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Single-Photon Excitation Lost in the Multi-Exciton Maze of a Nanocrystal

W. Witzel in lieu of Al. L. Efros

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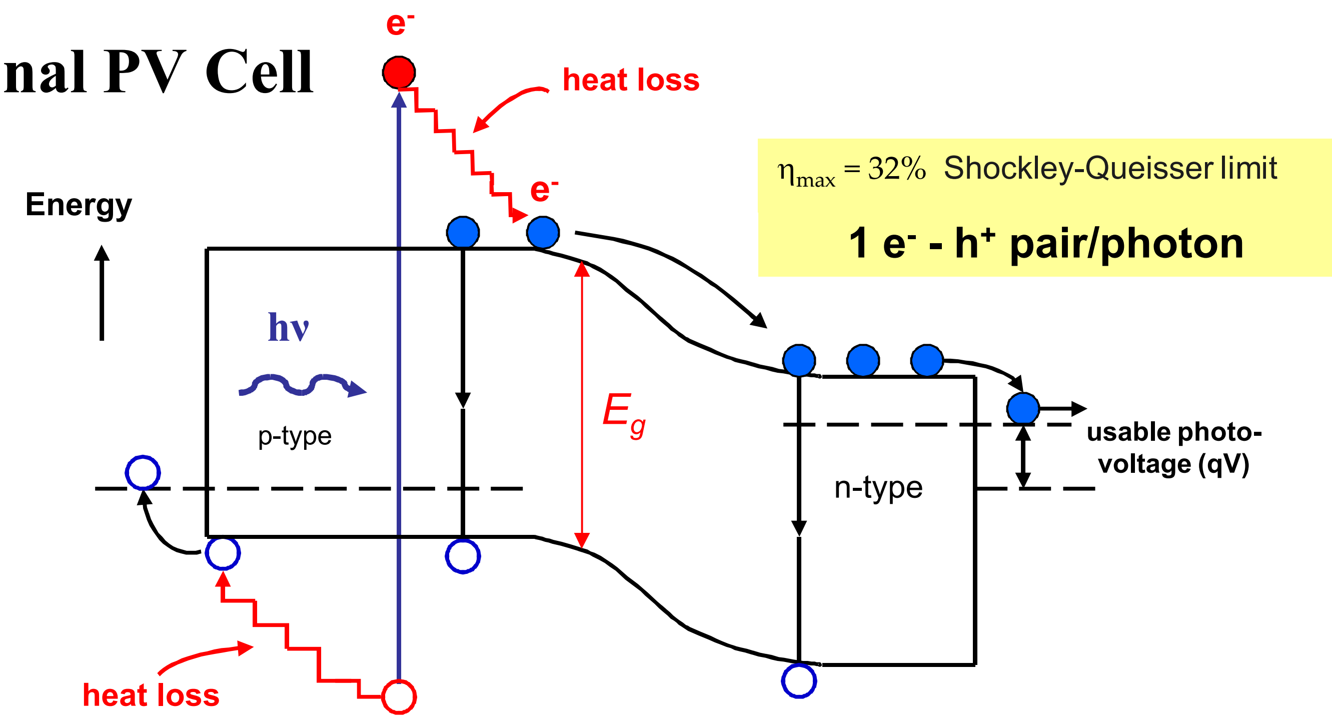
Solar Energy Conversion

Clean and renewable energy is the most challenging problem of our generation

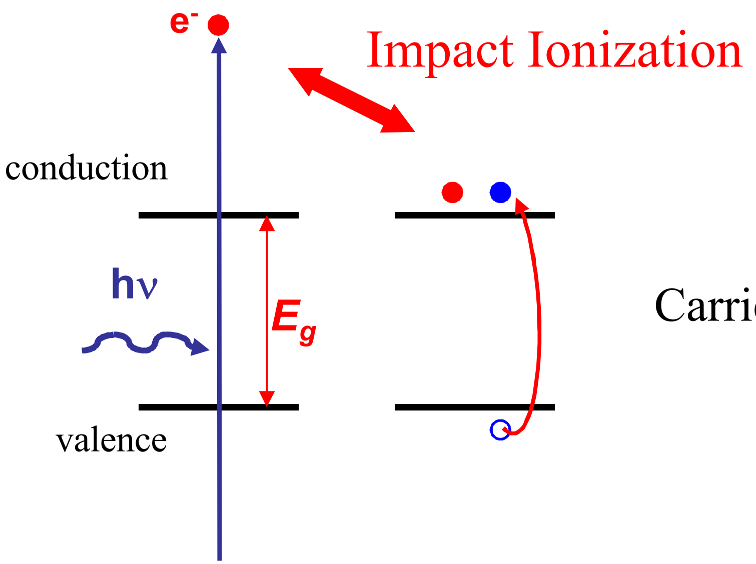
Conventional PV Cell



Can we utilize the excess energy: hν - E_g ??

Carrier Multiplication

Can we utilize the excess energy: $h\nu$ - E_g ?

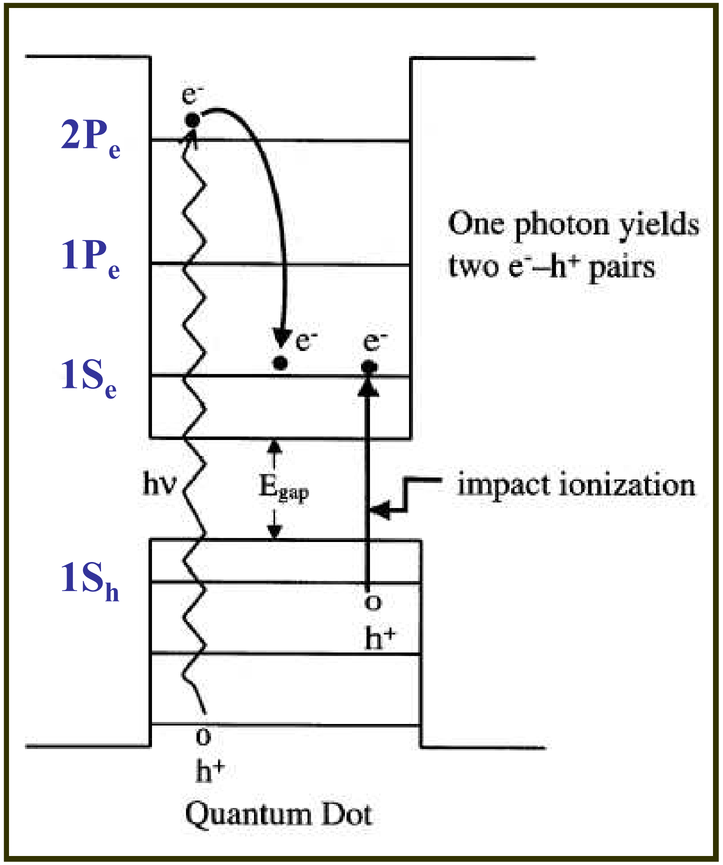


Carrier multiplication if $h\nu - E_g > E_g$

However carrier multiplication is inefficient in bulk:

- Impact ionization rate in bulk is very small
- Thermalization rate is much faster than impact ionization rate

Carrier Multiplication in Nanocrystals

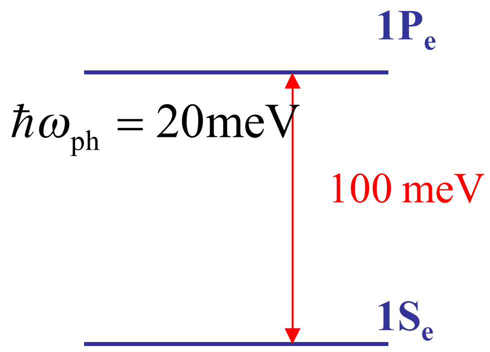


A. J. Nozik, Physica E 14 (2002), 115-120.

- Impact ionization is an inverse Auger process
  Auger processes enhanced in nanocrystals

$$\langle 2P_e | v(r_1, r_2) | \, 1S_e \, 1S_e \, 1S_h \rangle$$

- Discrete e-h spectra ⟶ Phonon bottleneck
  Carrier thermalization is suppressed

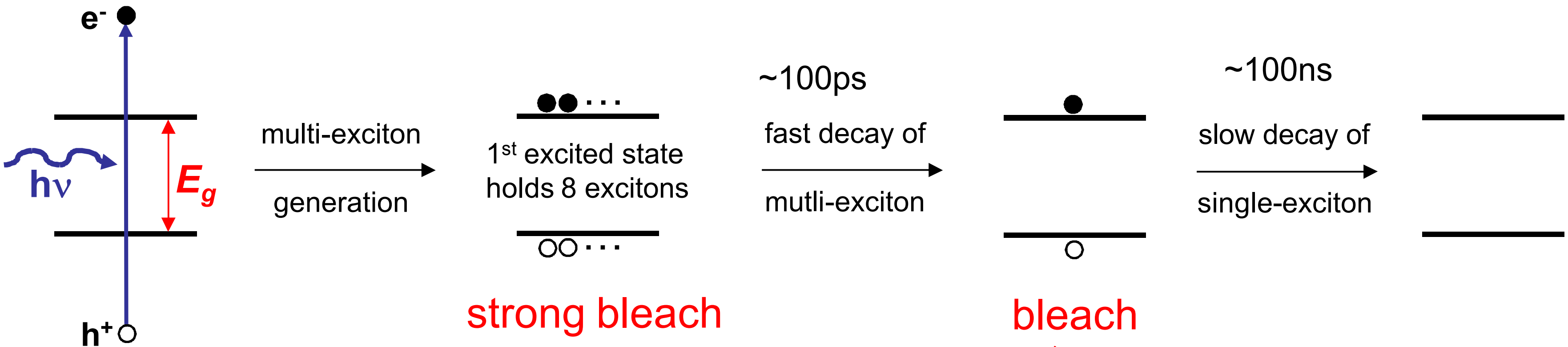


Impact ionization can compete successfully with thermalization !!

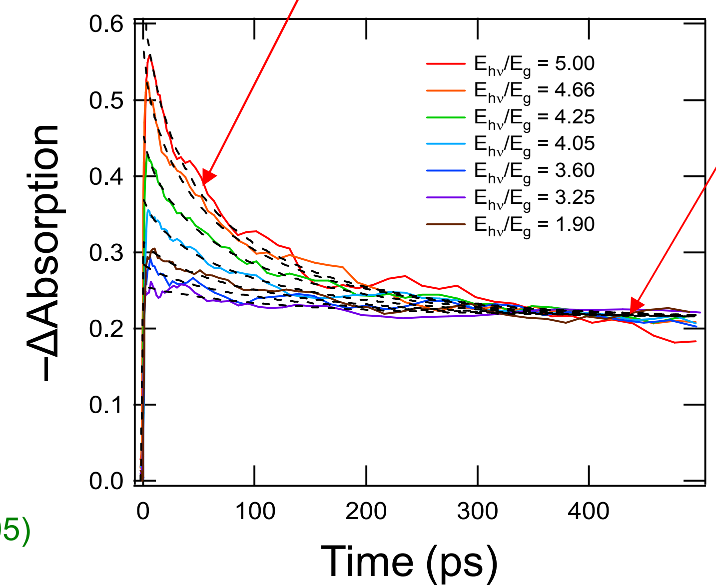
Multiple Excitons Generated by One Photon

Effect first observed in transient absorption dynamics in PbSe nanocrystals

R.Schaller & V. Klimov, PRL **92** *186601* (2004)



Experimental Evidence



R.Ellingson, et.al.
NanoLetters **5,** 865 (2005)

Band-edge transient bleach:

$$-\Delta\alpha_{1S} \sim F$$

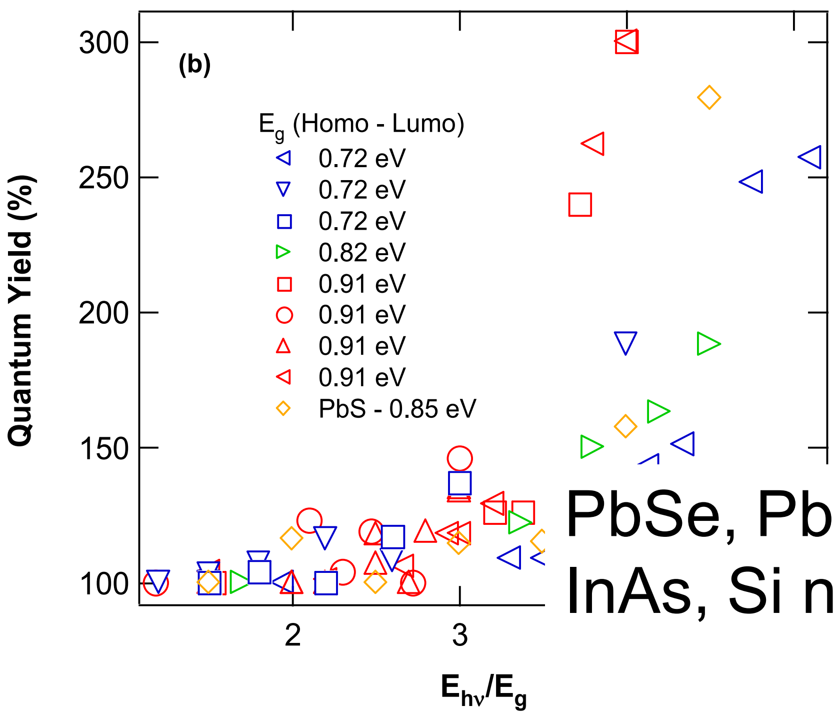
filling factor: $F = \dfrac{n_e + n_h}{8}$

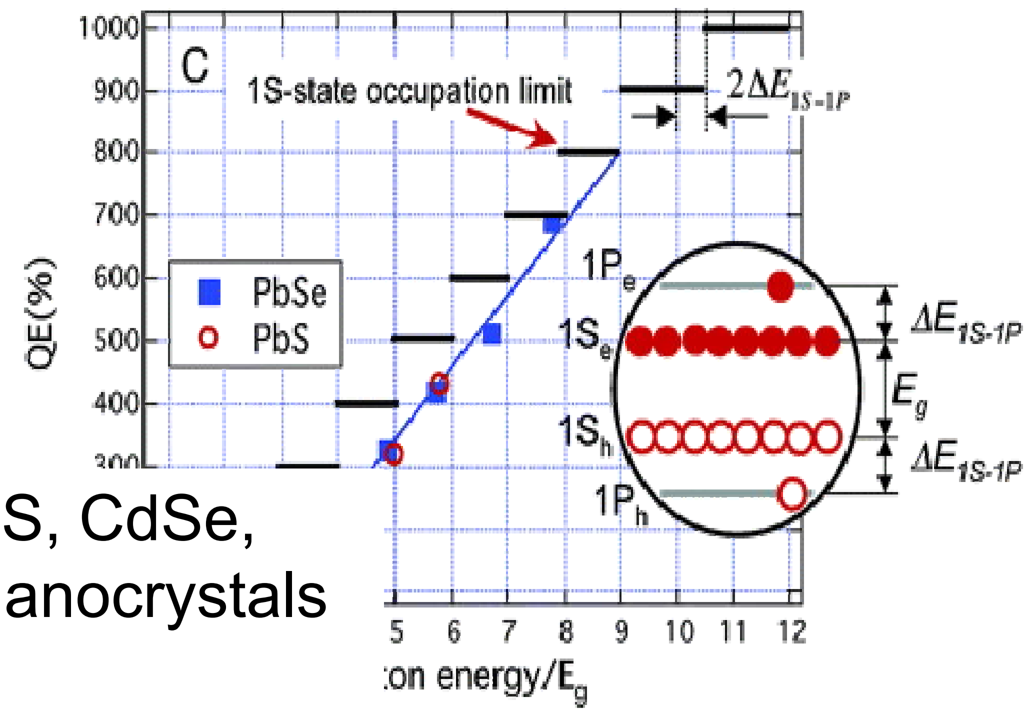
$n_e \le 8$ and $n_h \le 8$

For single exciton: $F=1/4$,
two excitons: $F=1/2$

Quantum Yield of Multi-Exciton Generation

Quantum Yield measured by transient bleach: **QY=(n_e+n_h)100%**





PbSe, PbS, CdSe, InAs, Si nanocrystals

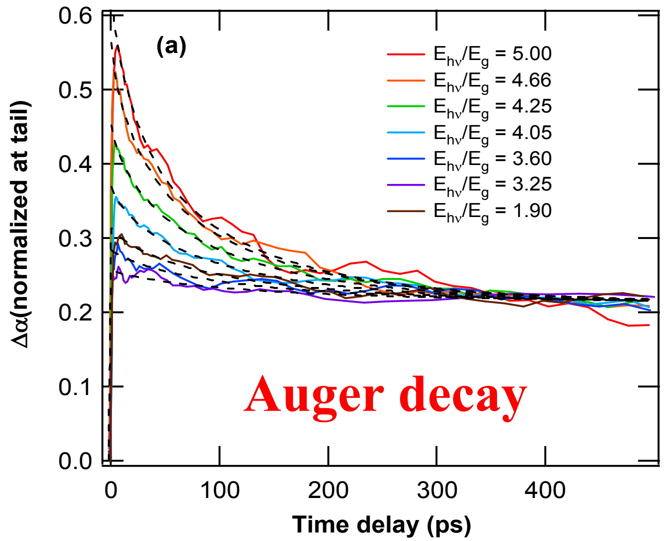
R.Ellingson, et.al. NanoLetters 5

Using various techniques

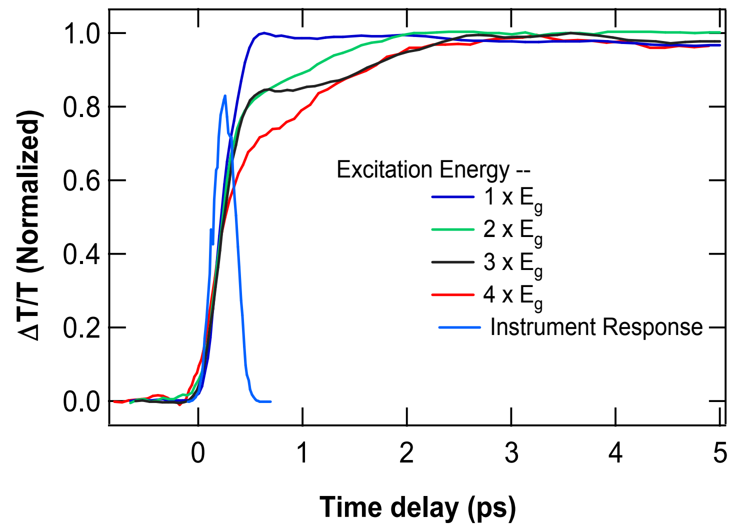
al., NanoLetters, **6**, 424 (2006)

What is the reason of such high efficiency?

Impact Ionization?



Bleach build up



R.Ellingson, et.al. NanoLetters (2005)

Puzzle:

- Decay time ~100 ps (Auger process)
- Rise time ~2-3 ps (Inverse Auger process)

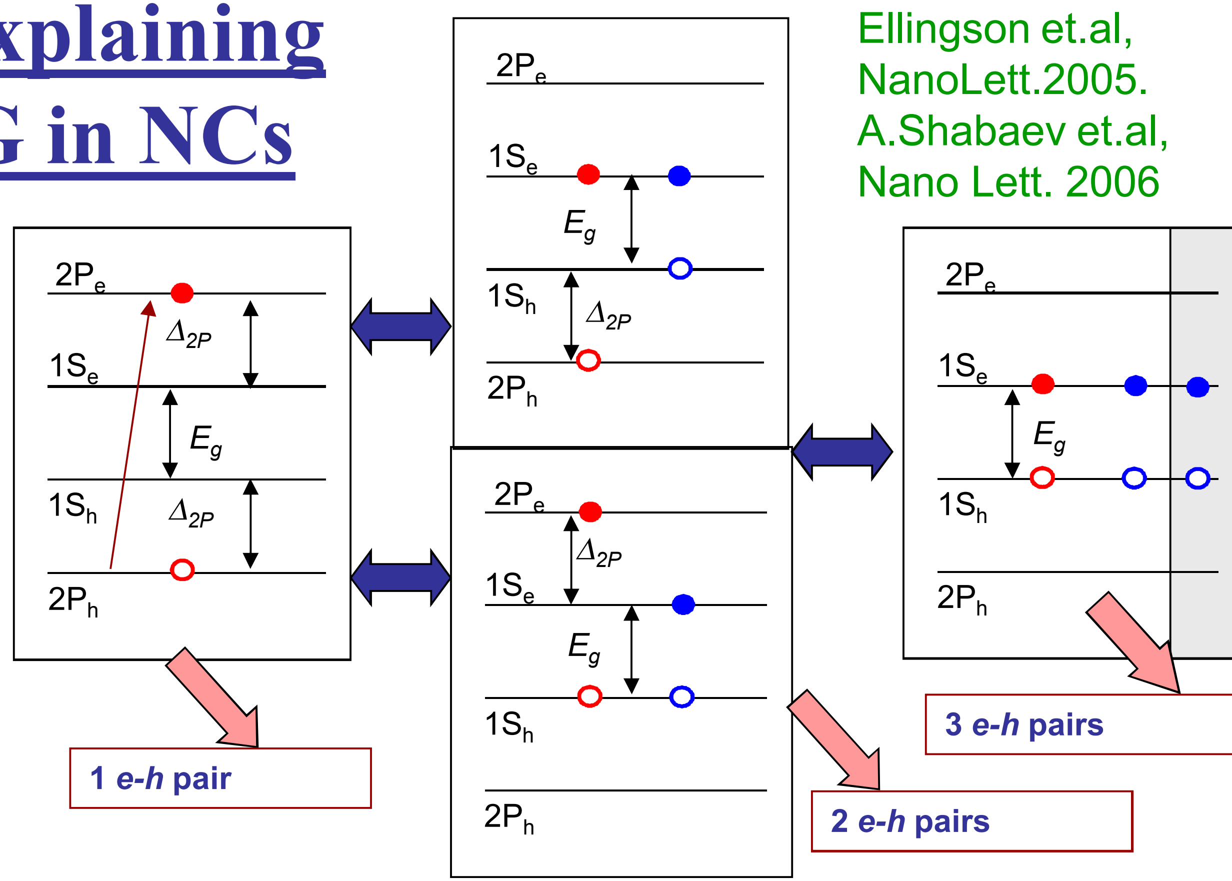
Rise time consistent only with carrier thermalization time.

Creation of a coherent superposition of a single and several electron-hole pairs.

Two Models Explaining Efficient MEG in NCs

Coherent superposition model:

light $\hbar\,\omega$



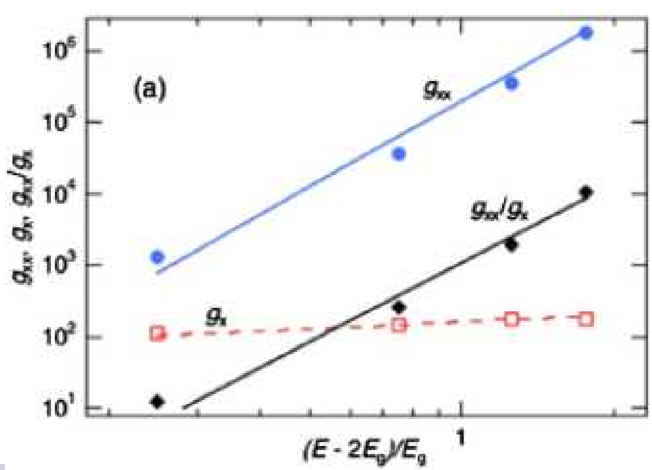
Ellingson et.al, NanoLett.2005.
A.Shabaev et.al, Nano Lett. 2006

Basis: single electron or hole states are not eigenstates of a NC.

Non- Coherent models:

Basis: the density of the biexciton states is much larger that the exciton one

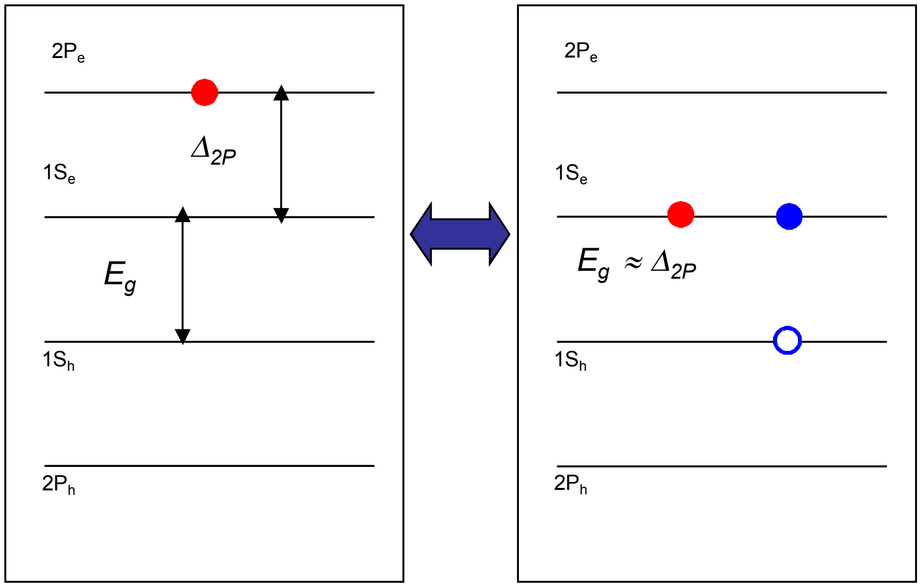
Schaller, Agranovich, Klimov, Nature Phys, 2005.

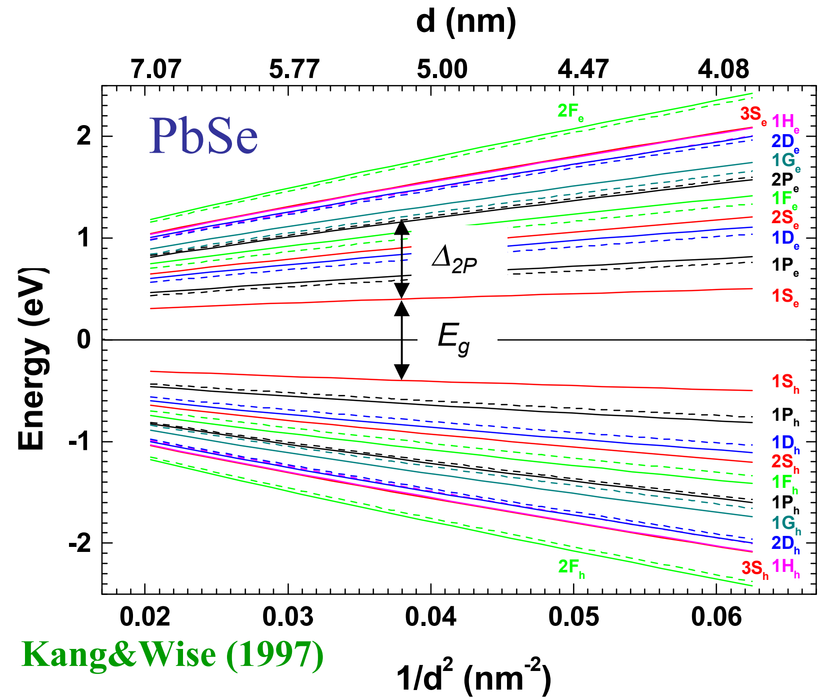


Putasov, Klimov, PRB 2007

States with Energy Larger than Energy Gap

Electron in the $2P_e$ state:



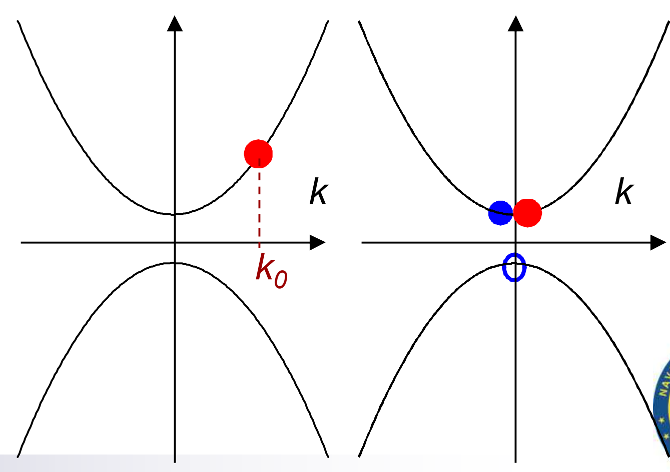


Two states are degenerate and coupled:

$\langle 2P_e|v(r_1,r_2)|\ 1S_e\ 1S_e\ 1S_h\rangle$ 🕒0

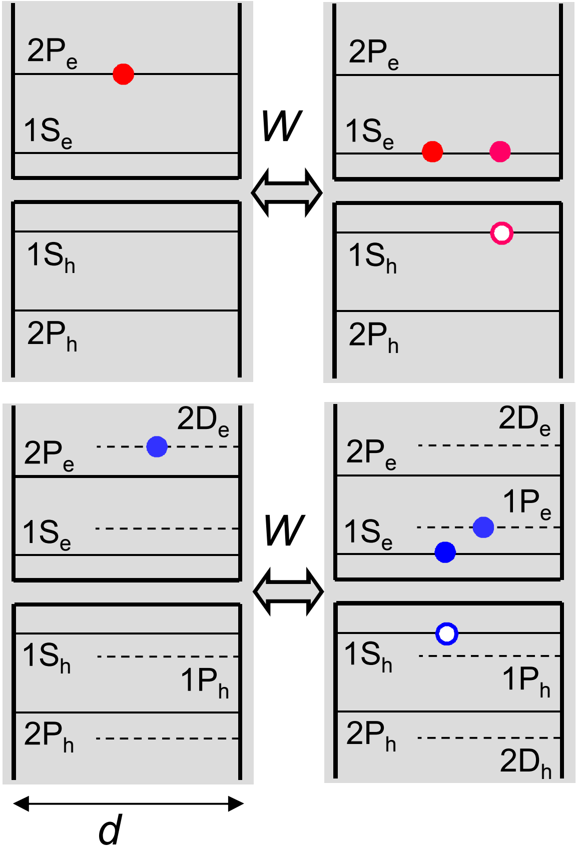
Single electron approximation is not valid for these carriers !!!

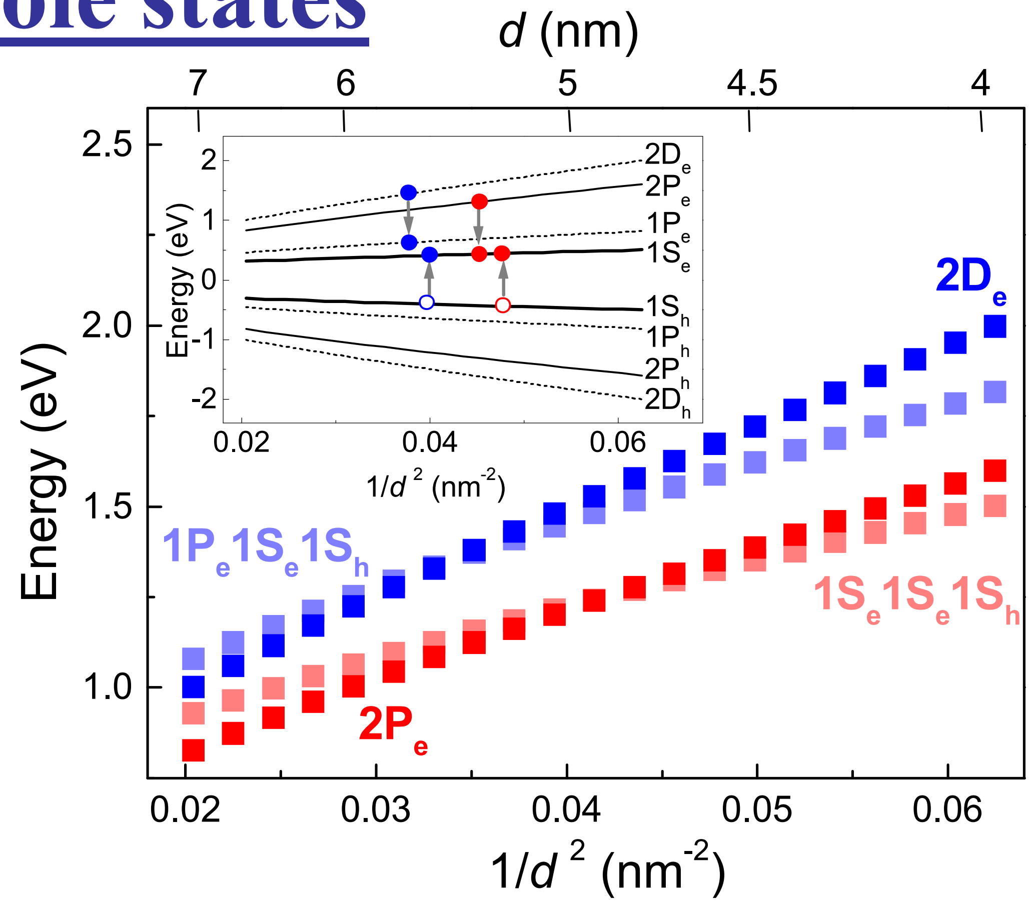
In bulk:



Two degenerate states BUT uncoupled

Multi-electron-hole states





Valence and conduction bands in PbSe are almost symmetrical: ***$2P_h$ and $2D_h$* hole states are strongly coupled with trion states.**

$\Psi_{2Pe,\,2De}$ =50%| **electron⇧** + 50%|**trion⇧**

Wave functions of the mixed electron and hole states:

$$\Psi^{\nu,e}_{"nL"} = \alpha^{\nu,e}_{nL}\,|nL_e\rangle + \sum_{k,i,m} \beta^{\nu,e}_{nL}(k,i,m)\left|kL^k_e iL^i_e mL^m_h\right\rangle$$

electron **trion**

$$\Psi^{\nu,h}_{"nL"} = \alpha^{\nu,h}_{nL}\,|nL_h\rangle + \sum_{k,i,m} \beta^{\nu,h}_{nL}(k,i,m)\left|kL^k_h iL^i_h mL^m_e\right\rangle$$

hole **trion**

Non-Coherent Models of the MEG

Use the Fermi Golden Rule: $$P_{ex \to biex} = \frac{2\pi}{\hbar} W^2 \rho_{biex}(\hbar\omega)$$

where W🕔 <ex|$v(r_1,r_2)$| biex> and ρ_{biex} is the density of the biexciton states.

The FGR is an approximation !!!!

The rate of formation of ONE excited J- bi-exciton state from the optically created exciton:

$$P_{ex \to J-biex} = \frac{W_J^2(\gamma_1+\gamma_2)}{(E_{ex}-E_J)^2/4 + W_J^2(1+\gamma_1/\gamma_2) + (\gamma_1+\gamma_2)^2\hbar^2}$$

where E_{ex} and E_J are the exciton and J- bi-exciton energies, W_j🕔 <ex|$v(r_1,r_2)$|J-biex>, γ_1 and γ_2 are the exciton and biexciton relaxation rate:

The total transition rate: $$P_{ex \to biex} = \sum_J P_{ex \to J-biex}$$

How do we get the FGR ?

We assume: **1.** $\gamma_2 >> W_J/\hbar$ $$\Rightarrow P_{ex \to J-biex} \approx \frac{W_J^2}{\gamma_2 \hbar^2}$$

2. $W^2 = \langle W_J^2 \rangle$

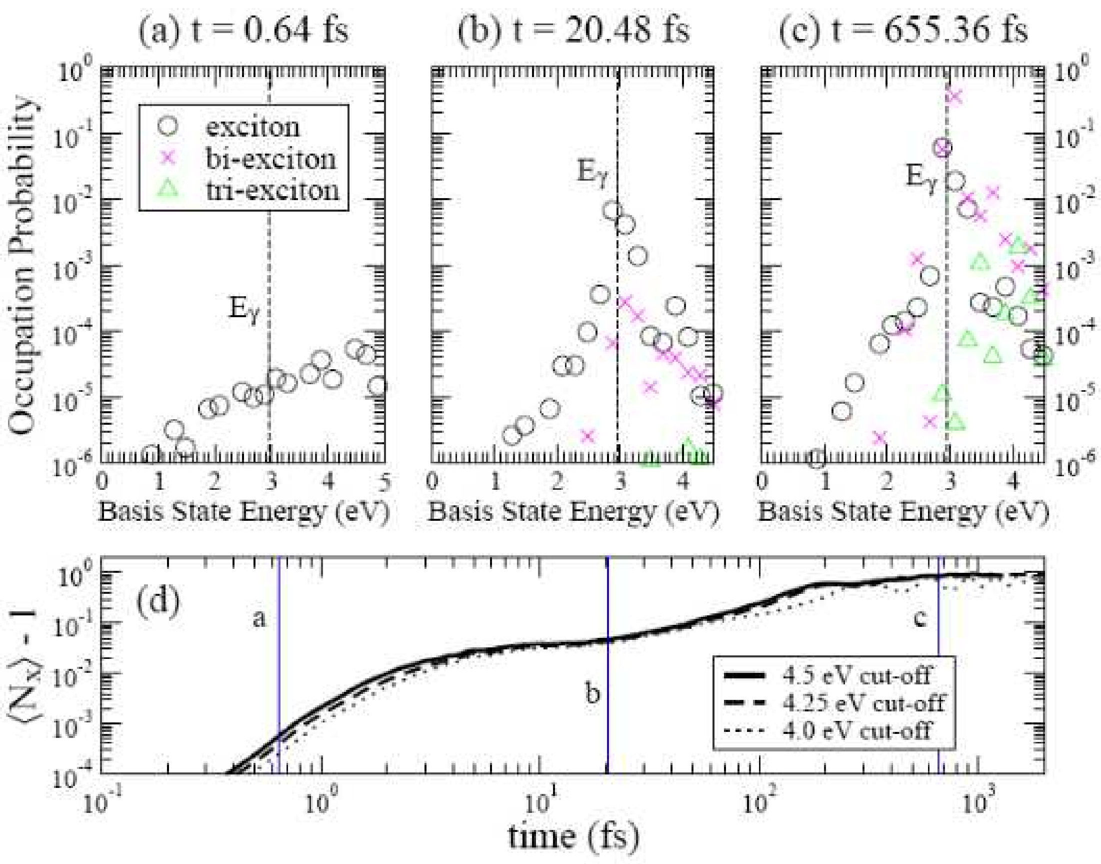
3. The number J-biex states where the is exciton transferred: $$N_J \approx \rho_{biex} \hbar \gamma_2$$

Quantum simulation of multiple-exciton generation

Closed system evolution: the initial single-photon state excites electronic states, which evolve ONLY through Columbic interaction :

$$\hbar \frac{d\,|\Psi(t)\rangle}{dt} = -i\hat{H}\,|\Psi(t)\rangle$$

H is the Hamiltonian, which includes all Columbic interactions.



Time dependent evolution of $2^eP_{1/2}$ -2^h $P_{1/2}$ excitation created by a single photon

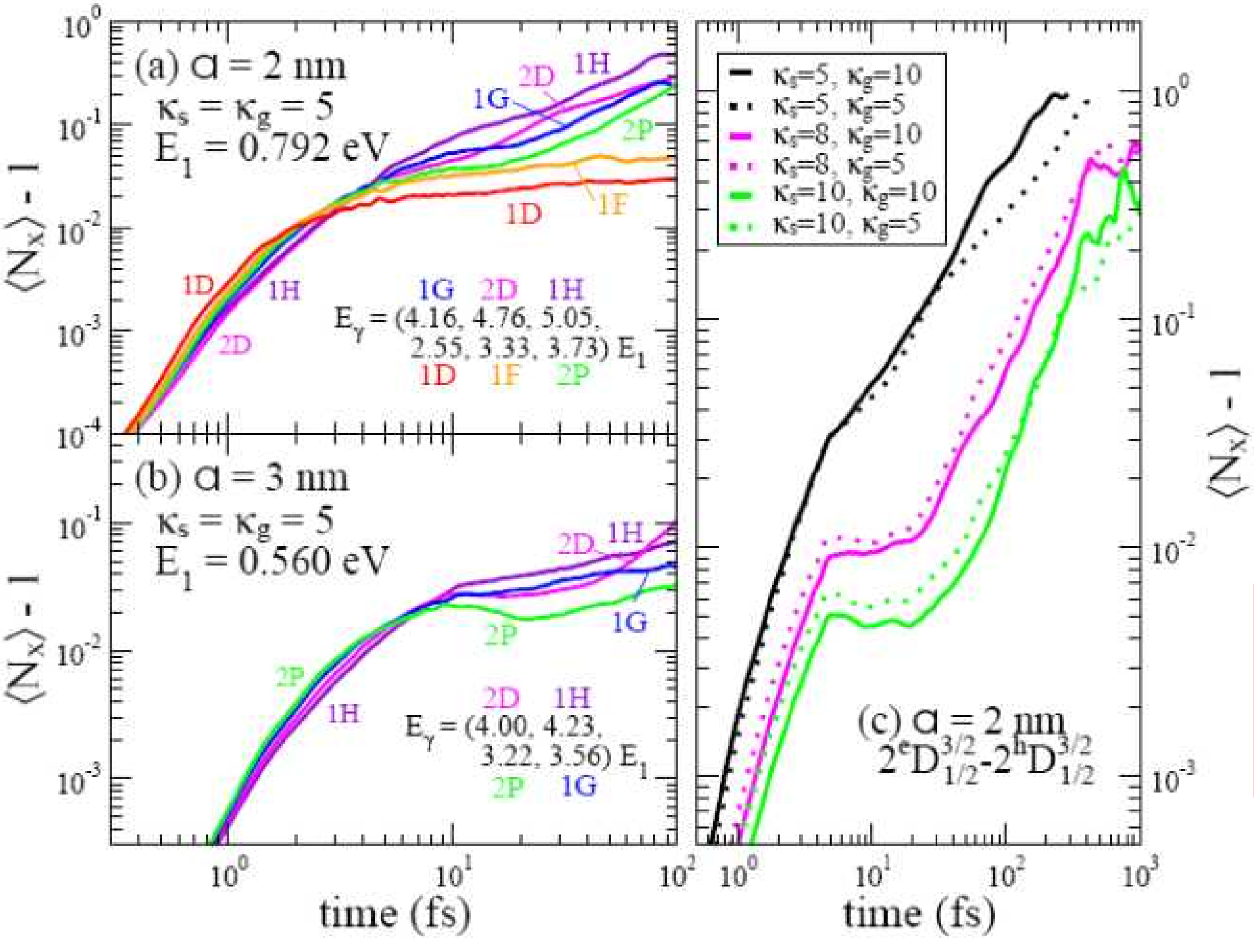
2nm radius PbSe NC: $\kappa_s = \kappa_g = 5$, $E_\gamma = 2.95$ eV

Occupation probability:

$$\| \langle k \,|\, \Psi(t) \rangle \|^2$$

of exciton, bi-exciton and tri-exciton states (k=1,2, and 3)

MEG Dependence on Coulomb Strength and Excitation Energy



No oscillation of <N$_x$>(t), even if MEG is efficient.

Oscillations are seen in cross-over behavior.

Rabi oscillations:

$$P(t) = \frac{W^2}{2\Omega^2\hbar^2}[1-\cos(2\Omega t)]$$

where

$$\Omega\hbar = \sqrt{W^2 + (E_{ex} - E_J)^2/4}$$

At $t \ll 1/\Omega$: $P(t) \approx \frac{W^2}{\hbar^2} t^2$

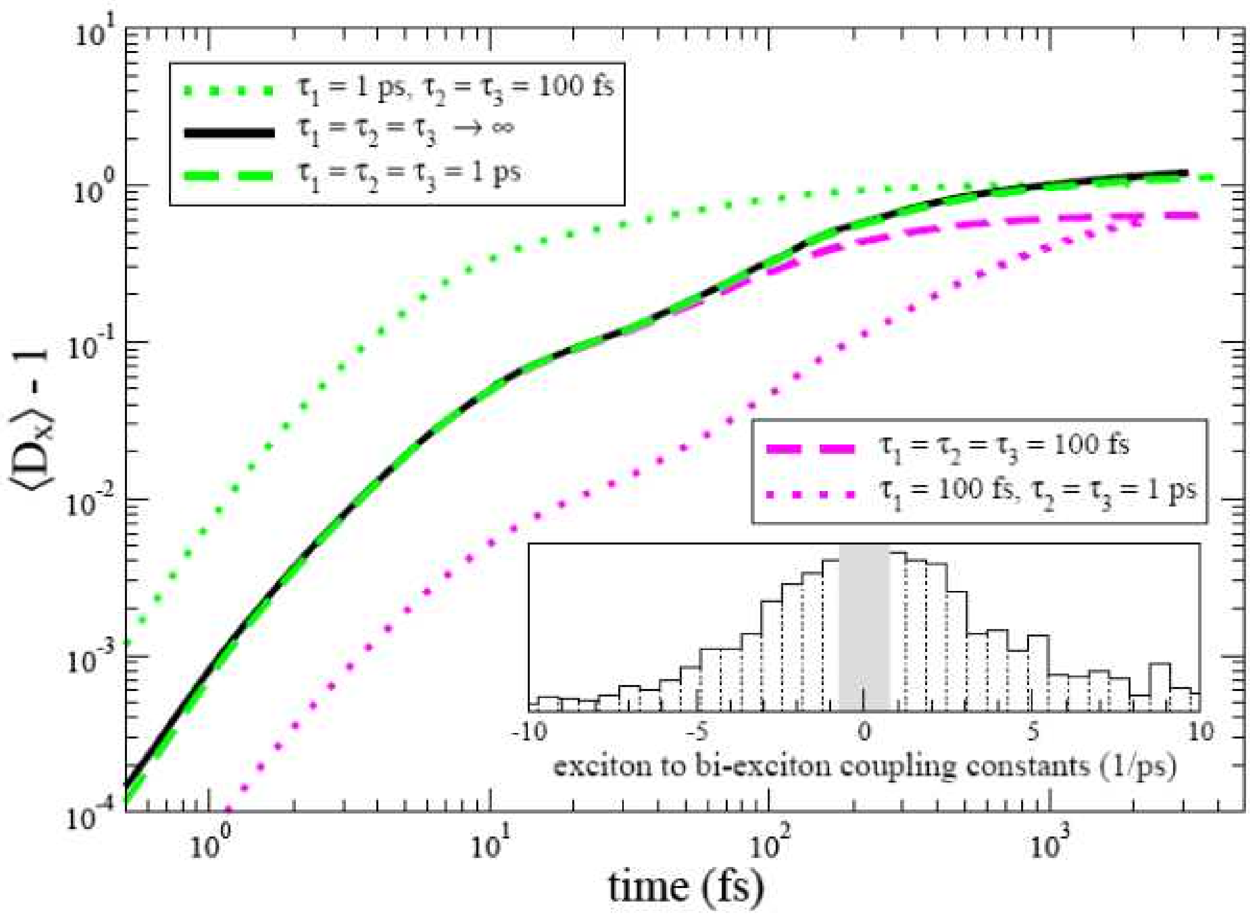
Independent of detuning !!!

Max values:

$$P(t = \pi/2\Omega) = \frac{W^2}{W^2 + (E_{ex} - E_J)^2/4}$$

Effect of Exciton and Bi-exciton Relaxation

In 2 nm radius PbSe NCs under excitation at the $1^eH_{1/2}$-$1^h H_{1/2}$ transition: E_γ=5.05 E_1=4 eV



Exciton-biexciton coupling time: 300 fs

Saturation value for MEG depends only on exciton relaxation time, τ_1

Summary

- Our calculations unambiguously demonstrate that highly efficient MEG can be observed in small nanocrystals.
- The effect is enhanced by a high density of biexciton states and strong coupling with optically created excitons.
- The fast multi-exciton thermalization accelerates the formation of multiexciton in the ground state and improve extraction efficiency of electron-hole pair from the NCs