

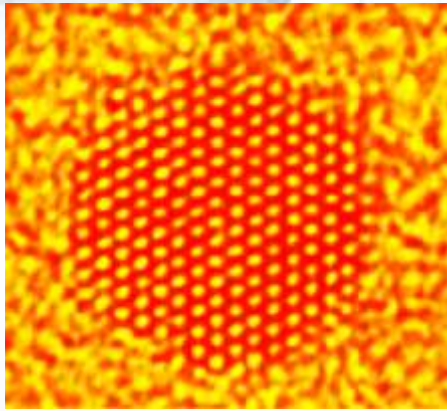
Multi-exciton generation in bulk and nanocrystalline semiconductors: mechanism, efficiency, and interest for solar cells?

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IEMN – ISEN - Lille – France

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1098 SJ, Amsterdam, The Netherlands

- I – Motivation
- II – Review of experimental results
- III – Theory of MEG by impact ionization
- IV – Measurements of MEG in bulk PbS & PbSe by THz spectroscopy
- V – Results and discussion

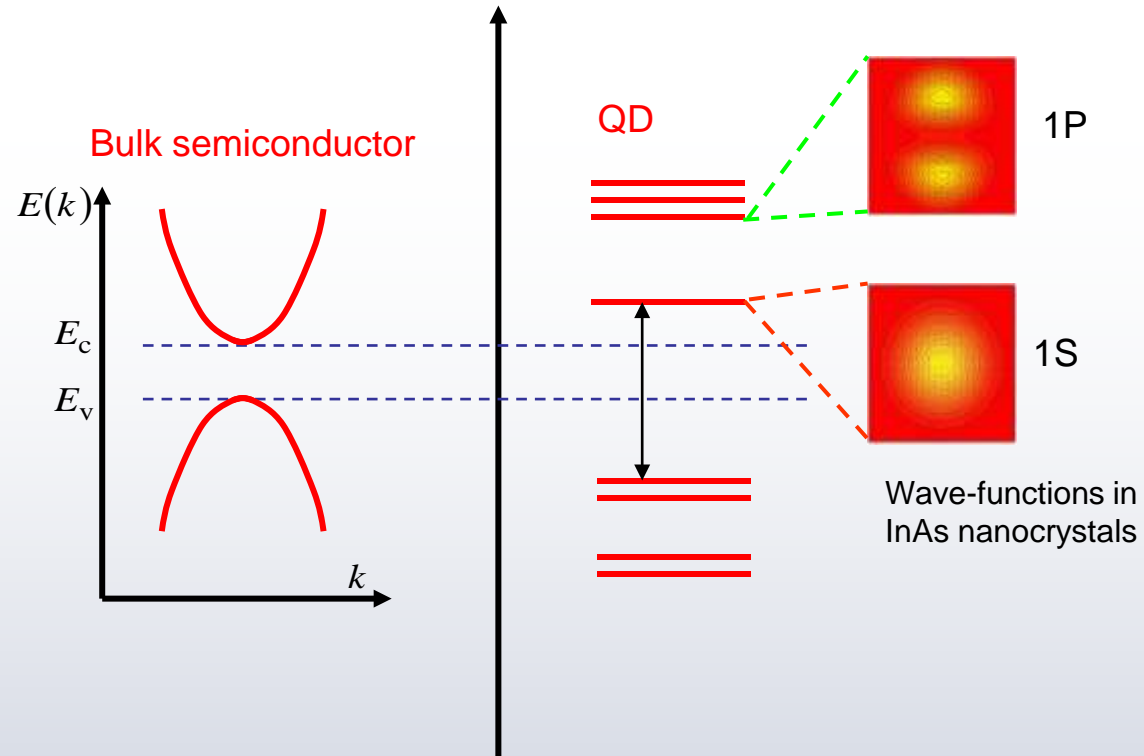
Semiconductor QDs



CdSe Nanocrystal
(P. Alivisatos, Berkeley)

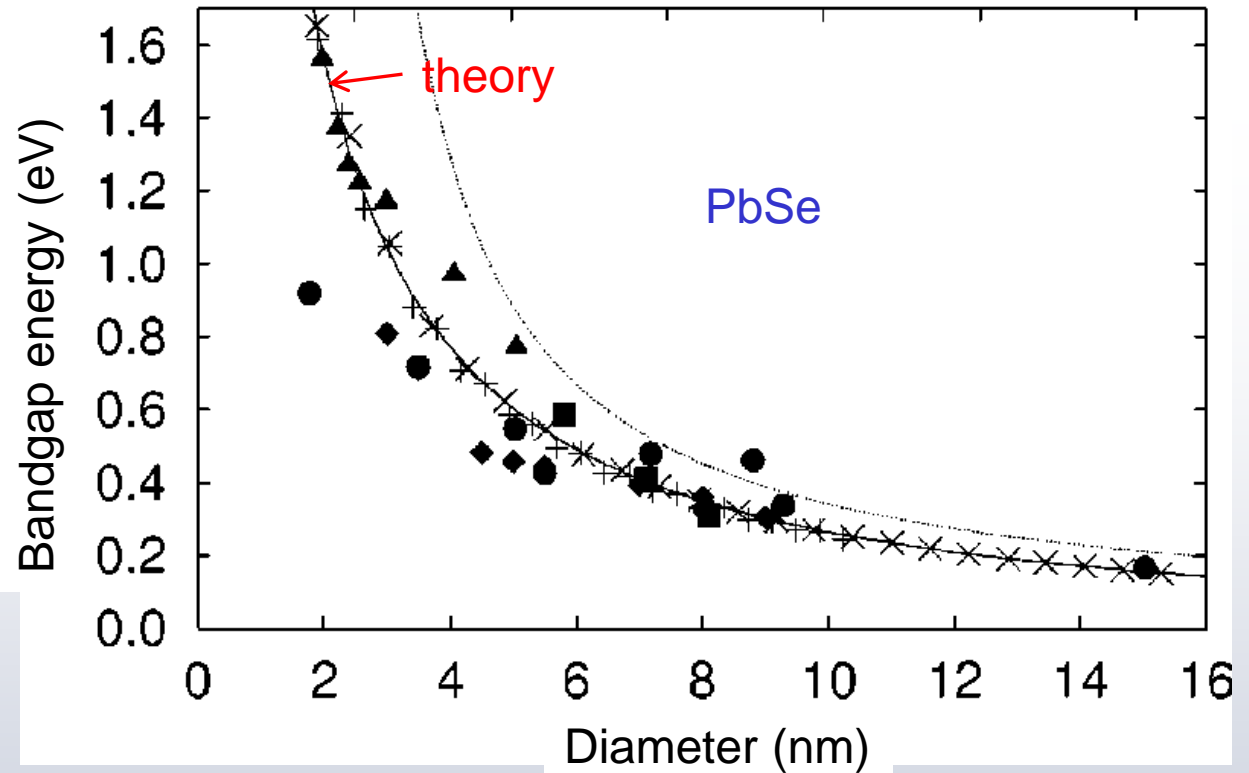
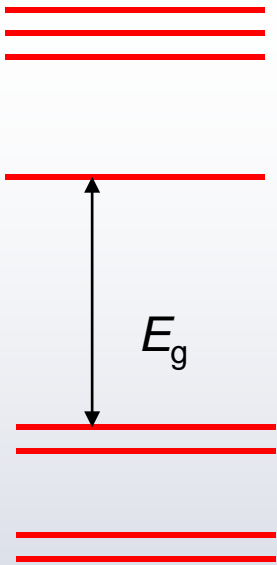


PL of CdSe/ZnS core-shell nanocrystals
in chloroform (H. Weller, Hamburg).



Quantum confinement in PbSe QDs

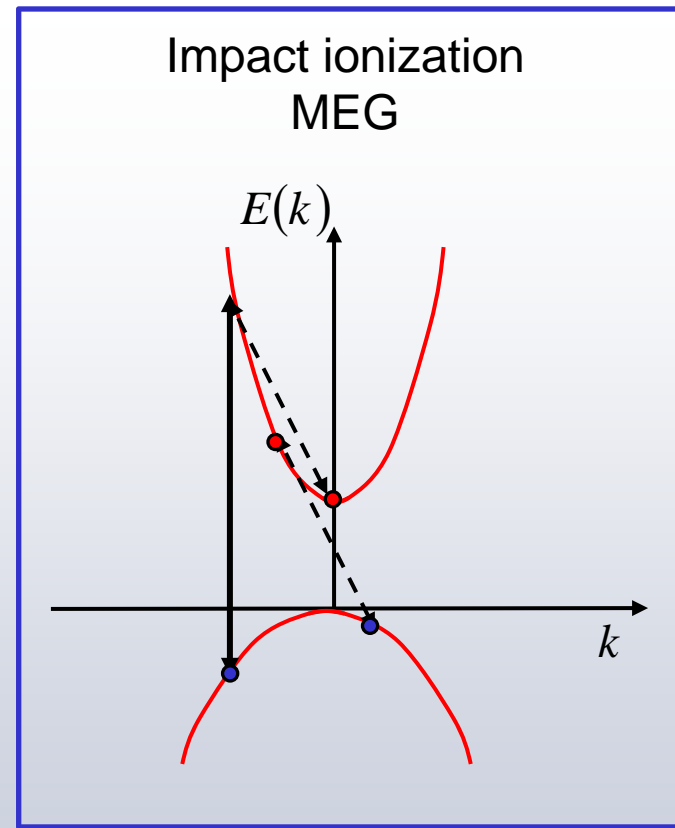
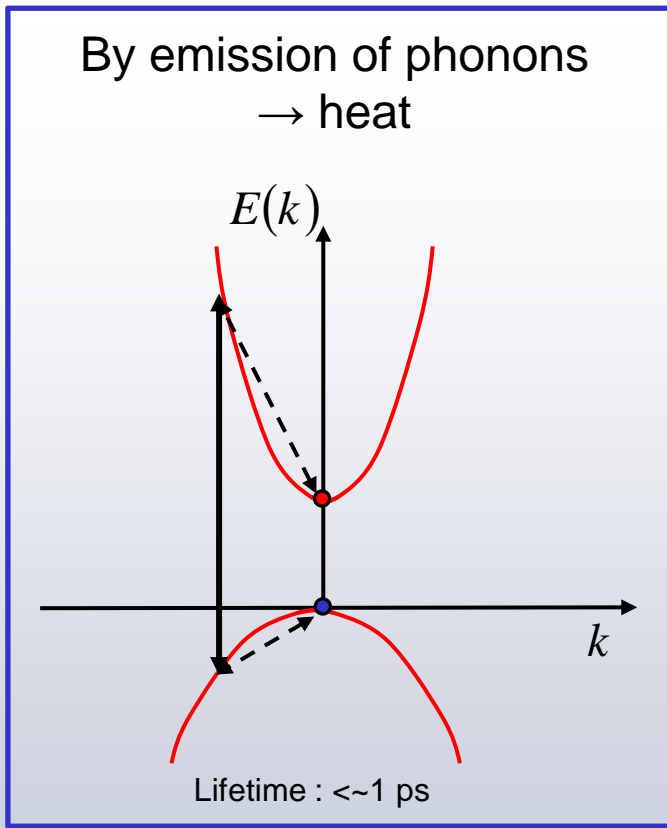
QD



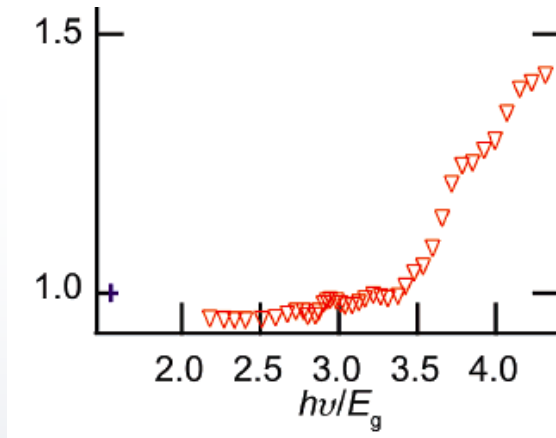
Bulk bandgap (~0.17 eV at 4K, 0.28 eV at 300K)

Efficiency of solar cells limited by the relaxation of hot carriers by emission of phonons

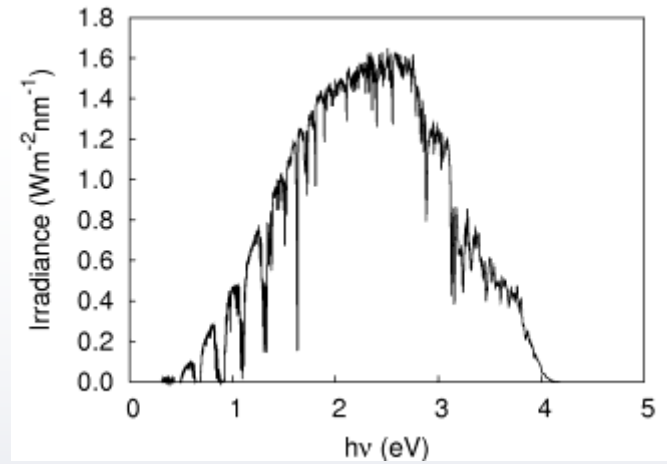
Relaxation pathways:



Bulk Si: impact ionization efficient only above ~ 3.8 eV



Number of photo-generated
excitons in bulk Si
Wolf et al, J. Appl. Phys. 1998



Solar spectrum

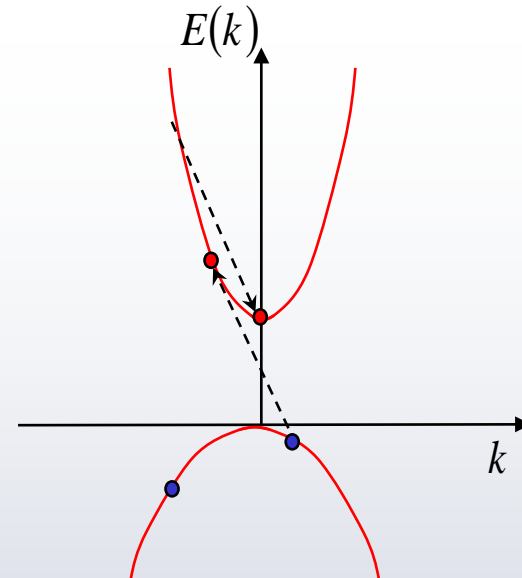
Schockley-Queisser limit
Limit for the efficiency of a single Si solar cell of about 30%.

MEG in QDs for solar cells ?

02 : Nozik claimed that impact ionization is enhanced in QDs

Nozik, Physica E 14, 115–120 (2002)

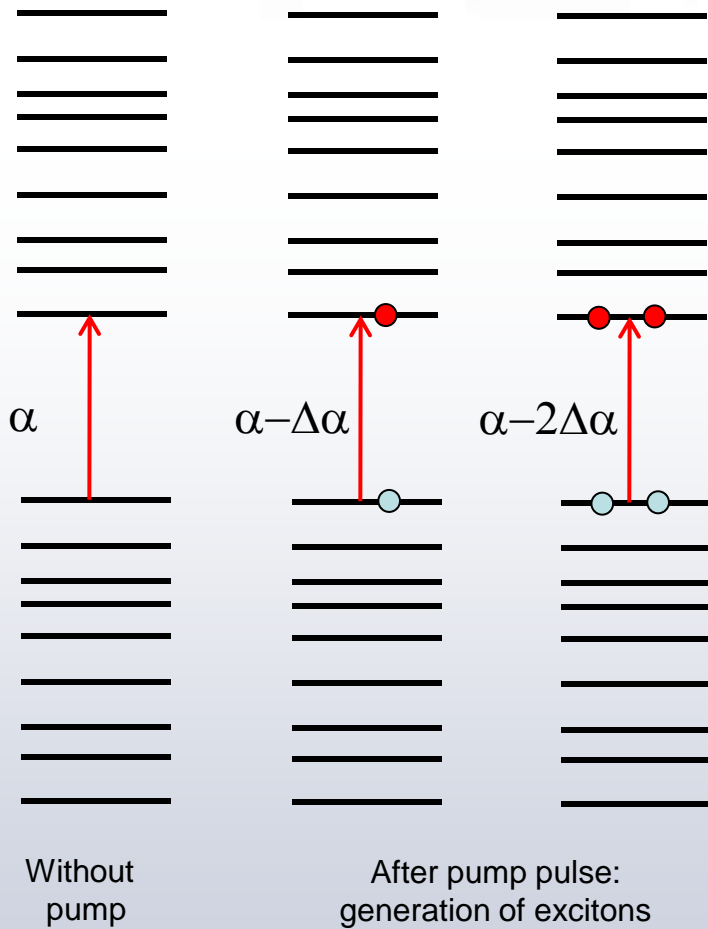
Argument: in bulk, conservation of E & k
in QDs, only E



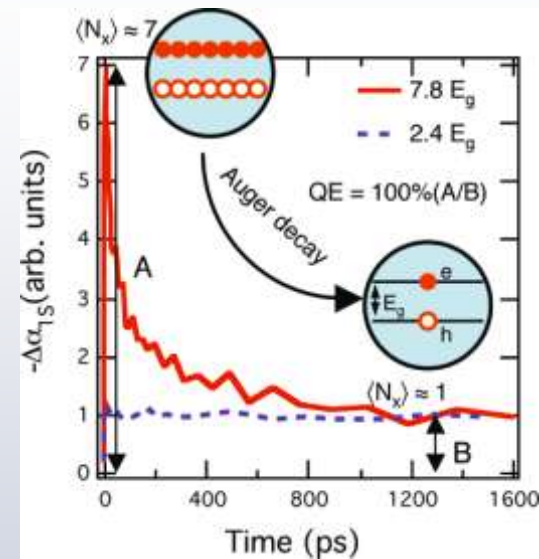
04 : group of Klimov reported efficient MEG in PbSe QDs

Schaller & Klimov, Phys. Rev. Lett. 92, 186601 (2004).

MEG in QDs: experiments

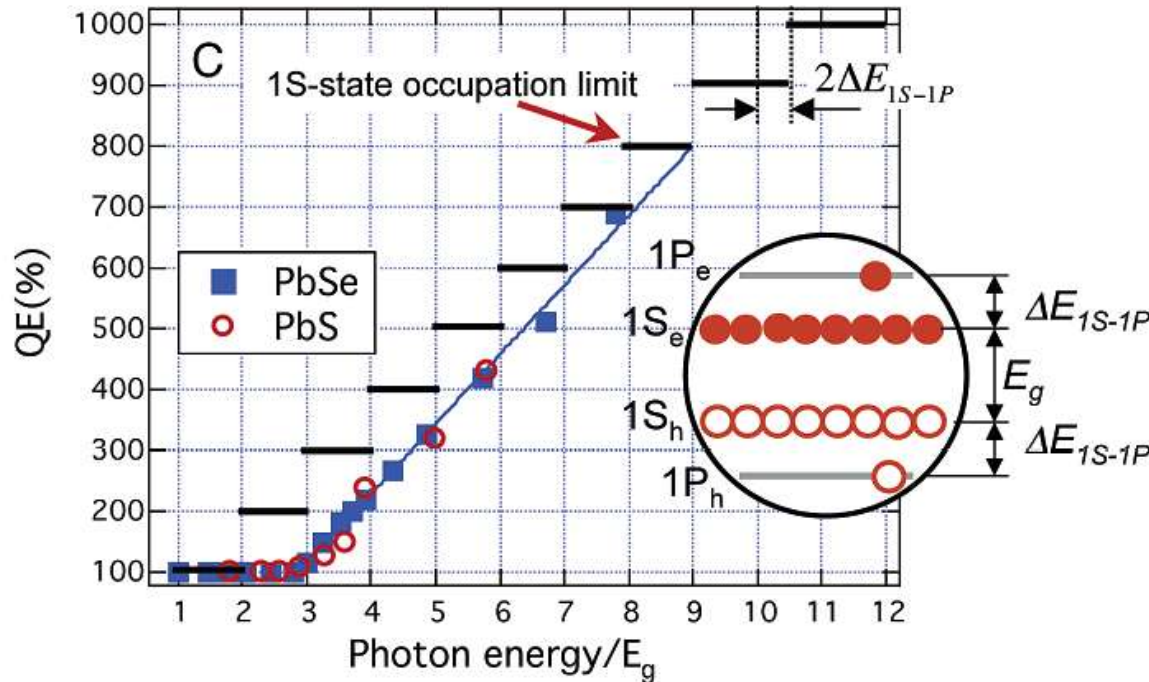


The exciton multiplicity is measured by transient absorption experiments
Population $\propto \Delta\alpha$



V. I. Klimov, J. Phys. Chem. B, Vol. 110, No. 34, 2006

MEG in QDs: controversy



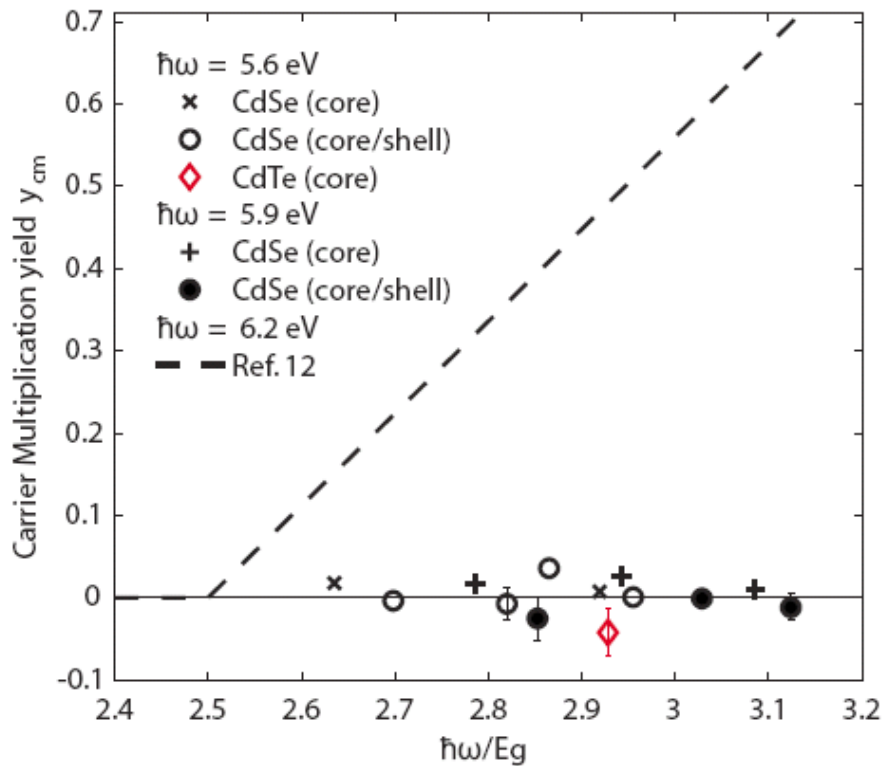
PbSe QDs
Up to 7 excitons!!!

R.D. Schaller et al, Nano Lett. 6, 424 (2006).

Controversy: Our calculations showed that these high MEG yields cannot be explained by impact ionization in QDs (Allan & Delerue, PRB 2006; PRB 2008)

Controversy :

Transient PL measurements of Nair et al. : no MEG !



Transient PL

Nair and Bawendi
PRB 76, 081304 R (2007)

MEG in QDs: controversy

- InAs QDs:

MEG observed:

- Klimov, Nano Lett. 7, p3469, 2007
- Pijpers/Bonn, JPC, 111, p4146, 2007

No MEG:

- Pijpers/Bonn, JPC, 112, p4783, 2008
- Ben Lulu, Nano Lett. 8, p1207, 2008

- CdSe QDs:

MEG observed:

- Klimov, APL 87, p253102, 2005

No MEG:

- Bawendi, PRB, 76, 081304, 2007

- PbS QDs:

MEG observed:

- Nozik, Nano Lett, 5, p865, 2006

No MEG:

- Bawendi, PRB, 78, 125325, 2008

- PbSe QDs:

Efficient MEG:

- Klimov: PRL(2004), Nano Lett. (2006, 2008), Nature Phys. (2005), APL (2005)
- Nozik: Nano Lett. (2006), JACS (2006)

Intermediate:

- Siebbeles, Nano Lett., 8, p1713, 2008

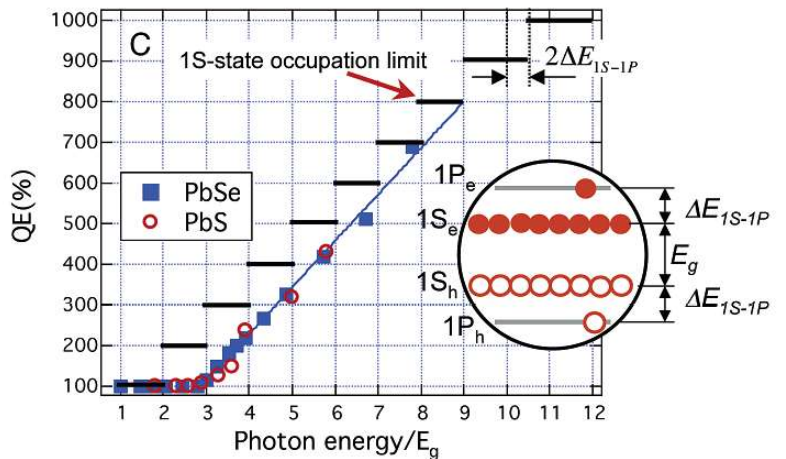
Inefficient MEG:

- Bawendi, PRB, 78, 125325, 2008
- Klimov, Accounts Chem. Res. (2008)



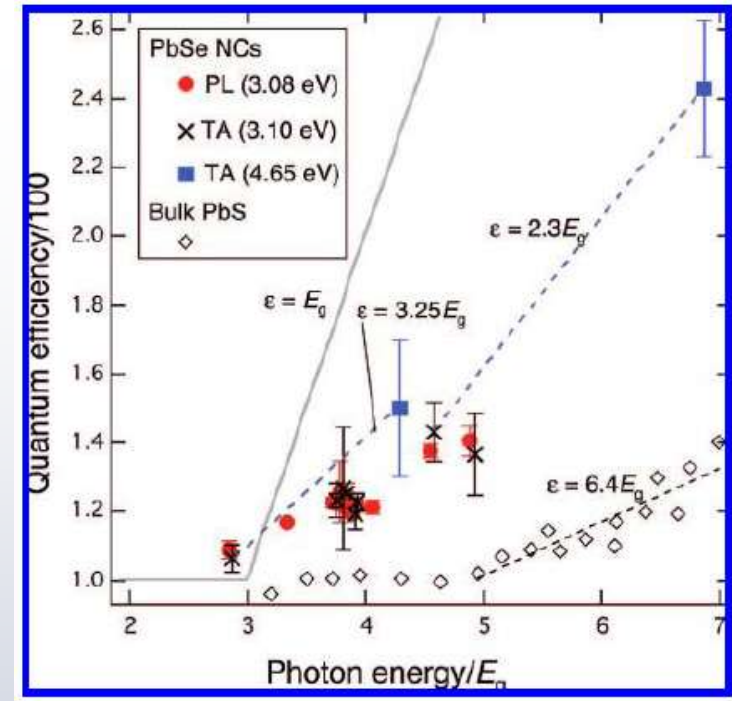
MEG in QDs: controversy

PbSe : recent results of Klimov et al confirm MEG but with a lower efficiency!



Previous results of Klimov group

R.D. Schaller et al, Nano Lett. 6, 424 (2006).



New results of Klimov group

J. A. McGuire, et al, Acc. Chem. Res (2008).

Objectives :

Theory & simulation \Rightarrow real efficiency of these processes

Calculation of the impact ionization rates

Calculation of the number of generated excitons

Big questions :

Impact ionization in QDs : is it more or less efficient than in bulk ?

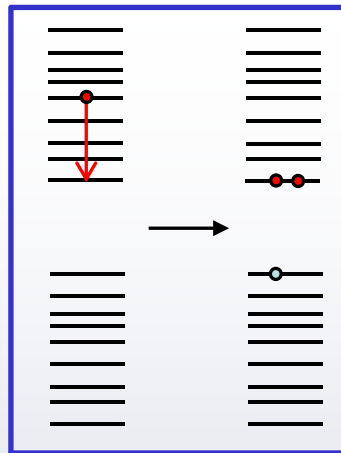
Can we justify the highest MEG yields reported in early works ? **NO**

Can we justify the lower MEG yields reported recently ?

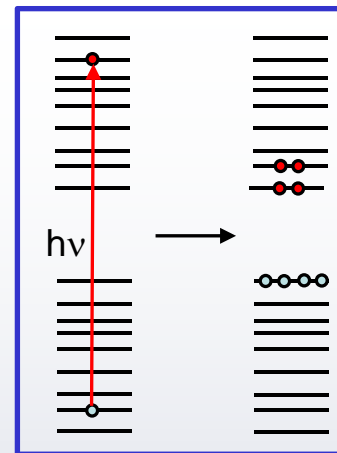
Can we generate more excitons in QDs than in bulk ?

Interest of MEG in QDs for solar cells ?

Transitions induced by e-e interactions:



Impact ionization

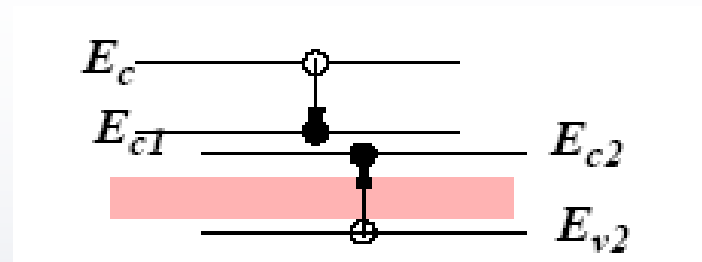
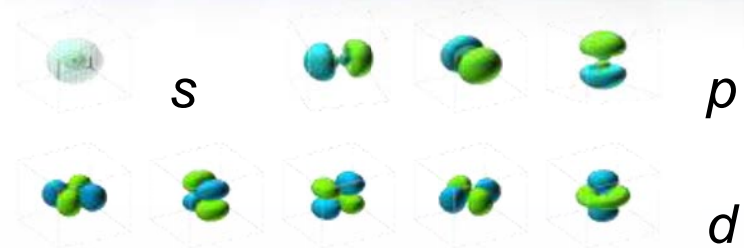


Multi-exciton generation

$$W \propto \left| \langle \varphi_1 \varphi_2 | V | \varphi_3 \varphi_4 \rangle \right|^2$$

Transition rate?

Electronic states calculated in tight binding
 Calculation of the dielectric screening (RPA)
 Calculation of the screened Coulomb interaction
 Fermi golden rule → transition rate



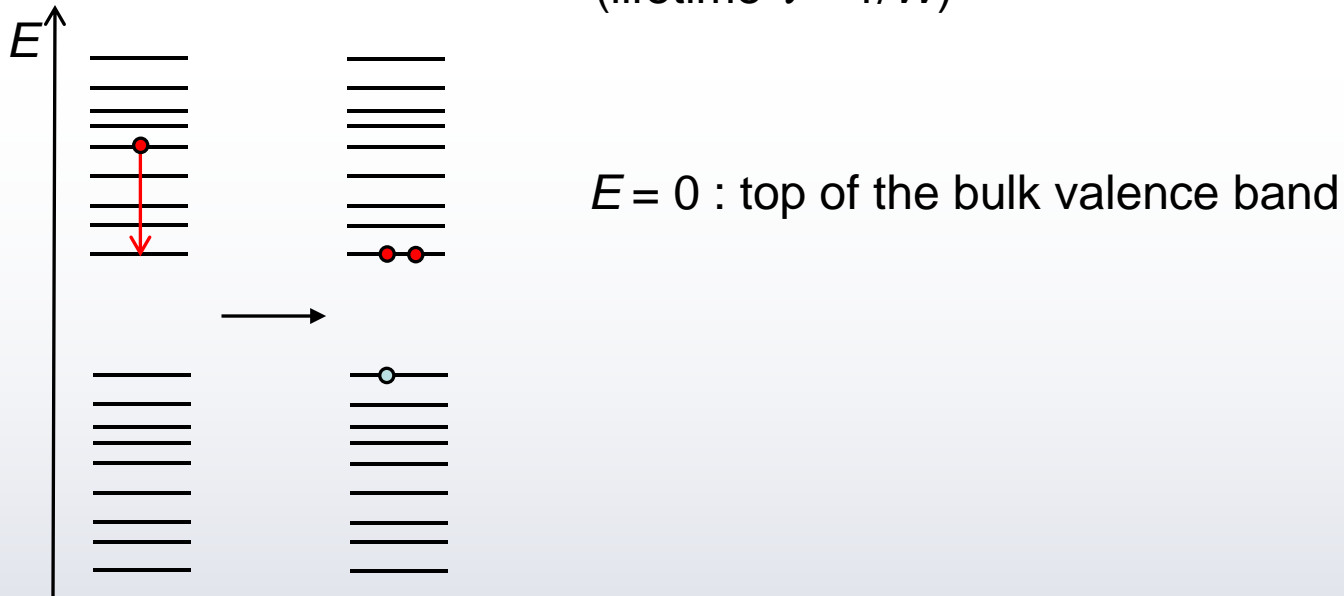
$$W = \frac{2\pi}{\hbar} \sum_{i,f} p(i) |\langle f | V | i \rangle|^2 \delta(E_f - E_i)$$

$|i\rangle, |f\rangle$: Slater determinants built on tight binding wave-functions

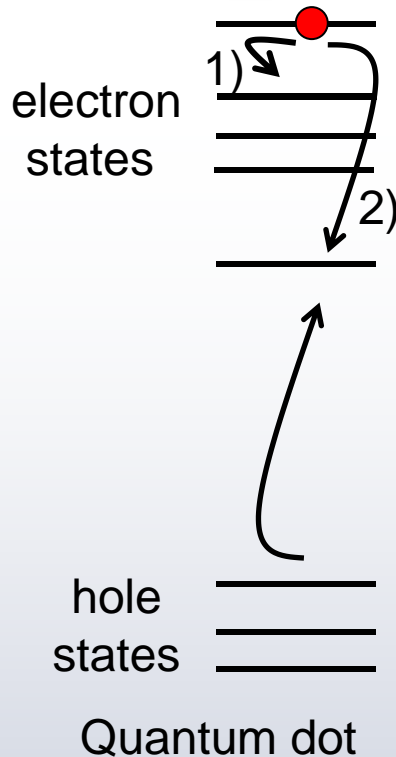
$$V(r, r') = \int \varepsilon^{-1}(r, r'') \frac{e^2}{|r - r''|} d^3 r''$$

Theory of MEG : impact ionization

- 1) Calculation of the impact ionization rate W versus energy E
(lifetime $\tau = 1/W$)



- 2) Calculation of the number of photogenerated excitons per photon
(MEG efficiency)



Calculation of MEG efficiency

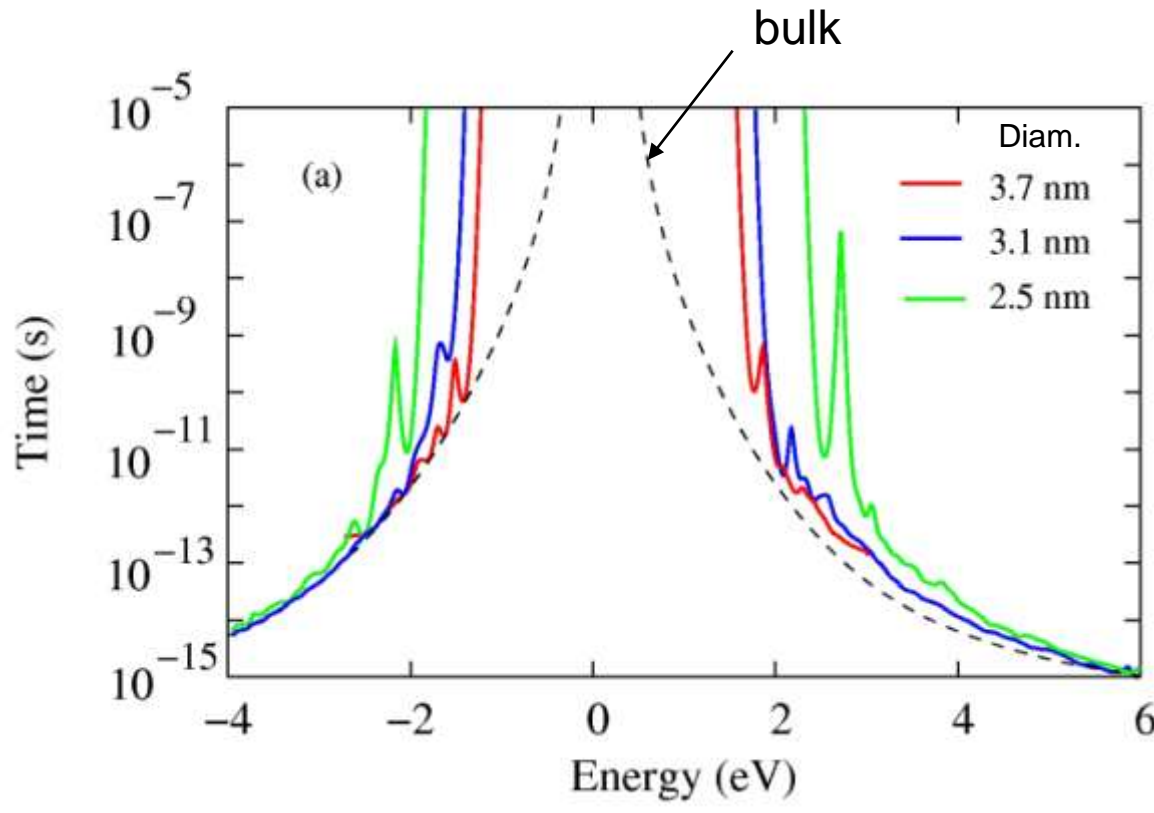
MEG efficiency is result of competition between:

- 1) multi-phonon relaxation
- 2) impact ionization

- 1) multi-phonon relaxation: assume one (energy-independent) relaxation time τ_{phonon}
- 2) impact ionization: using calculated lifetimes
- 3) numerical simulation of the relaxation

Impact ionization lifetime in PbSe nanocrystals

$$\tau = 1/W$$



$$E > 0 : E_c$$
$$E < 0 : E_v$$

(0 = top of bulk valence band)

G. Allan et al, PRB 73, 205423 (2006)

Impact ionization process :

Impact ionization is always less efficient in QDs than in bulk

Reasons :

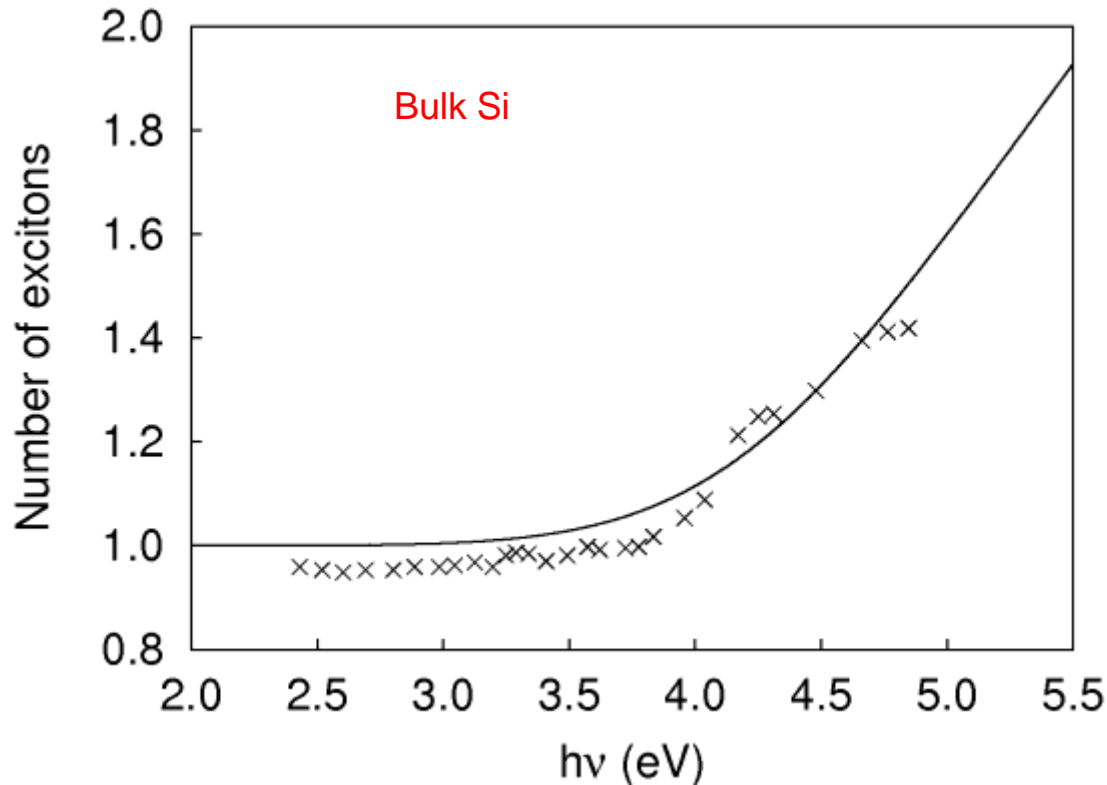
1) The momentum conservation rule plays no role.

In bulk, k conservation can be ignored.

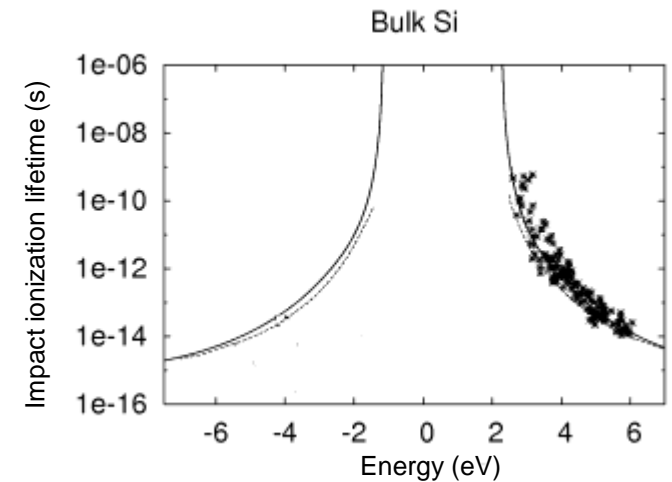
E.O. Kane, Phys. Rev., 159 (1967)

2) The density of final states (per unit volume) is smaller in QDs than in bulk

A test case: bulk Si



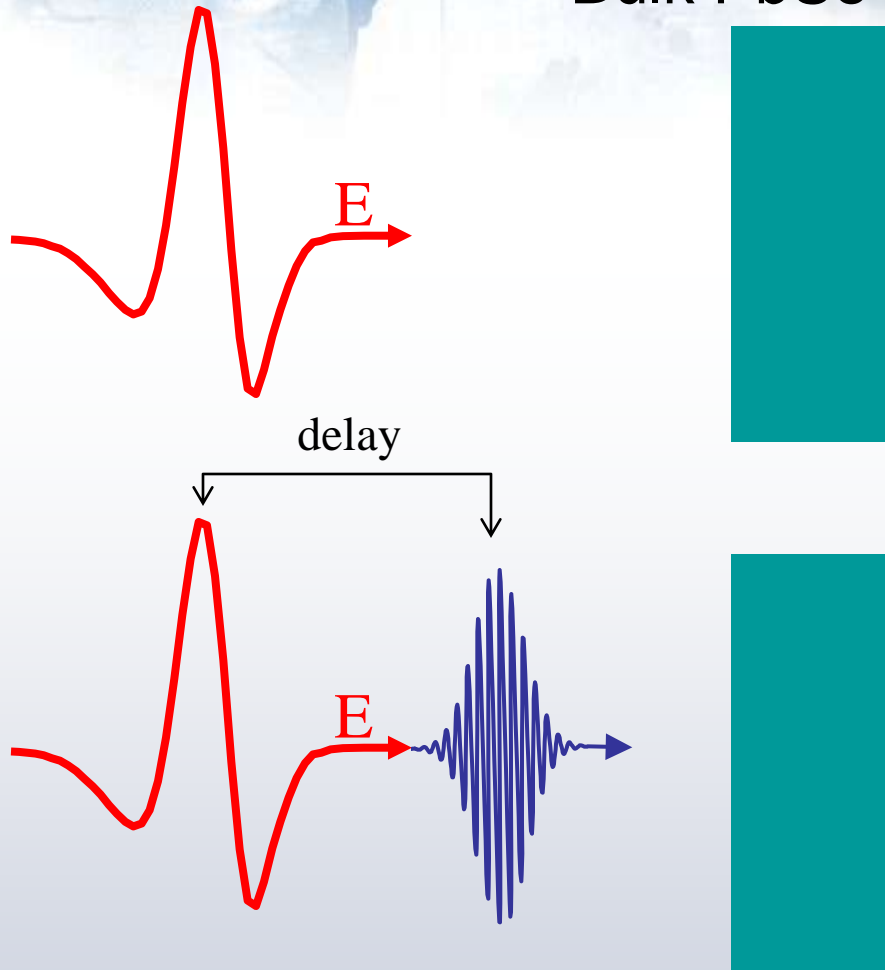
Line : our calculations. $\tau_{\text{phonon}} = 0.5$ ps
x = experiments (Wolf et al, J. Appl. Phys. 1998)



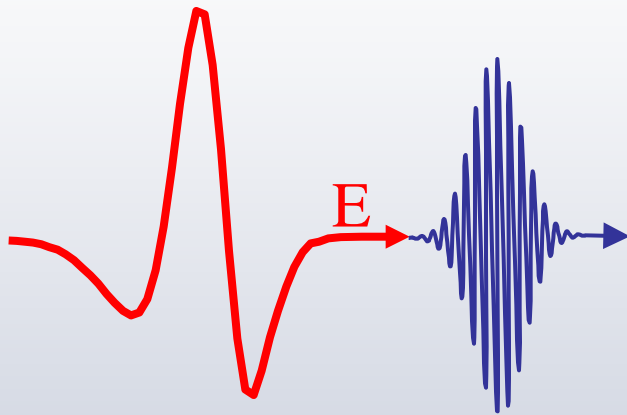
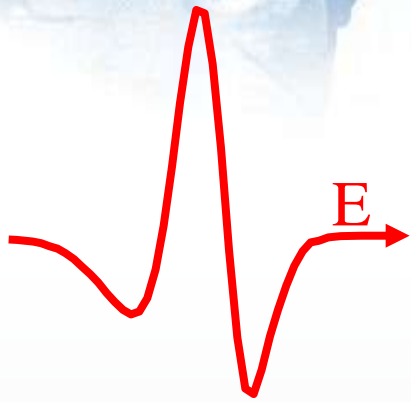
Line : our calculations.
Dashed line: Sano et al, JAP 75, 5102 (94)
* = Kunikiyo et al, Proceedings of the 1993 international Workshop on VLSI Process and Device Modeling, 1993 VPAD, p. 40.

Probing free charges with THz spectroscopy

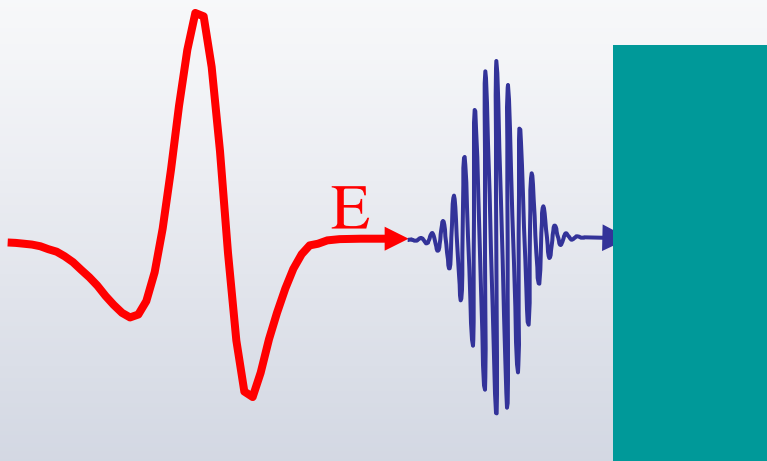
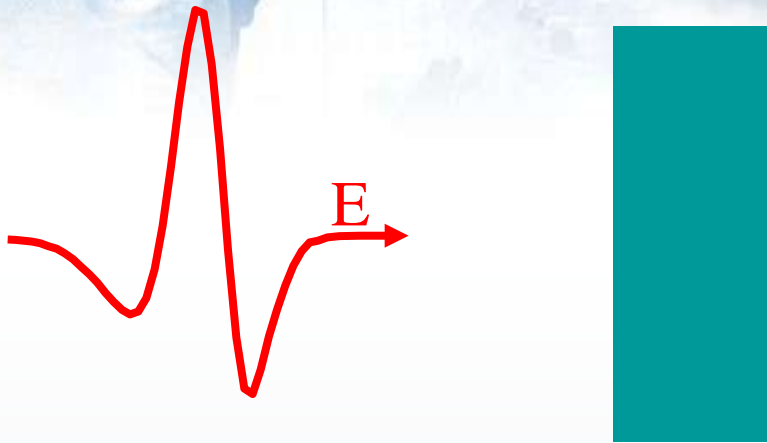
Bulk PbSe / PbS



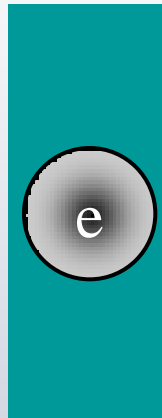
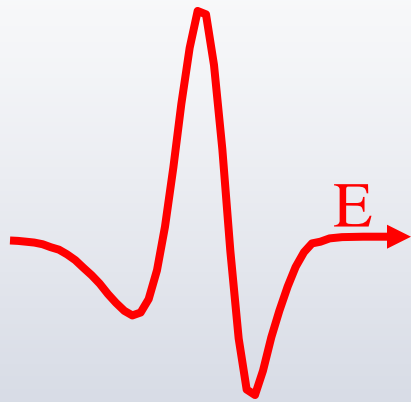
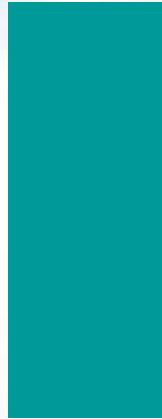
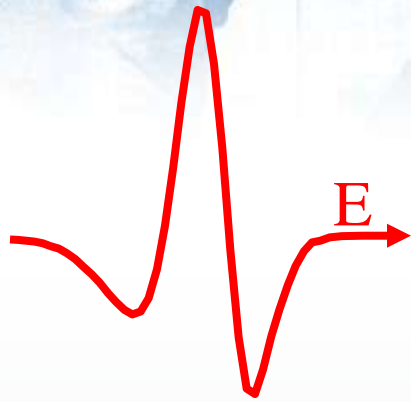
Probing free charges with THz spectroscopy



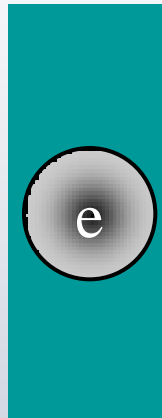
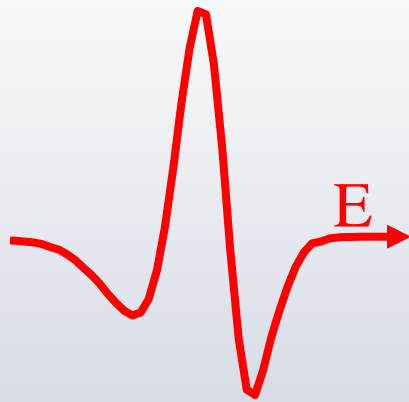
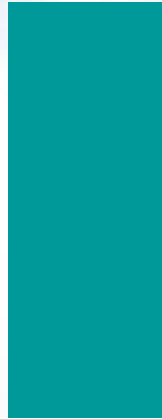
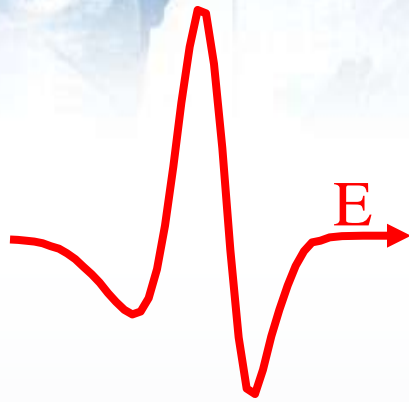
Probing free charges with THz spectroscopy



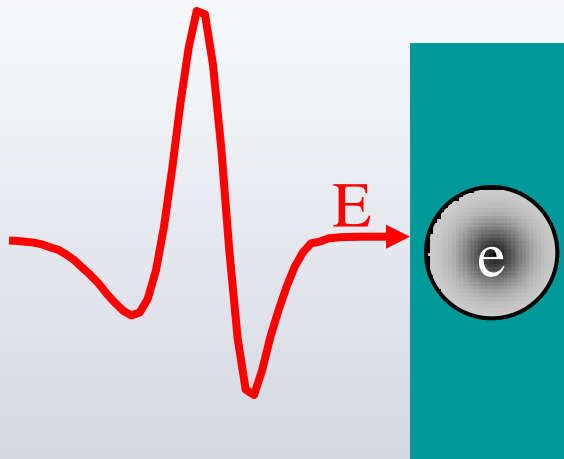
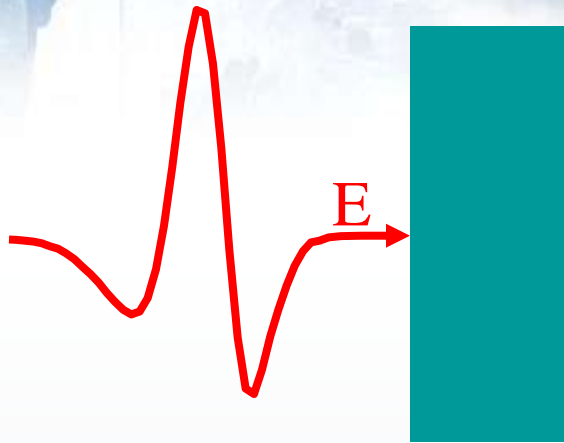
Probing free charges with THz spectroscopy



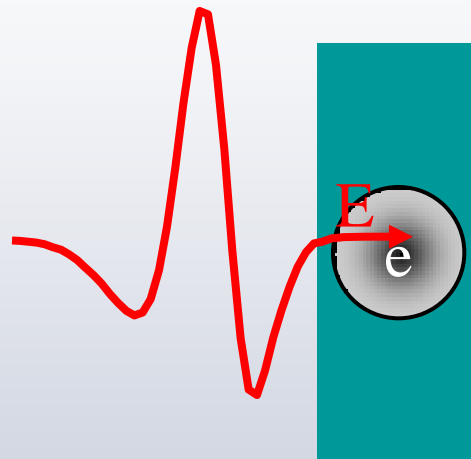
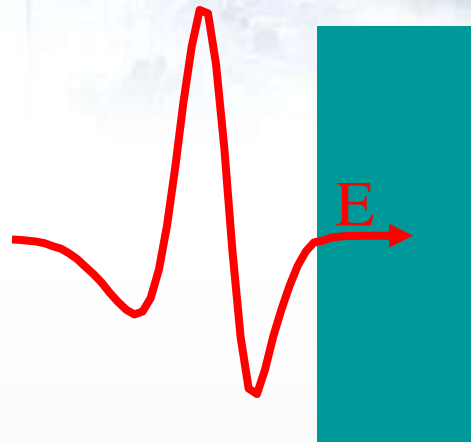
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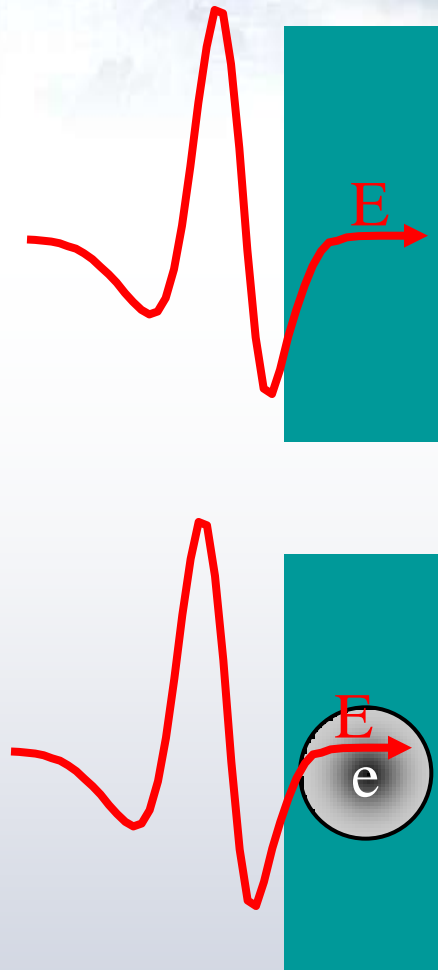
Probing free charges with THz spectroscopy



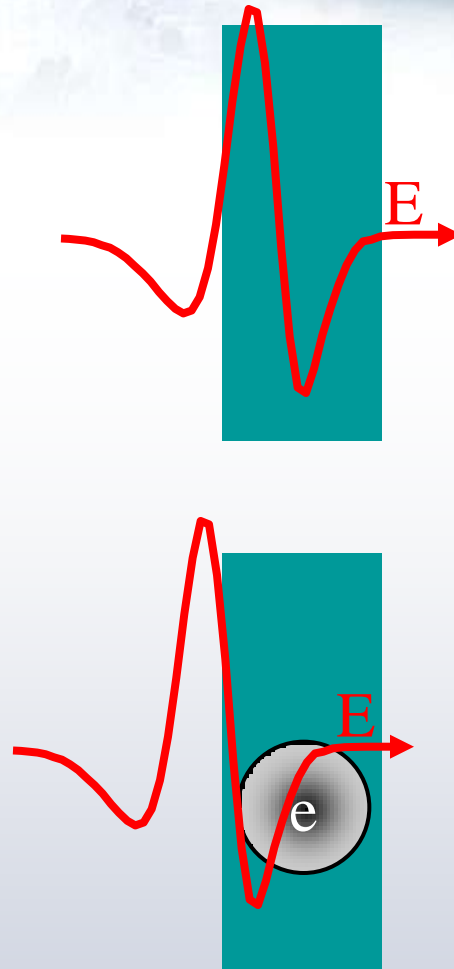
Probing free charges with THz spectroscopy



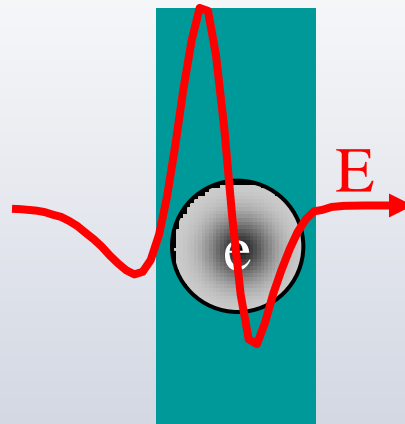
Probing free charges with THz spectroscopy



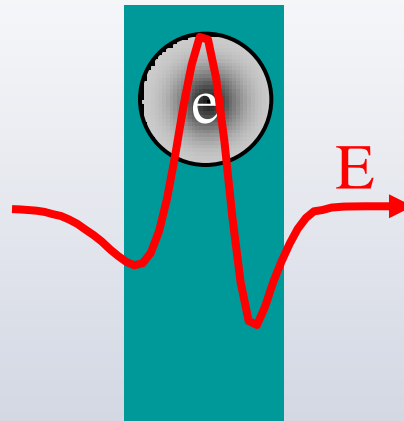
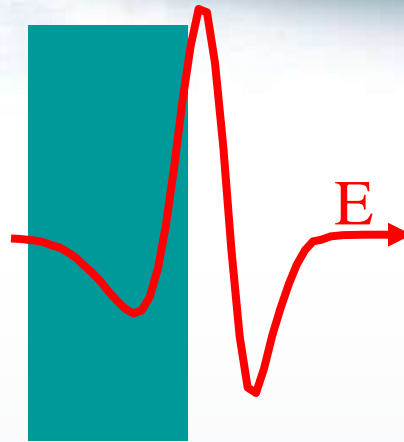
Probing free charges with THz spectroscopy



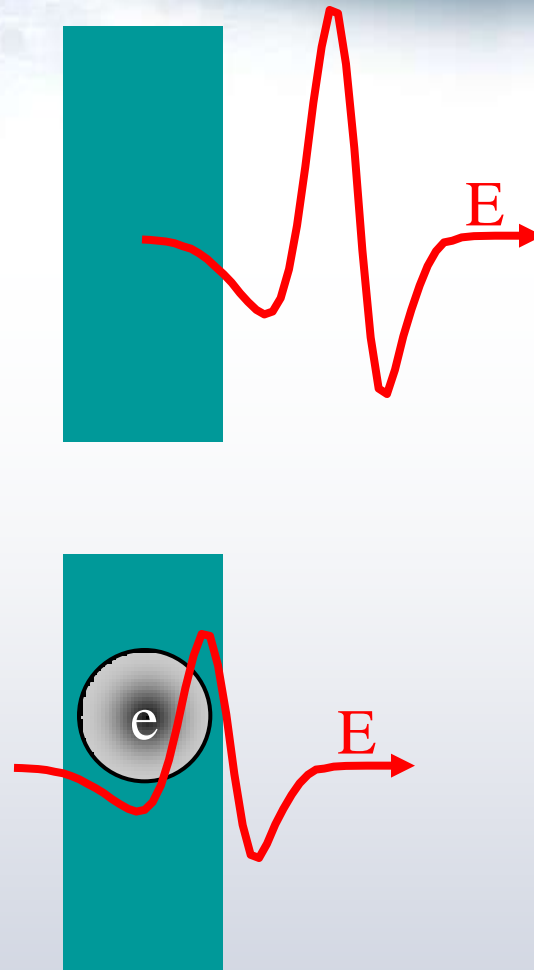
Probing free charges with THz spectroscopy



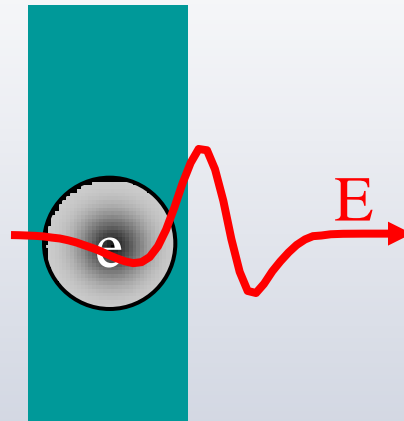
Probing free charges with THz spectroscopy



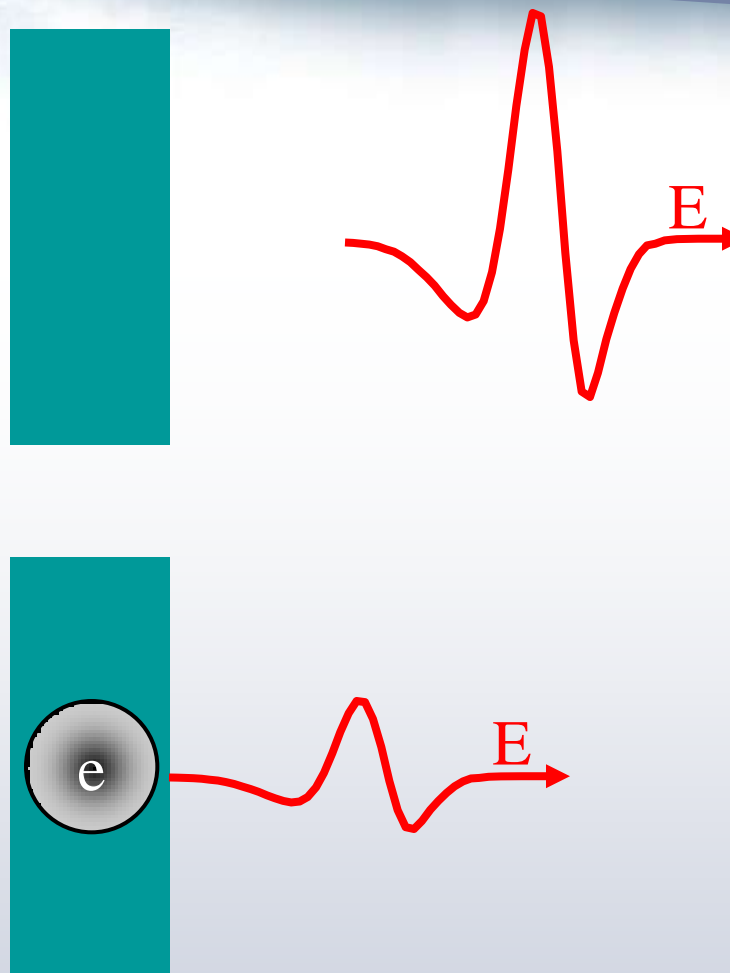
Probing free charges with THz spectroscopy



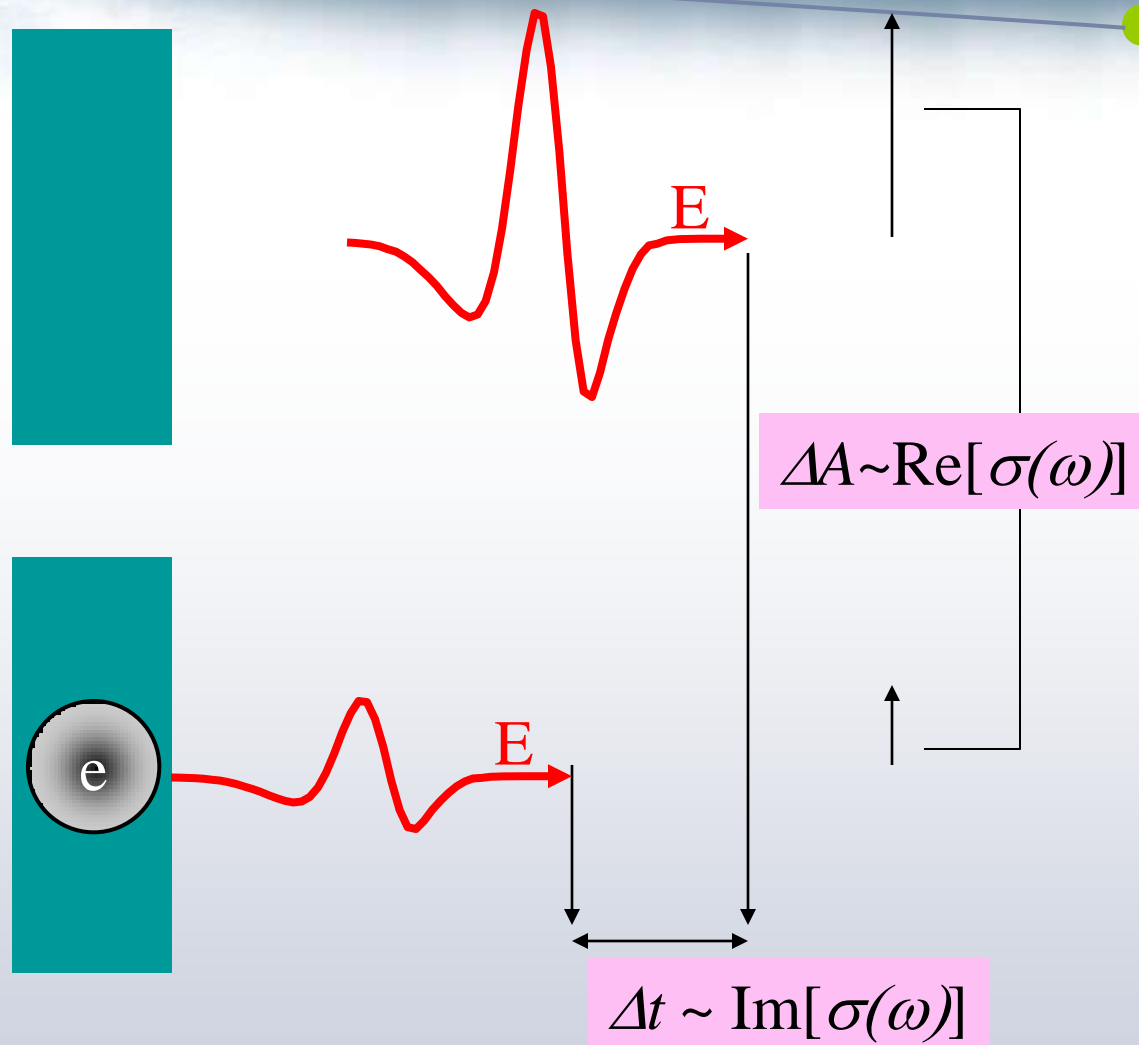
Probing free charges with THz spectroscopy



Probing free charges with THz spectroscopy

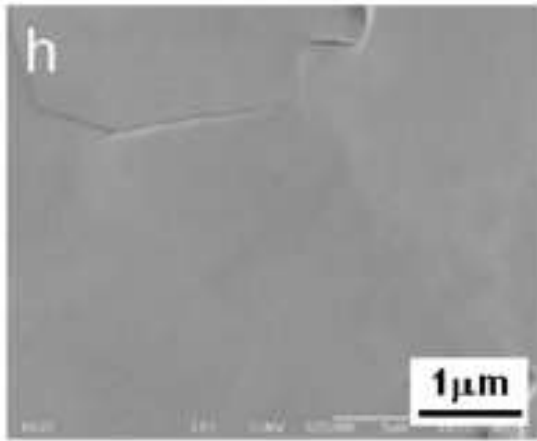


Probing free charges with THz spectroscopy

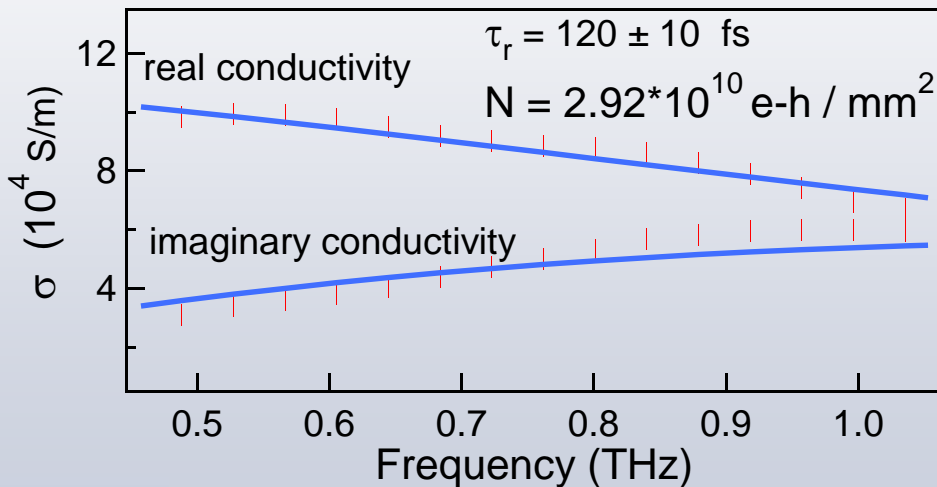
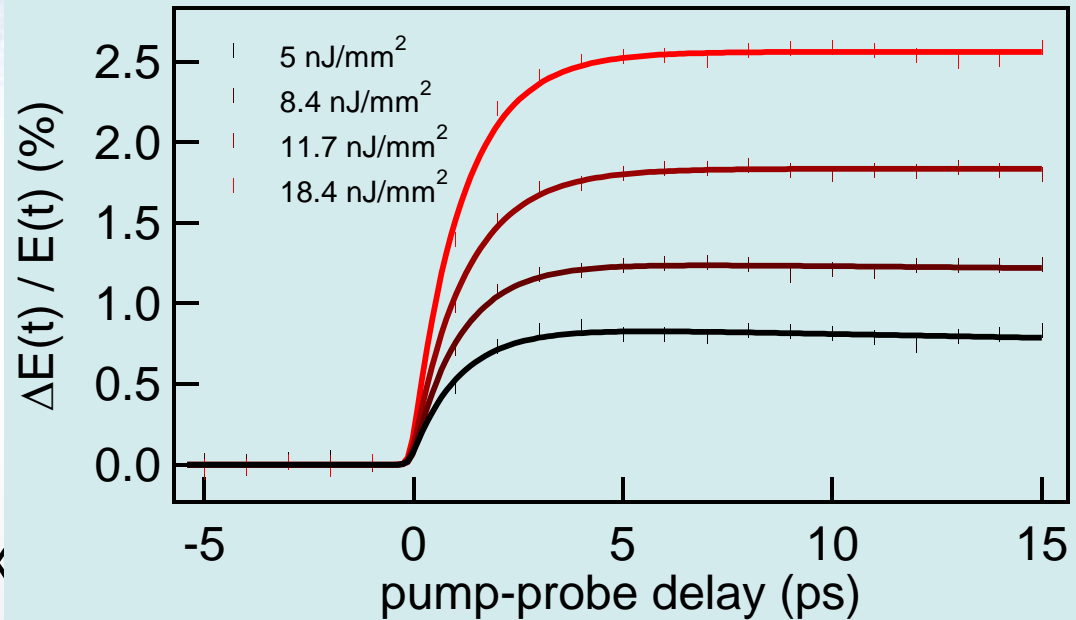


Through carrier-phonon interactions energy can be dissipated – THz absorption

Drude model for conductivity of free carriers



PbS, 266nm pump (11x)



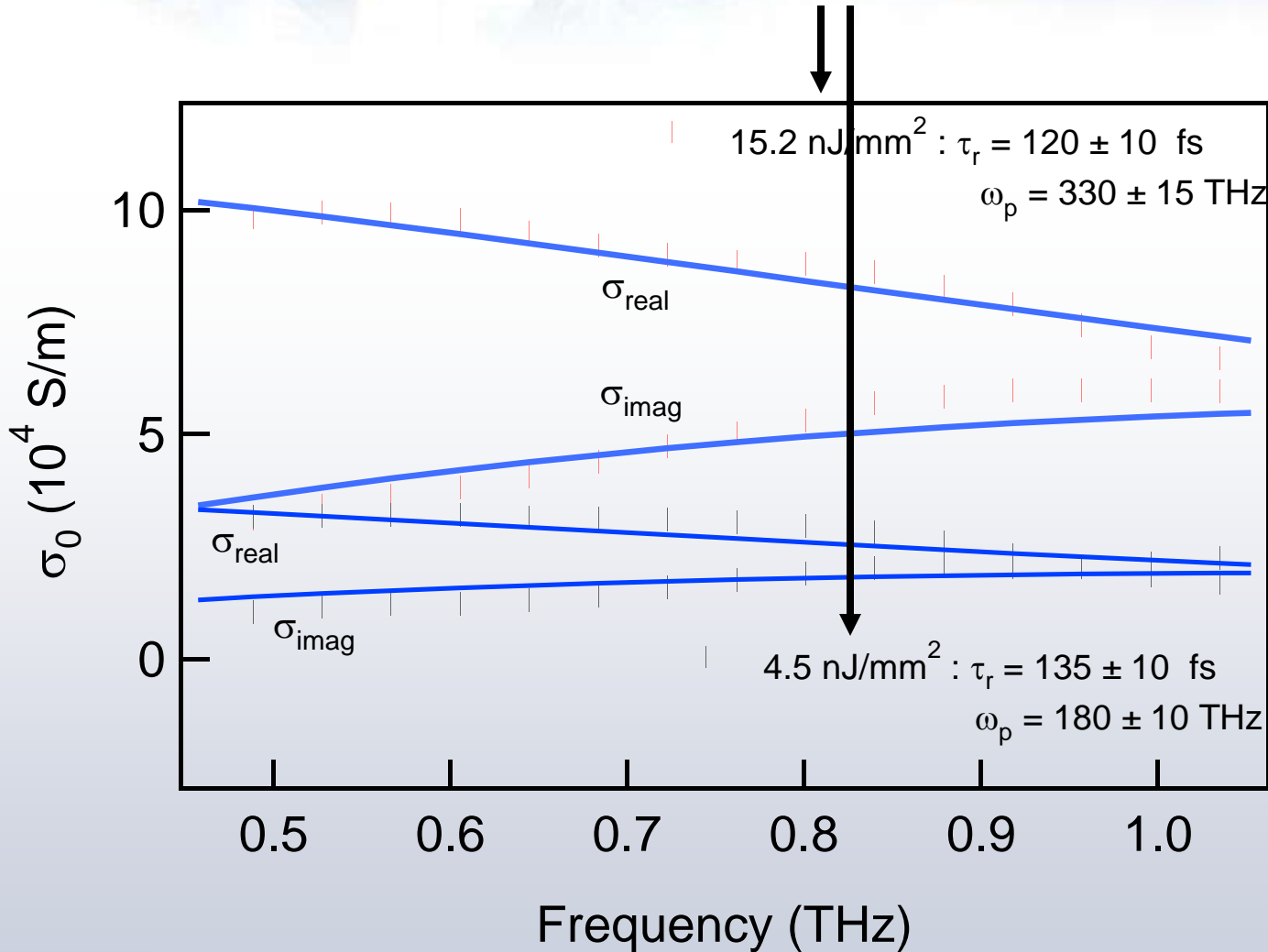
THz spectroscopy allows us to quantify carrier density picoseconds after excitation

Frequency dependence

Plasma frequency: $\omega_p^2 = \frac{e^2 N}{\epsilon_0 m^*}$

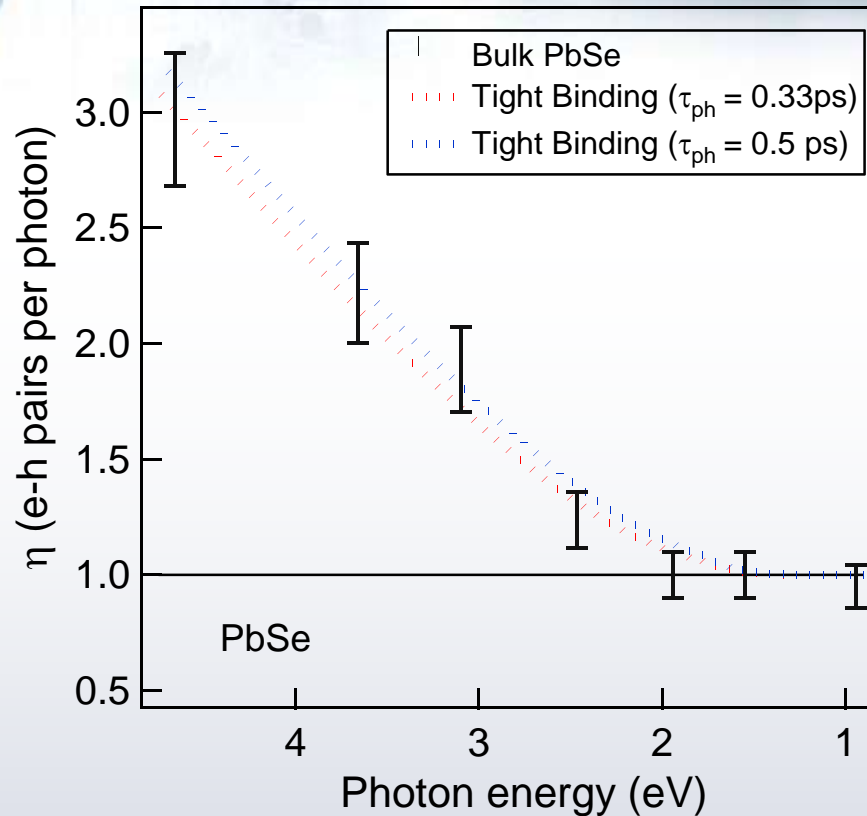
Wavelength-dependent MEG

Same absorbed photon flux



266 nm
 3.05 ± 0.15
e-h / photon

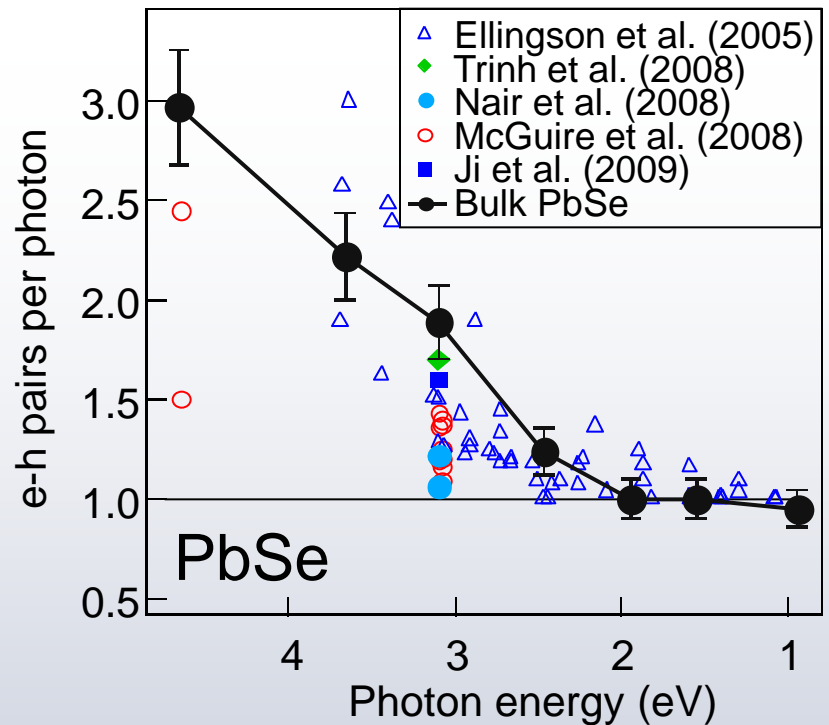
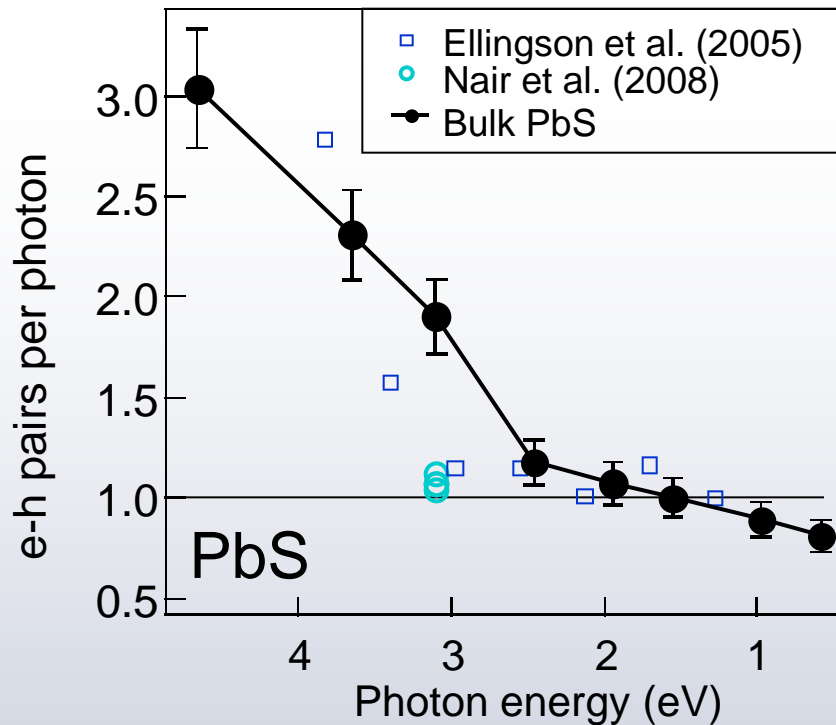
800 nm:
 1.03 ± 0.05
e-h / photon



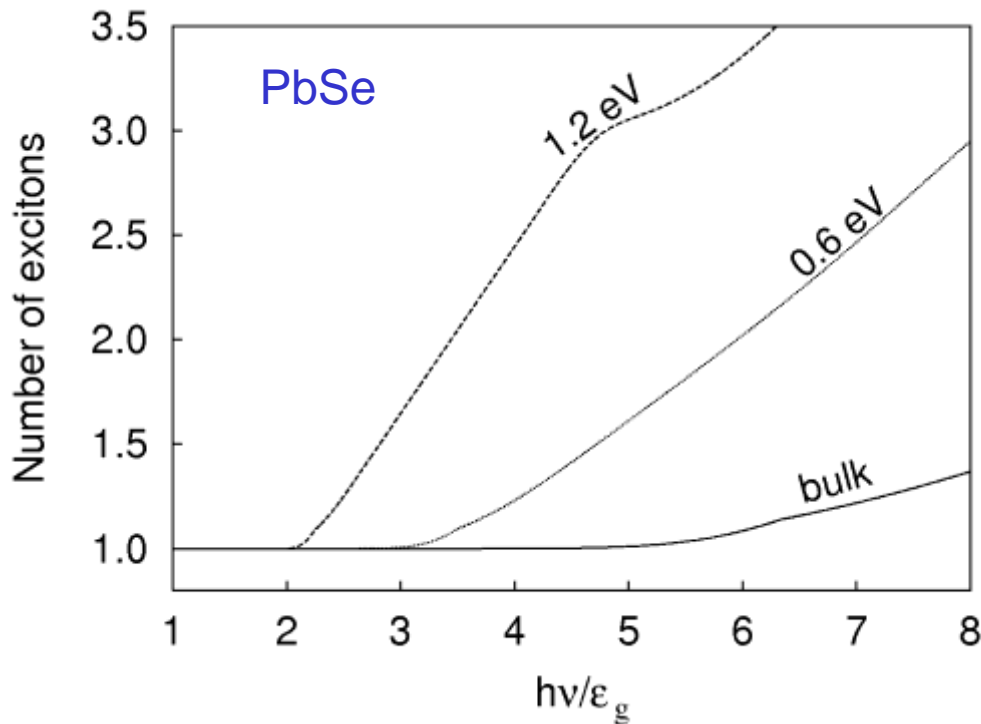
Conclusion:

Theory explains the MEG efficiency in bulk PbSe and Si for similar values of the phonon relaxation lifetime ($\sim 0.5 ps$)

Comparison between experimental data



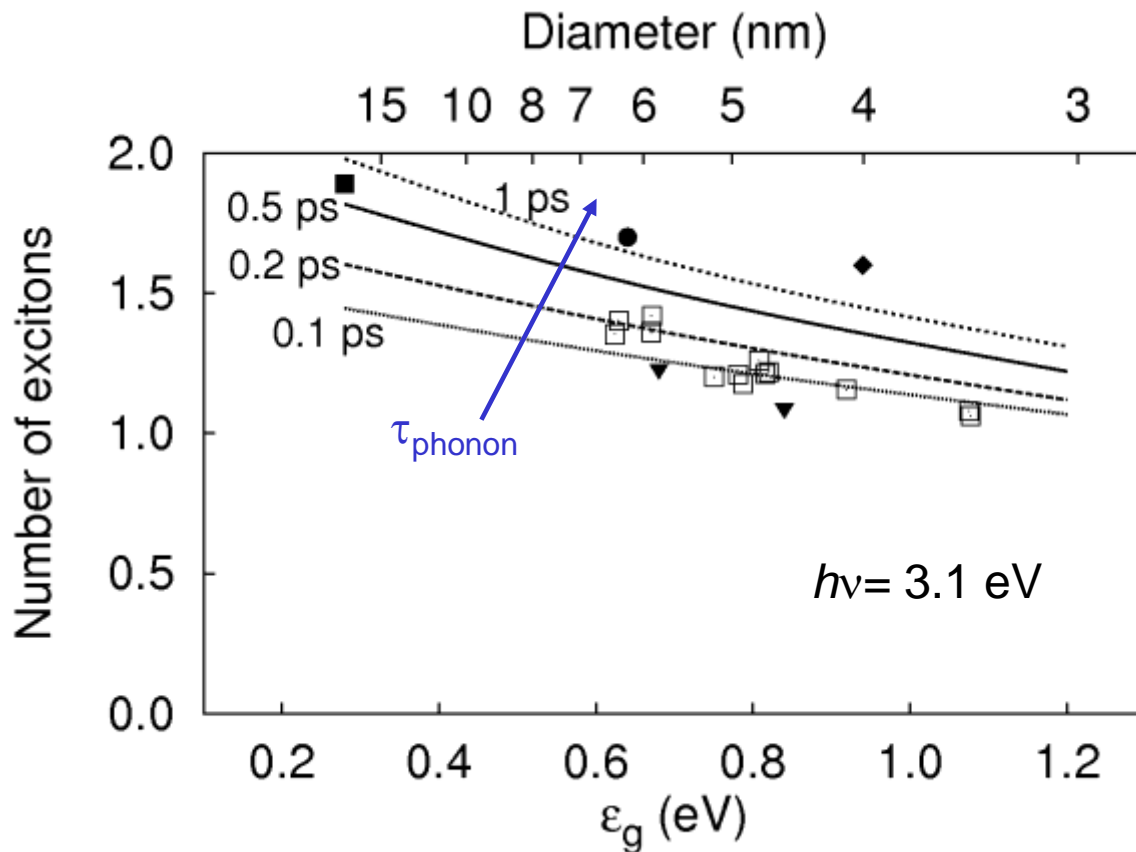
Comparison between bulk & QDs



Lines : our calculations.

$$\tau_{\text{phonon}} = 0.5 \text{ ps}$$

PbSe: evolution from bulk to QDs



Lines : our calculations.

Recent experimental results:

□ : Klimov 08

▼ : Nair et al 08

● : Trinh 08

■ : bulk PbSe

Observations of MEG in bulk *and* QDs can be fully accounted for by Impact Ionization – no need for other mechanisms (coherent superposition of single and multi-exciton wavefunctions[#]; occurrence of virtual single exciton states*.)

[#] Ellingson, R. J. et al. *Nano Lett.* 5, 865-871 (2005).

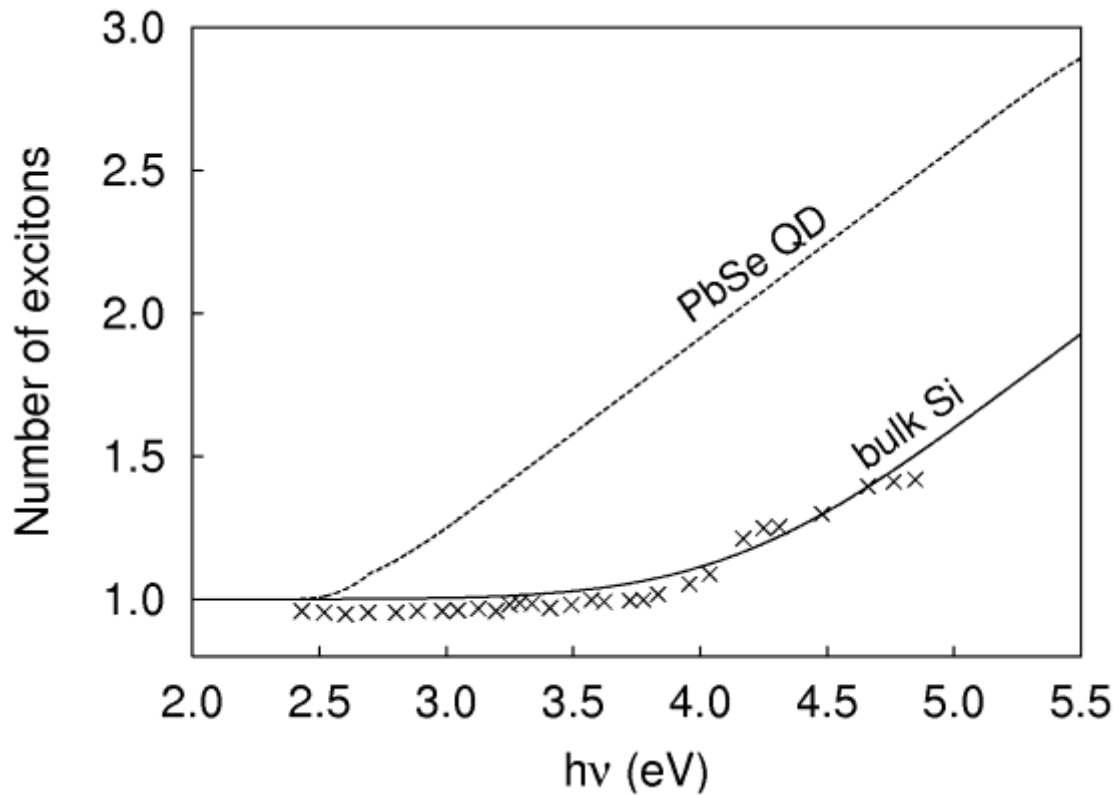
* Schaller, R. D., *Nature Phys.* 1, 189-194 (2005).

Big questions....

- Impact ionization in QDs : is it more or less efficient than in bulk ? **LESS**
- Can we justify the highest MEG yields reported in early works ? **NO**
- Can we justify the lower MEG yields reported recently ? **YES**
- Can we generate more excitons in QDs than in bulk ? **NO** (at constant hv)
- Interest of MEG in QDs for solar cells ?

Interest for solar cells ?

Comparison : **PbSe QDs** / **bulk Si** (gap = 1.2 eV)



Lines : our calculations.
 $\tau_{\text{phonon}} = 0.5 \text{ ps}$

x : Wolf, M.; Brendel, R.; Werner, J. H.; Queisser, H. J. J. Appl. Phys. 1998

Interest for solar cells ?

$$\text{Energy efficiency} = \frac{\text{number of excitons} * \text{energy gap}}{\text{photon energy } h\nu}$$

Energy efficiency of PbSe under solar illumination:

Gap (eV)	Without MEG	With MEG	Gain = Ratio with/without
0.28 (bulk)	0.199	0.217	1.09
0.60 (QD)	0.381	0.400	1.05
1.20 (QD)	0.476	0.485	1.02

Small gain value : most of the photon flux is below the MEG threshold
Even for PbSe QDs, the importance of MEG for solar cells remains minor.

Interest for solar cells ?

- Impact ionization in QDs : is it more or less efficient than in bulk ? **LESS**
- Can we justify the highest MEG yields reported in early works ? **NO**
- Can we justify the lower MEG yields reported recently ? **YES**
- Can we generate more excitons in QDs than in bulk ? **NO** (at constant $h\nu$)
- Interest of MEG in QDs for solar cells ? **MINOR**
- (with present materials)

✓MEG efficiency :

PbSe QDs < bulk PbSe

PbSe QDs (1.2 eV gap) > bulk Si (1.2 eV gap)

✓Even for PbSe QDs, the importance of MEG for solar cells remains minor.

G. Allan and C. Delerue, Phys. Rev. B 73, 205423 (2006)

G. Allan and C. Delerue, Phys. Rev. B 77, 125340 (2008)

G. Allan and C. Delerue, Phys. Rev. B 79, 195324 (2009).

J. J. H. Pijpers, R. Ulbricht, K.J. Tielrooij, A. Osherov, Y. Golan, C. Delerue, G. Allan & M. Bonn, Nature Physics 5, 811 (2009)

C. Delerue, G. Allan, J.J.H. Pijpers, and M. Bonn, submitted.

