = E_{1D_{5/2}} - E_{1S_{3/2}}$$

Coulomb energy: $e^2/\epsilon a$

Crystal field: Δ_{cf}=25meV

Exchange energies:

$\varepsilon_{ex,S}$ and $\varepsilon_{ex,P}$

Band edge excitons and their oscillator transition strengths is described by 16x16 matrix

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Effect of Coulomb Potential on Exciton Levels

The $l = 0$ term in expansion of Coulomb potential shifts both the electron and hole levels

$$H^{l=0}_{1S_{3/2},1S_{3/2}} = \frac{qe}{\epsilon a}\left(M^h_{1S_{3/2}} - M^e_{1S_e}\right)\hat{\mathbb{I}}\ , \qquad H^{l=0}_{1P_{3/2},1P_{3/2}} = \frac{qe}{\epsilon a}\left(M^h_{1P_{3/2}} - M^e_{1S_e}\right)\hat{\mathbb{I}}\ .$$

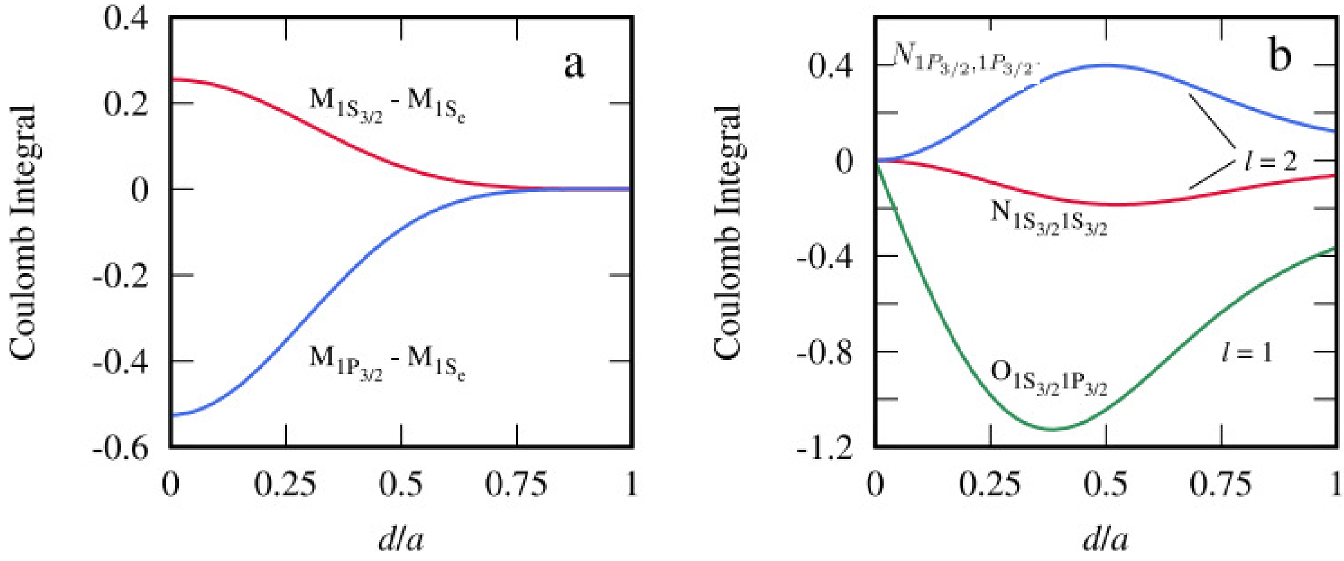
The l=2 term additionally splits the hole levels with projection ±1/2 and ±3/2:

$$H^{l=2}_{1S_{3/2},1S_{3/2}} = \frac{qe}{\epsilon a} N_{1S_{3/2},1S_{3/2}} \tilde{H}_{l=2}\ , \qquad H_{1P_{3/2},1P_{3/2}} = \frac{qe}{\epsilon a} N_{1P_{3/2},1P_{3/2}} \tilde{H}_{l=2}\ .$$

The l=1 odd term mixes up $1S_{3/2}$ and $1P_{3/2}$ hole sublevels:

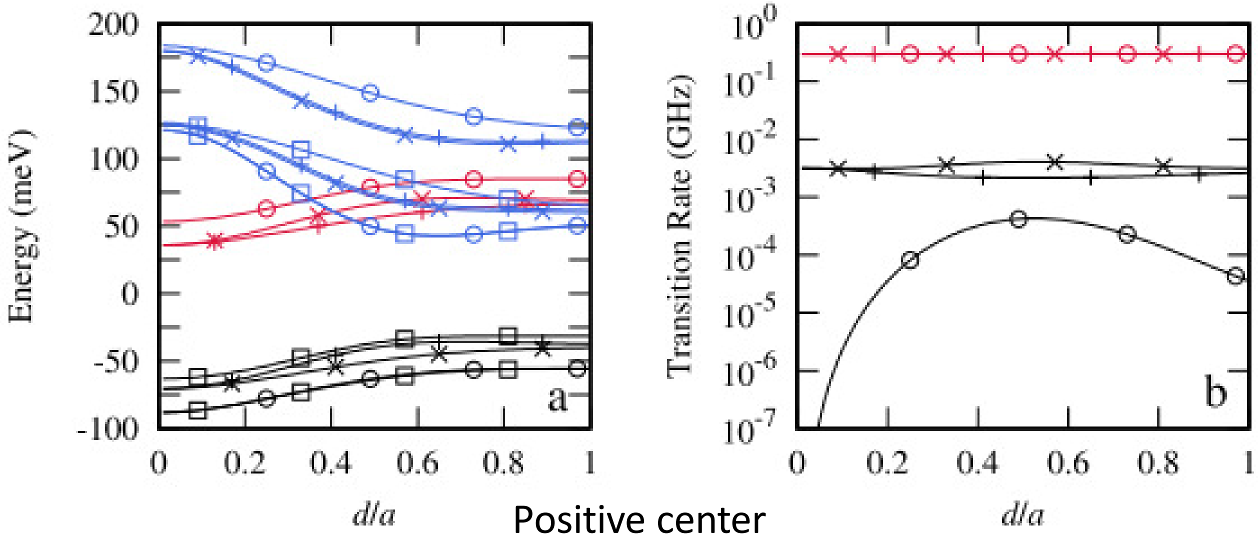
$$H_{1S_{3/2},1P_{3/2}} = \frac{qe}{\epsilon a}\ O_{1S_{3/2},1P_{3/2}} \begin{pmatrix} \sqrt{\frac{3}{5}}b_z & \sqrt{\frac{2}{5}}b_- & 0 & 0 \\ \sqrt{\frac{2}{5}}b_+ & \frac{b_z}{\sqrt{15}} & 2\sqrt{\frac{2}{15}}b_- & 0 \\ 0 & 2\sqrt{\frac{2}{15}}b_+ & -\frac{b_z}{\sqrt{15}} & \sqrt{\frac{2}{5}}b_- \\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

where $b_z(\theta_0, \phi_0)$, $b_\pm(\theta_0, \phi_0)$

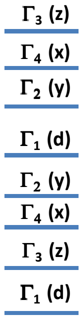


Exciton Level Structure in CdSe NC with Coulomb Center with Approximate Symmetry D_{2h}

Negative center



D_{2h} level structure



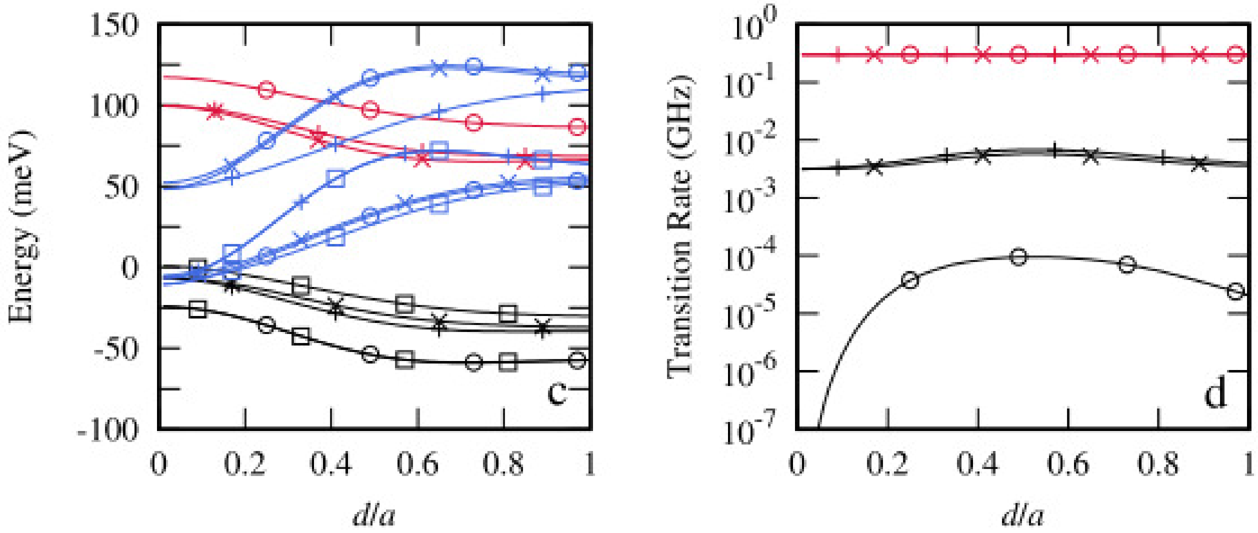
— $1S_e1P_{3/2}$ exciton manifold

— $1S_e1S_{3/2}$ exciton manifold

○ – (Γ_3, z), × – (Γ_2, y)

+ – (Γ_4, x), □ – (Γ_1, d).

Positive center



The radiative transition rates:

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

where

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

NC radius $a = 1.2$nm, $\phi_0 = 0,\ \theta_0 = \pi/4$, $\Delta_{ax} = 25$ meV.

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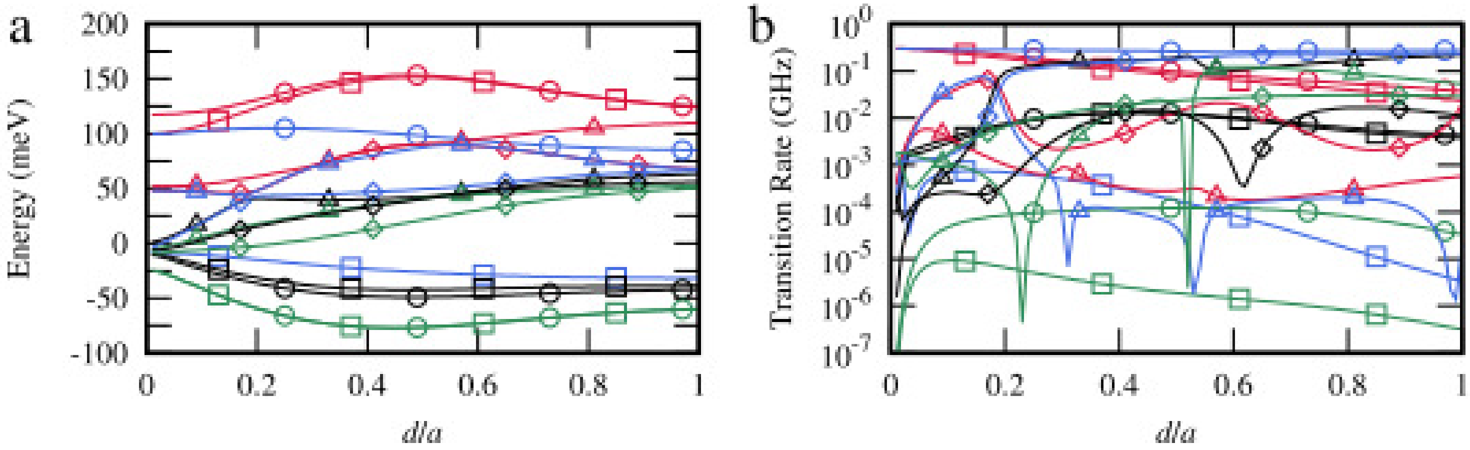
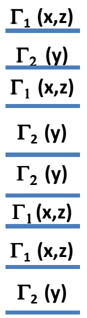
Exciton Level Structure in CdSe NC with Positive Coulomb Center with Symmetry C_s



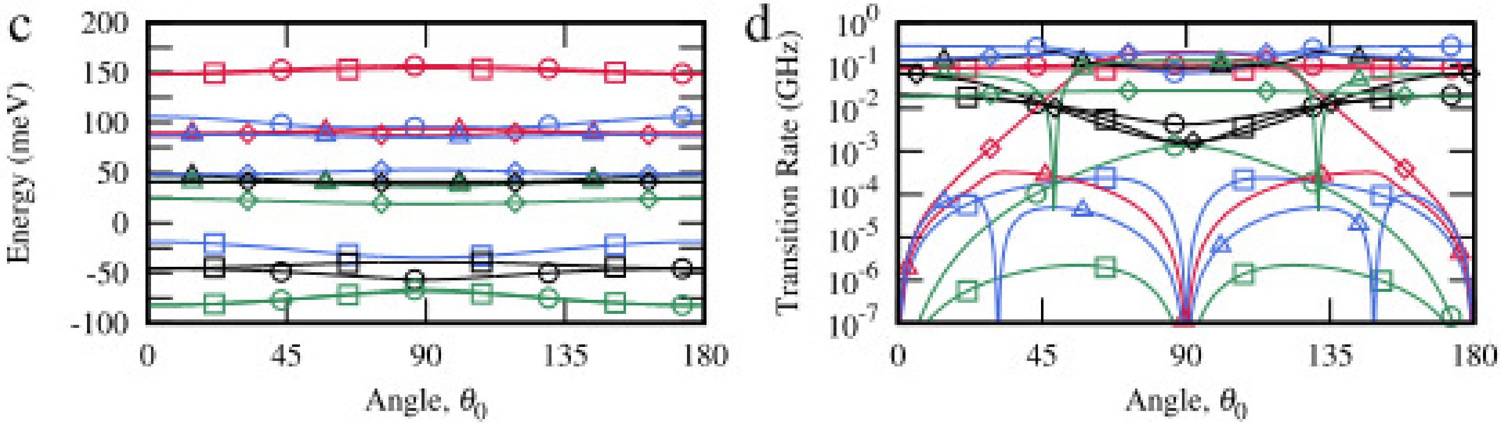
NC radius a = 1.2nm, $\phi_0 = 0,\ \theta_0 = \pi/4$, Δ_{ax} = 25 meV.

C_s level structure



○ and ◇ – (Γ_1, x, z)

□ and △ – (Γ_2, y)



NC radius a = 1.2nm, ϕ_0 =0, d/a = 0.5, and Δ_{ax} = 25 meV.

Lines with symbols ○ and □ and with symbols ◇ and △ are formed from the $1S_e\ 1S_{3/2}$ & $1S_e\ 1P_{3/2}$ exciton state manifold respectfully at small d/a .

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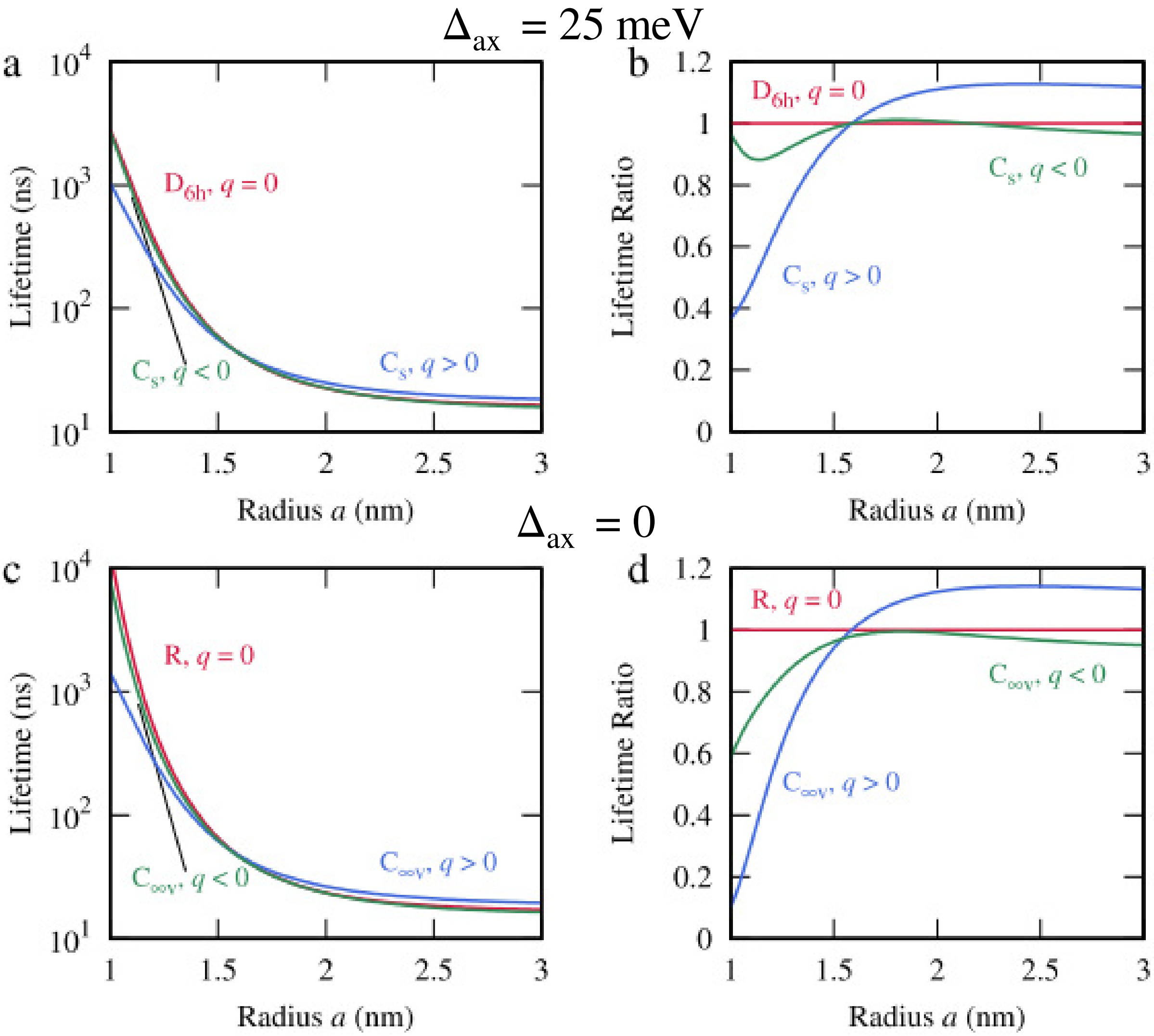
Room Temperature Lifetime of NCs with Coulomb Center

NC radiative decay rate is the thermally weighted average of the decay rates of all exciton sublevels:

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

where we assume that each exciton level with energy E_k is populated according to a Boltzmann distribution



Defects are positioned in the x, z plane at $d/a = 0.5$ and angle $\theta = \pi/4$

Ag Donors in CdSe Nanocrystals

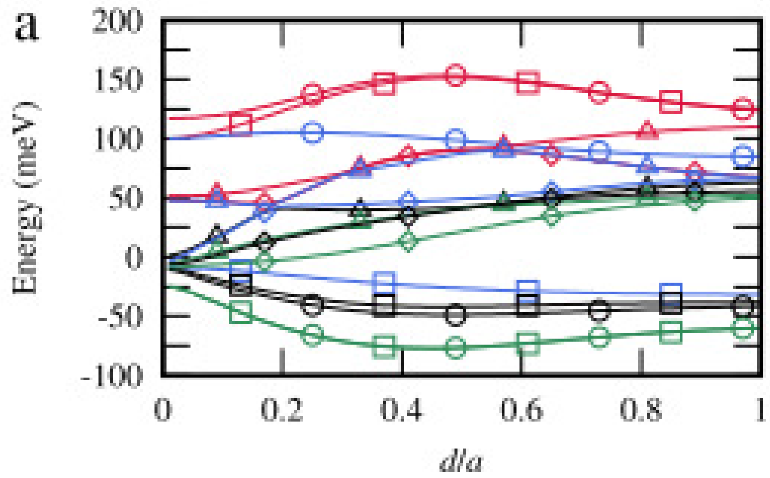
Ag donors in CdSe NC occupy an interstitial position in the CdSe lattice and are quite mobile at room temperature. The barrier height for Ag hopping is ~ 0.2 eV*

Typical hopping time at RT ~ 45ns, which is comparable with radiative decay time ~ 20ns

⬇

broadening of emission spectra and band edge absorption

At low temperatures interaction of positive Ag donors with the exciton could bring them to the d/a ~ 0.5 region , where exciton levels have smallest energy :

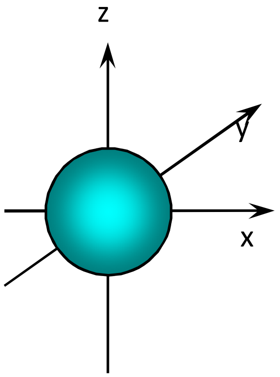


* Ott, F. D.; Spiegel, L.; Norris, D.J.; Erwin, S.C. Phys. Rev. Lett. 2014, **113**, 156803

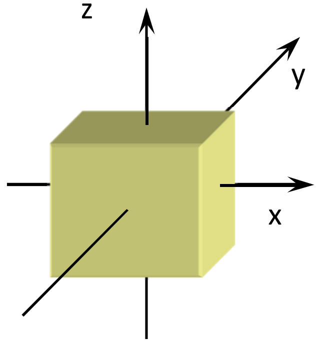
Cube Shape with no Hexagonal Crystal Field

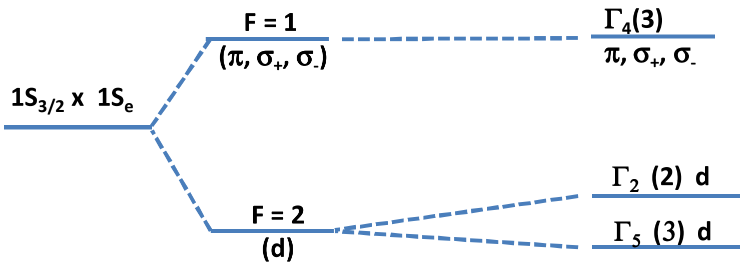
R

All Rot
i

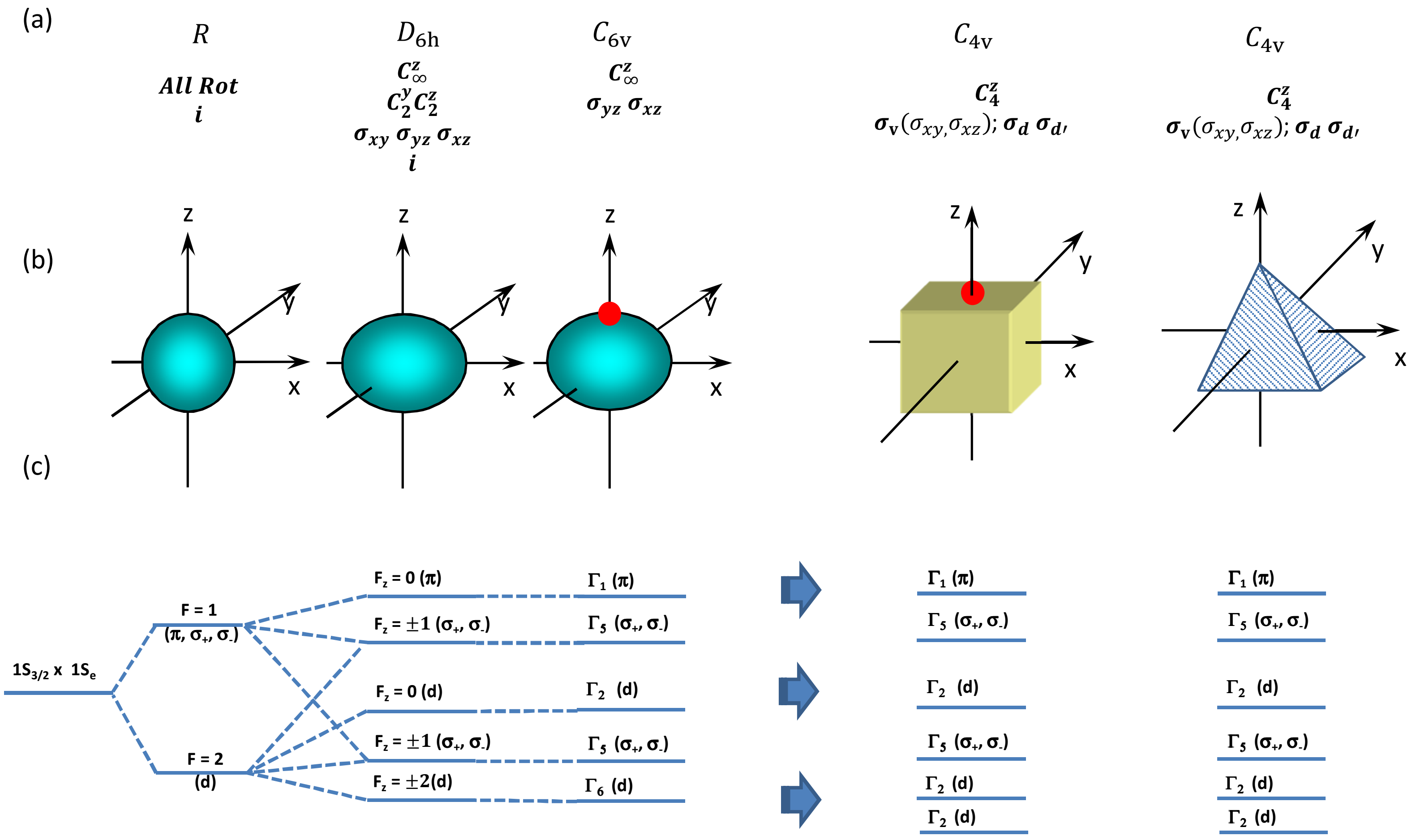


O_h





Cube and Pyramidal Shape CdSe NC with Hexagonal Crystal Field


(a)

R
All Rot
i

D_{6h}
C_∞^z
$C_2^y C_2^z$
$\sigma_{xy}\ \sigma_{yz}\ \sigma_{xz}$
i

C_{6v}
C_∞^z
$\sigma_{yz}\ \sigma_{xz}$

C_{4v}
C_4^z
$\sigma_v(\sigma_{xy},\sigma_{xz});\ \sigma_d\ \sigma_{d'}$

C_{4v}
C_4^z
$\sigma_v(\sigma_{xy},\sigma_{xz});\ \sigma_d\ \sigma_{d'}$

(b)

(c)

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

F = 1
$(\pi, \sigma_+, \sigma_-)$

F = 2
(d)

$F_z = 0\ (\pi)$
$F_z = \pm 1\ (\sigma_+, \sigma_-)$
$F_z = 0\ (d)$
$F_z = \pm 1\ (\sigma_+, \sigma_-)$
$F_z = \pm 2 (d)$

$\Gamma_1\ (\pi)$
$\Gamma_5\ (\sigma_+, \sigma_-)$
$\Gamma_2\ (d)$
$\Gamma_5\ (\sigma_+, \sigma_-)$
$\Gamma_6\ (d)$

$\Gamma_1\ (\pi)$
$\Gamma_5\ (\sigma_+, \sigma_-)$
$\Gamma_2\ (d)$
$\Gamma_5\ (\sigma_+, \sigma_-)$
$\Gamma_2\ (d)$
$\Gamma_2\ (d)$

$\Gamma_1\ (\pi)$
$\Gamma_5\ (\sigma_+, \sigma_-)$
$\Gamma_2\ (d)$
$\Gamma_5\ (\sigma_+, \sigma_-)$
$\Gamma_2\ (d)$
$\Gamma_2\ (d)$

CdSe NC with Hexagonal Crystal Field: Shape Perturbation to C_{3v}*

R

$\boldsymbol{All\ Rot}$

$\boldsymbol{i}$

D_{6h}

C^z_∞

$C^y_2 C^z_2$

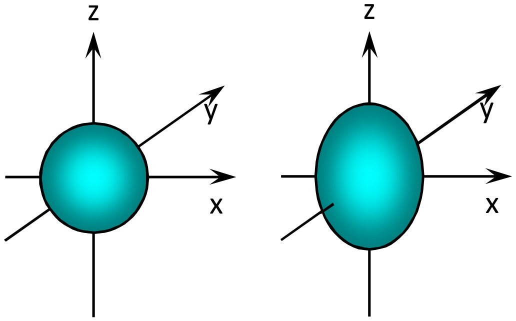
$\sigma_{xy}\ \sigma_{yz}\ \sigma_{xz}$

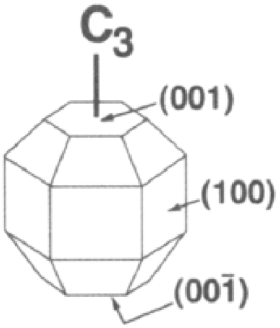
$\boldsymbol{i}$

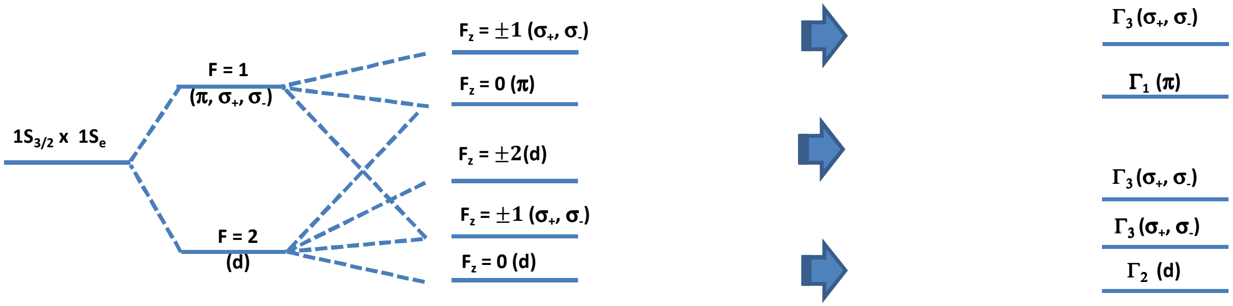
C_{3v}

C^z_3

$\sigma_{xz}\ \sigma_{x'z}\ \sigma_{x''z}$







$1S_{3/2}$ x $1S_e$

F = 1 (π, σ_+, σ_-)

F = 2 (d)

F_z = ±1 (σ_+, σ_-)

F_z = 0 (π)

F_z = ±2(d)

F_z = ±1 (σ_+, σ_-)

F_z = 0 (d)

Γ_3 (σ_+, σ_-)

Γ_1 (π)

Γ_3 (σ_+, σ_-)

Γ_3 (σ_+, σ_-)

Γ_2 (d)

J.J. Shiang, A. V. Kadavanich, R. K. Grubbs, and A.P. Alivisatos, J.Phys.Chem. 1995, **9**9, 17417.

Summary

1. The descent of the nanocrystal symmetry from spherical to point group C_s, which is characterized by just one reflection plane symmetry element, leads step by step to activation of all five $F = 2$, $F_z = \pm 2, \pm 1, 0$ excitons.
2. Even the ground exciton becomes optically active, which should be observable in low-temperature photoluminescence measurements.
3. For several intermediate symmetries the band edge exciton fine structure consists of sets of three linearly polarized mutually orthogonal dipoles plus a dark exciton, one of which is always the ground state.
4. We quantify the effect of symmetry descent on the exciton fine structure by introducing a charged Coulomb impurity in the nanocrystals.
5. The nanocrystal symmetry breaking by a Coulomb impurity shortens the radiative decay of nanocrystals even at room temperatures in qualitative agreement with the increase in PL efficiency observed in nanocrystals doped with positive Ag charge centers.