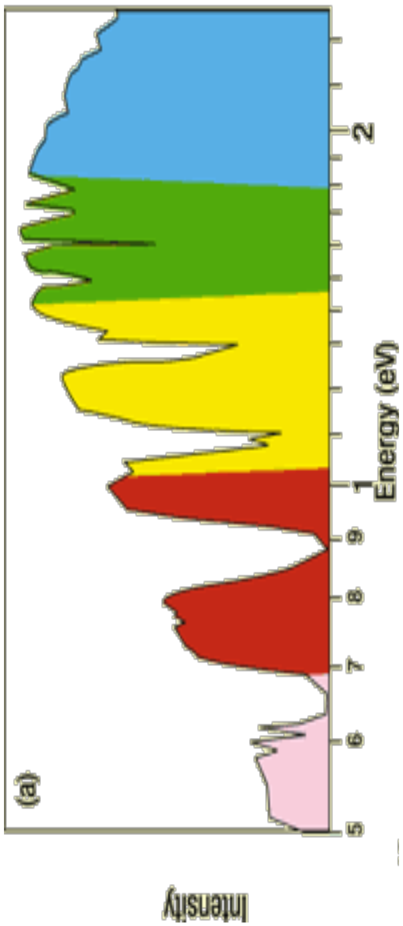
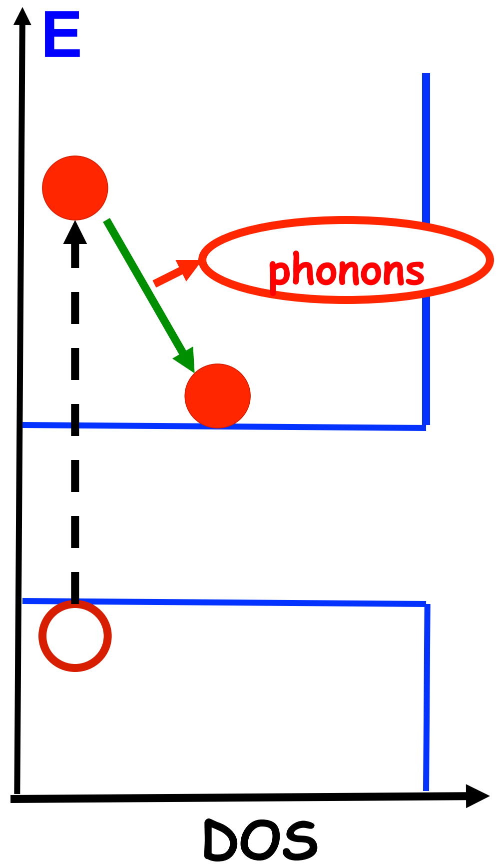
Ab initio studies of Nanoparticle Photovoltaics:
MEG, Exotic core phases & Complementary transport

G. Galli
F. Gygi
A. Gali
D. Rocca
M. Voros
S. Wippermann
I. Carbone
G. Zimanyi
(UC Davis)

S. Carter (UCSC)
T. Kaxiras (Harvard)

Solar Energy Conversion: Relaxation by phonons

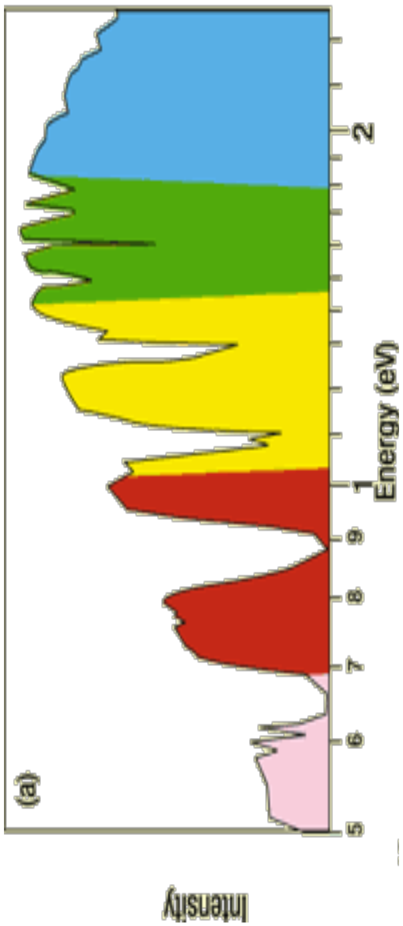


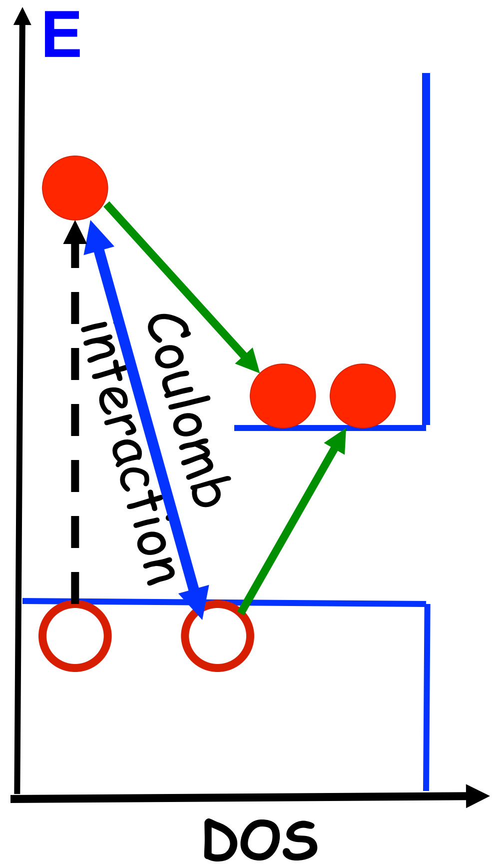


Loss at low energies:
no absorption below E(gap)

Loss at high energies:
electron that absorbed a high energy photon E>E(gap) relaxes to E~E(gap) by emitting phonons

Solar Energy Conversion: Relaxation by excitons





Keep energy of high energy photons in electronic sector:

Relaxation by Multiple Exciton Generation:

Photo-excited first exciton relaxes by exciting second exciton instead of phonons

X->XX process needs to be faster than e-ph relaxation

Max efficiency:
44% 1 Sun (Klimov 2005)
70% 1000 Sun (Nozik 2013)

Multiple Exciton Generation - 1957

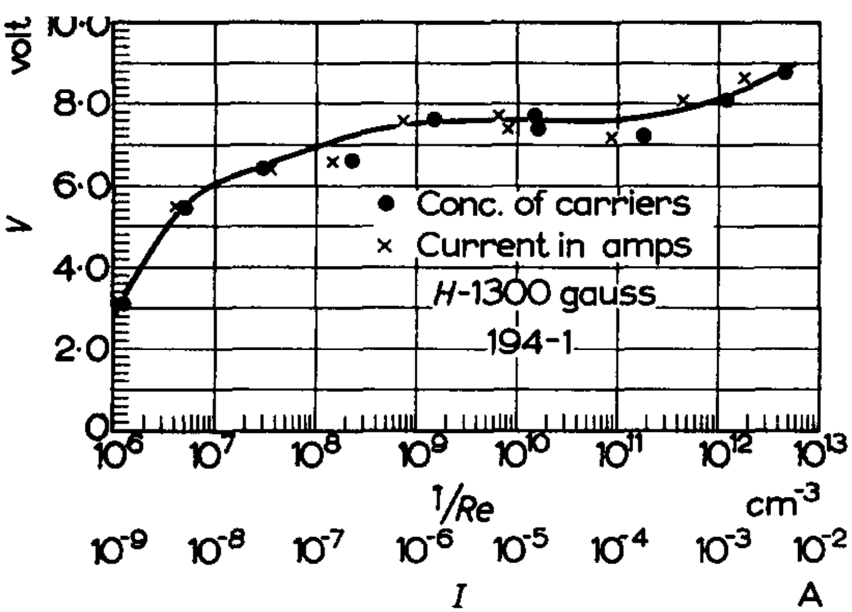
J. Phys. Chem. Solids. Pergamon Press 1957. Vol. 2. pp. 1–23.

IMPACT IONIZATION OF IMPURITIES IN GERMANIUM*

N. SCLAR† AND E. BURSTEIN

United States Naval Research Laboratory, Washington, D.C.

(*Received* 16 *September* 1956)



"Impact Ionization" has ~1% efficiency in bulk (Sclar 1957)

Multiple Exciton Generation

To save the exciton generation from the jaws of electron-phonon interaction:

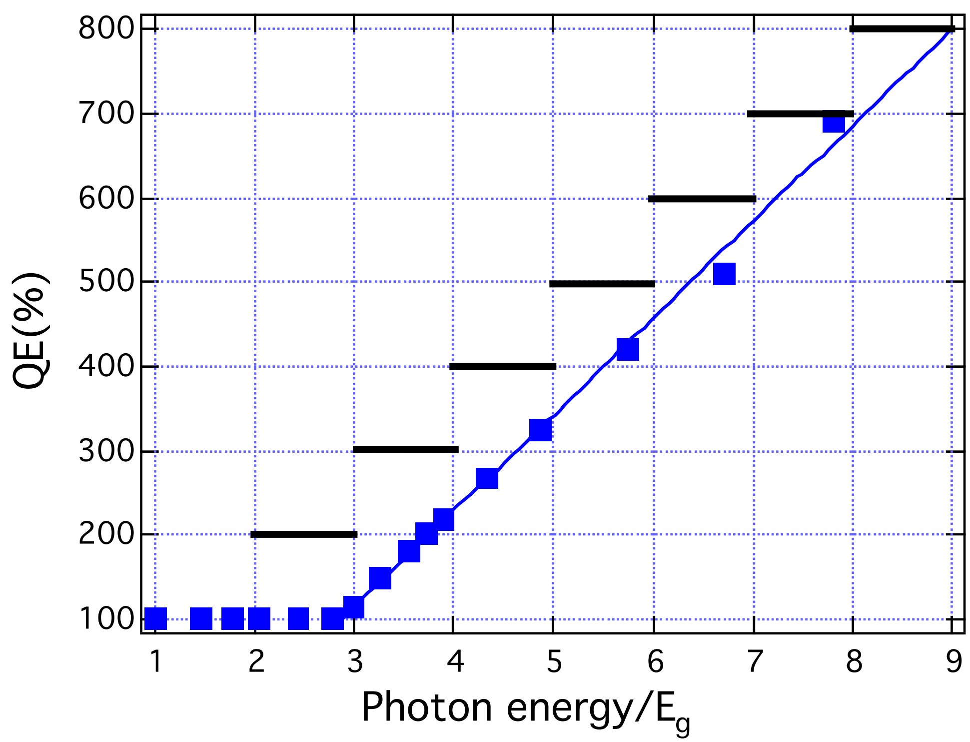
"We're going to need a bigger Coulomb interaction"

In nanoparticles electrons cannot avoid each other: screening is reduced, Coulomb interaction enhanced (Nozik 2001-2004)

MEG in Nanoparticles: The Discovery

Klimov, Schaller (2004) pump & probe:

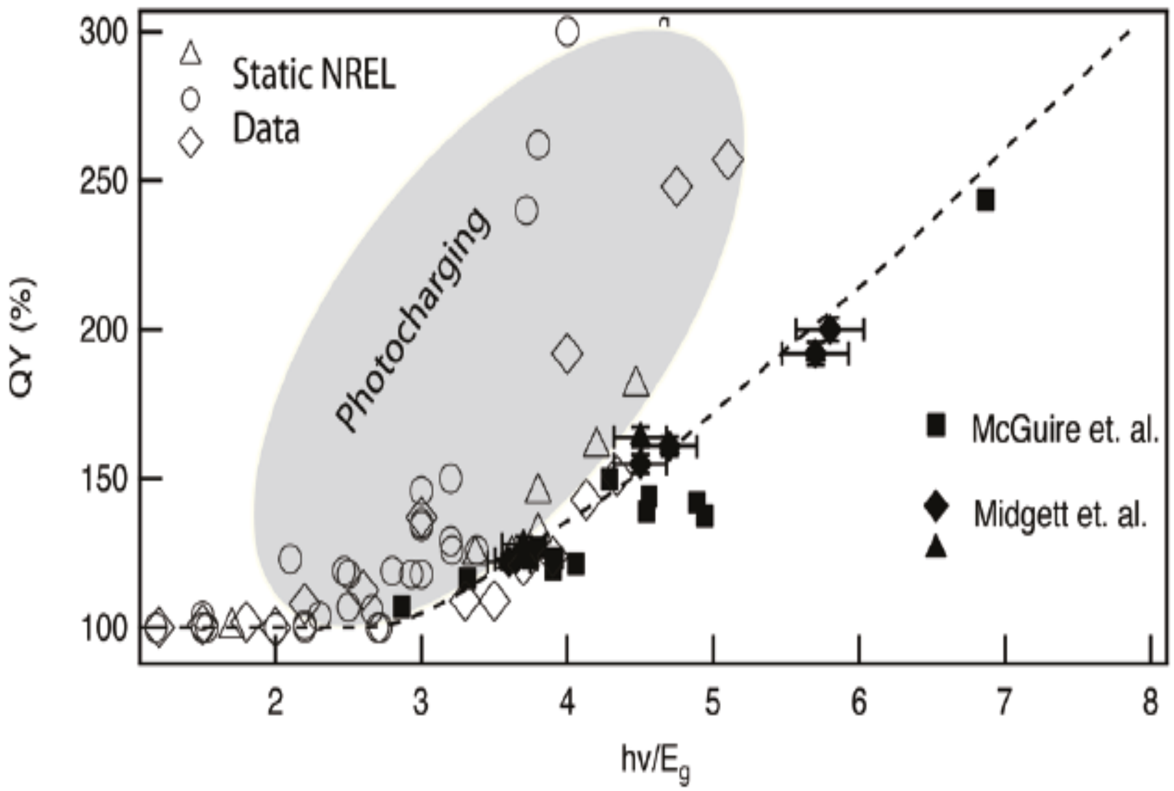
Quantum Yield (QY=#(electrons)/photon) up to 700%



MEG: Consensus Status (in solutions)

Beard (2011):

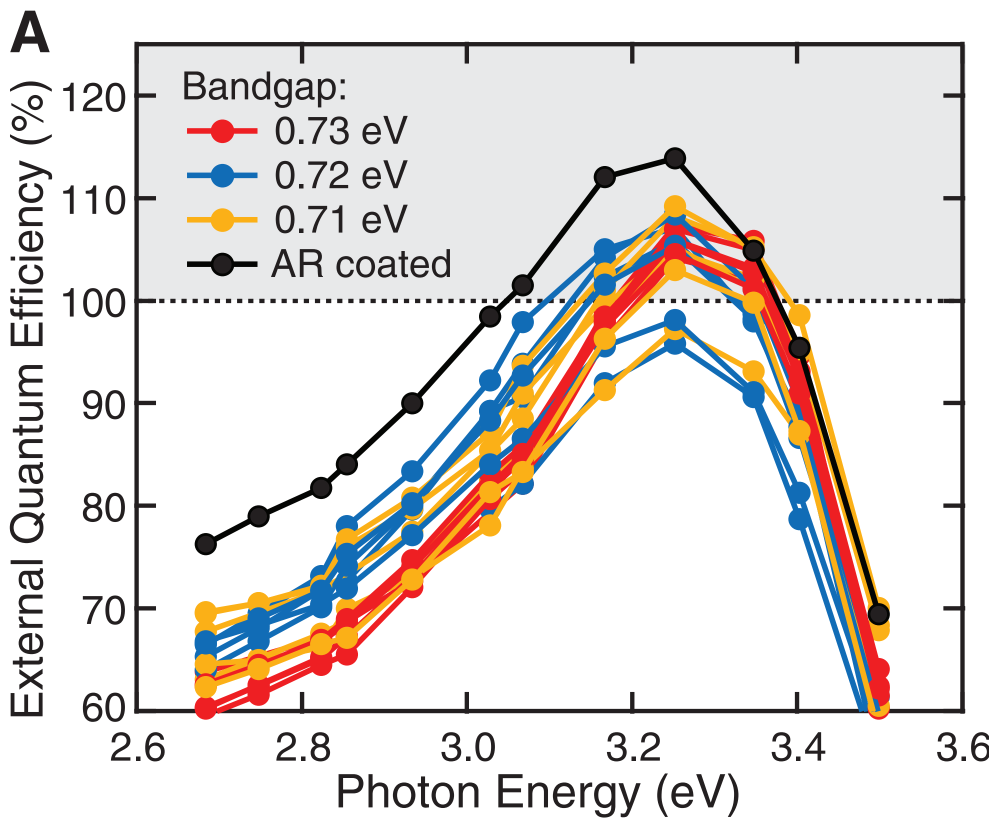
MEG is certainly present in NPs, albeit with lower efficiency



MEG first implemented in working solar cell: Dec. 2011

Peak External Photocurrent Quantum Efficiency Exceeding 100% via MEG in a Quantum Dot Solar Cell

Octavi E. Semonin,[1,2] Joseph M. Luther,[1] Sukgeun Choi,[1] Hsiang-Yu Chen,[1] Jianbo Gao,[1,3] Arthur J. Nozik,[1,4]* Matthew C. Beard[1]*



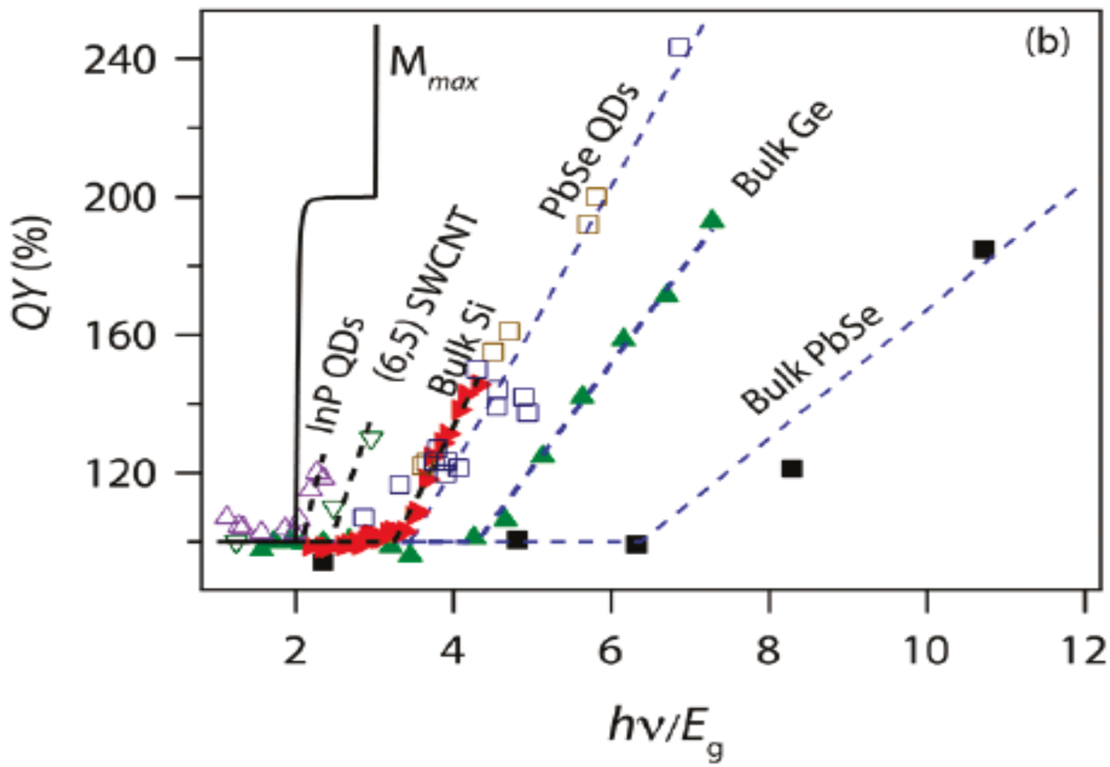
EQE > 100%:

Good

MEG: Absolute vs. Relative Energy scales

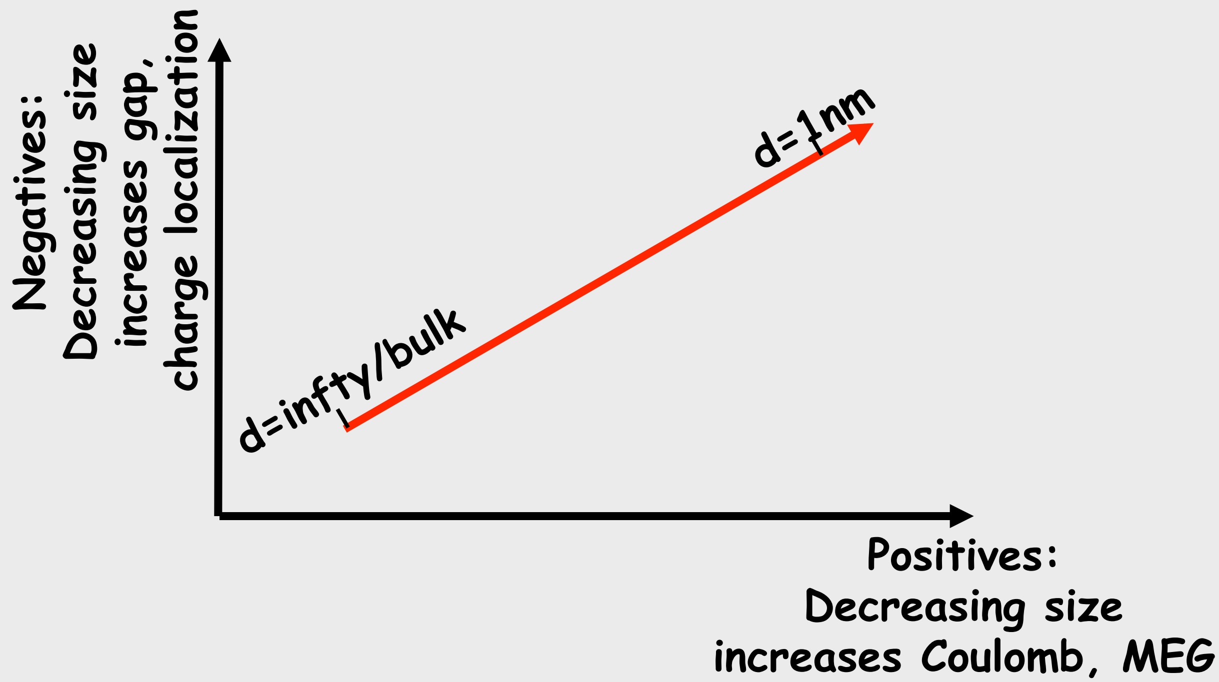
* Threshold energy bad: Eg is larger in NPs, so on absolute energy scales NP solar cells absorb smaller fraction of solar spectrum

* Coulomb strength -> Conversion efficiency enhanced: MEG more efficient in NPs than in bulk when gap increase is made implicit by plotting MEG on relative energy scale E/Eg



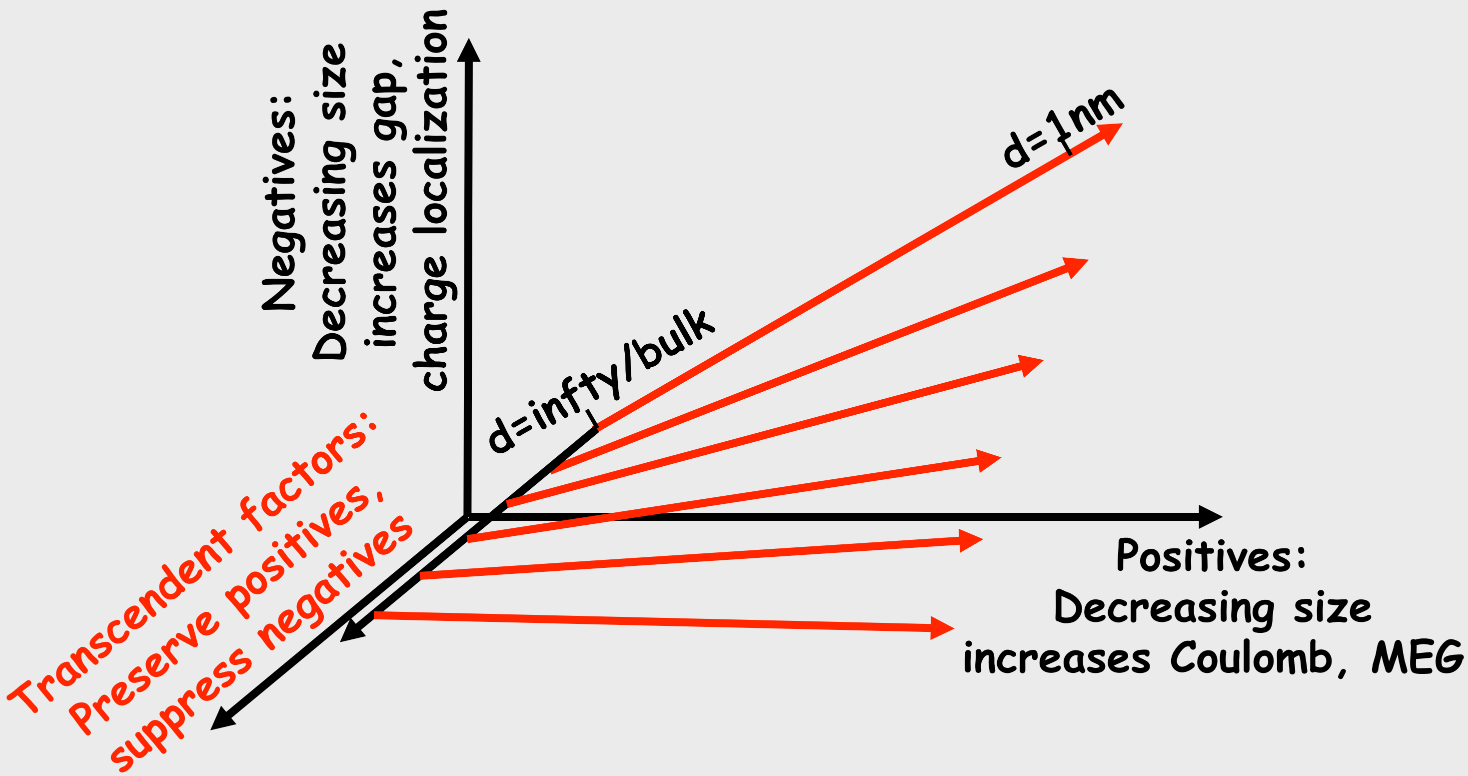
QCD - The Quantum Confinement Dilemma in Nanostructured Solar Cells

Decreasing size enhances MEG but introduces negatives



Transcending QCD in Nanostructured Solar Cells

Transcendent factors:
Preserve positives, suppress negatives



The Solar Collaborative at UC Davis/UCSC

1. To transcend QCD
2. To concentrate on non-toxic and earth abundant Si, Ge

MEG primarily demonstrated with toxic materials PbSe

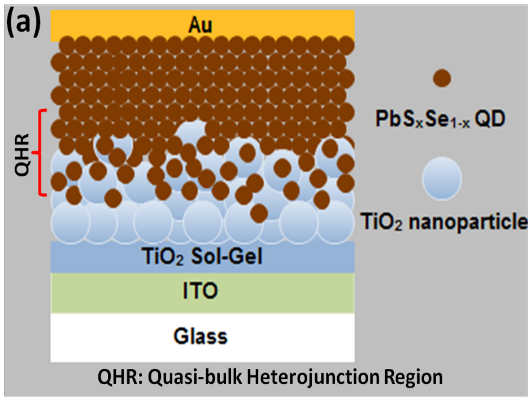
Experiment:

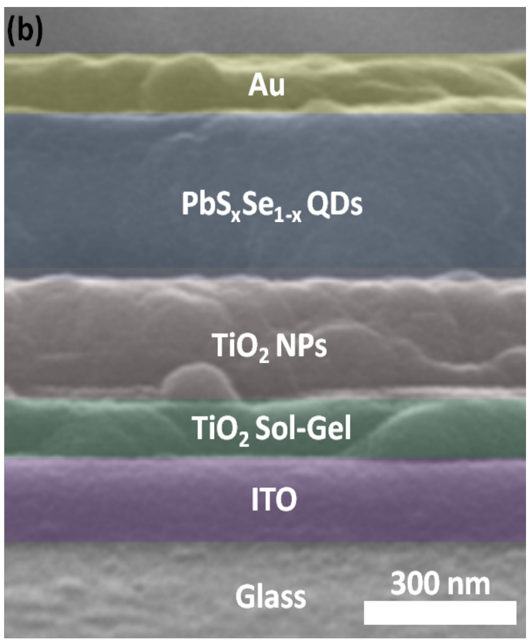
S.Kauzlarich – synthesize Si, Ge NPs
D.Larsen – characterize NPs with photoluminescence/transmission
S.Carter – assemble NPs into working solar cells

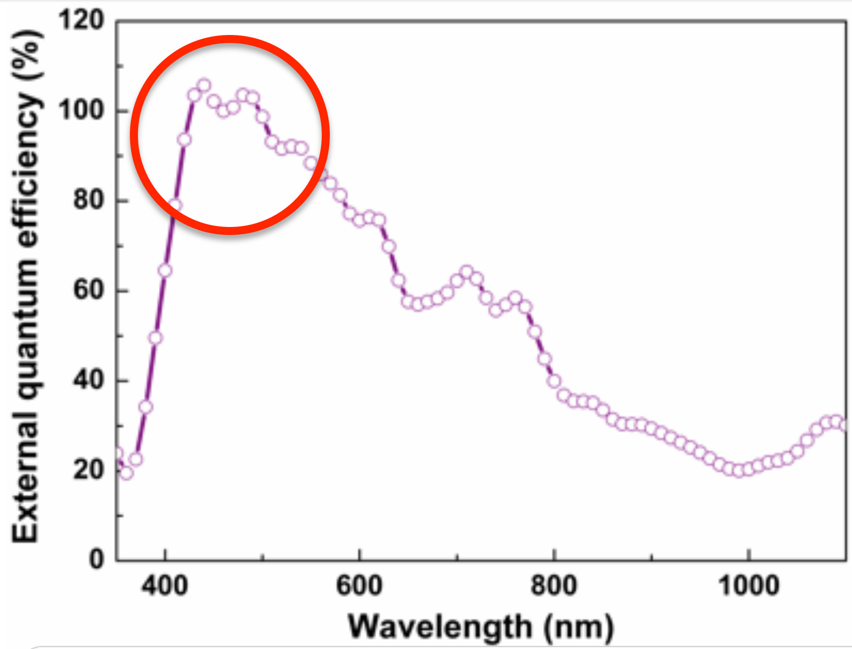
Theory:

G.Galli
F.Gygi
A.Gali
D.Rocca
M.Voros
S.Wippermann
I. Carbone

Observing Multiple Exciton Generation in a Functioning Solar Cell







Carter lab: EQE>100% in working solar cell

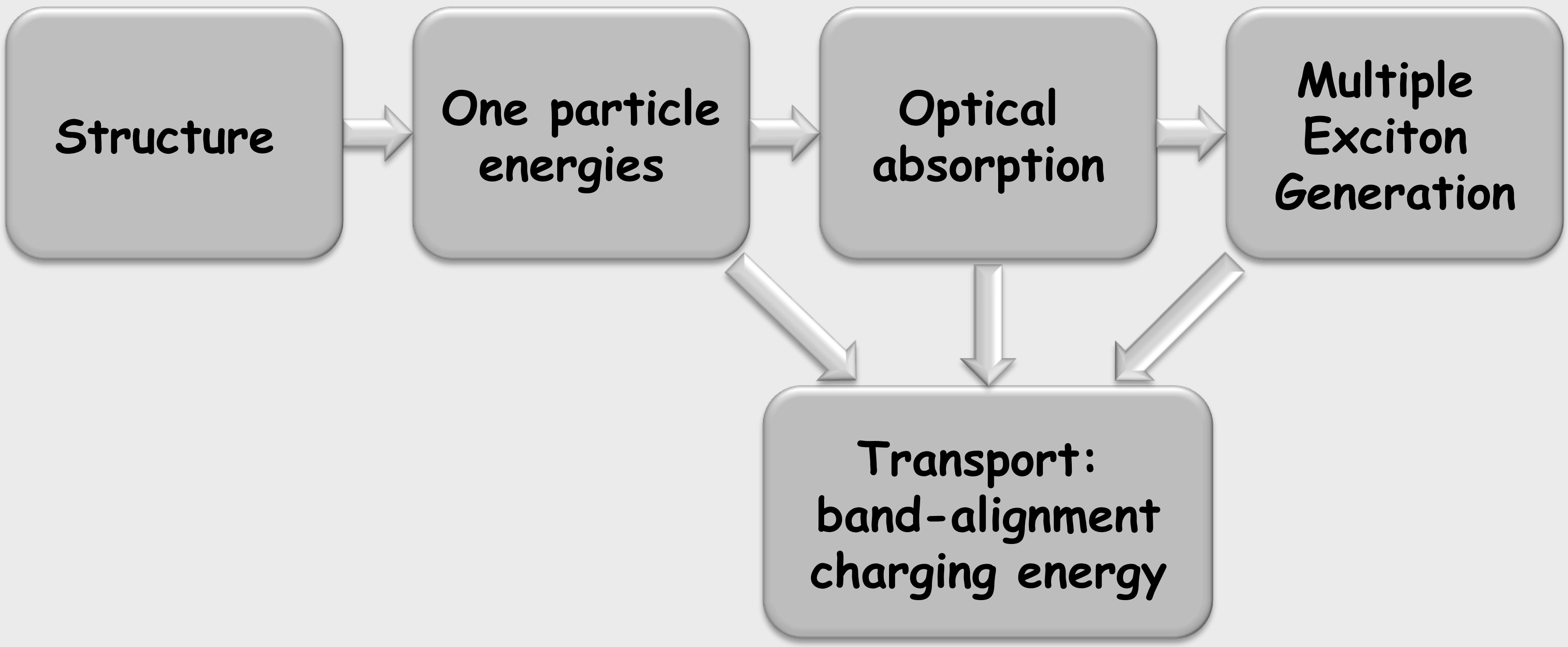
Optimized cell performance not by the use of hydrazine, but by varying the composition PbS_xSe_{1-x}.

Transcending QCD in Nanostructured Solar Cells

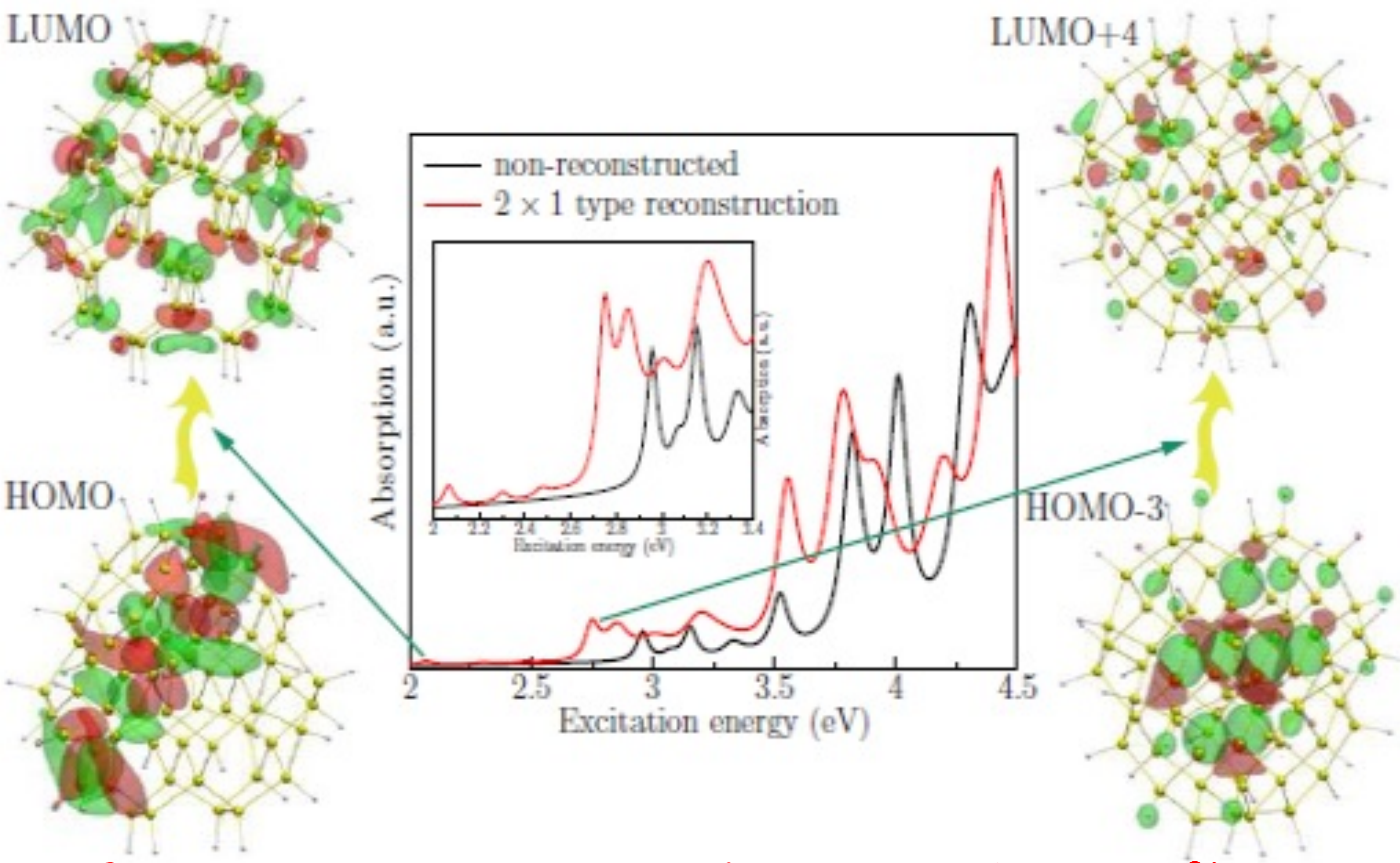
Transcendent factors:
preserve positives, suppress negatives

1. Surface reconstruction of nanoparticles
2. Shape engineering of nanoparticles: from dots to rods
3. Exotic core phase nanoparticles
4. Charge separation, transport and extraction

Theory Infrastructure



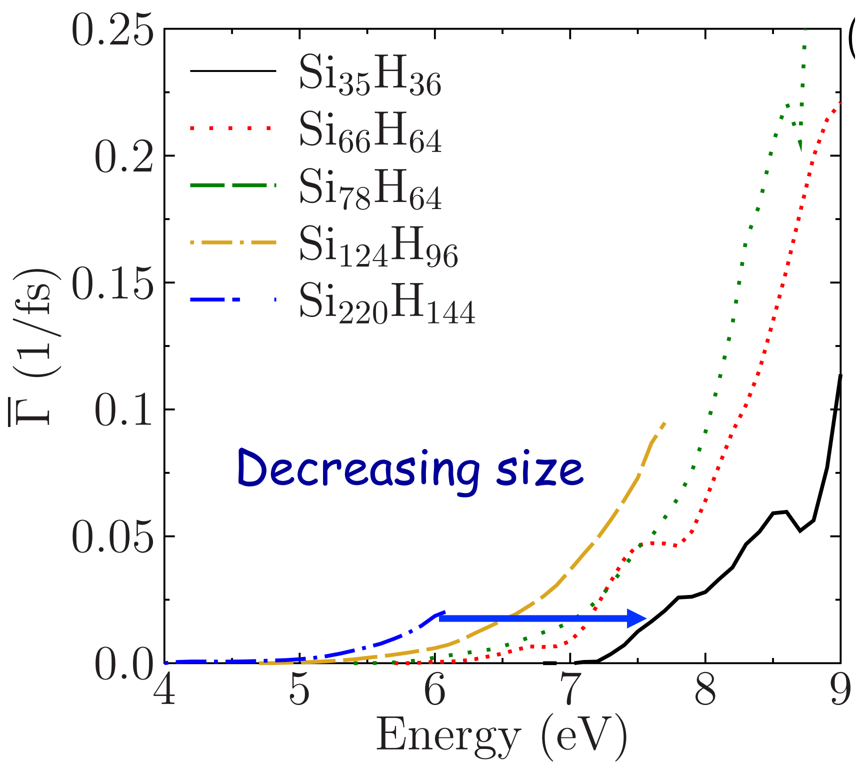
1. Surface Reconstruction Reduces the Gap

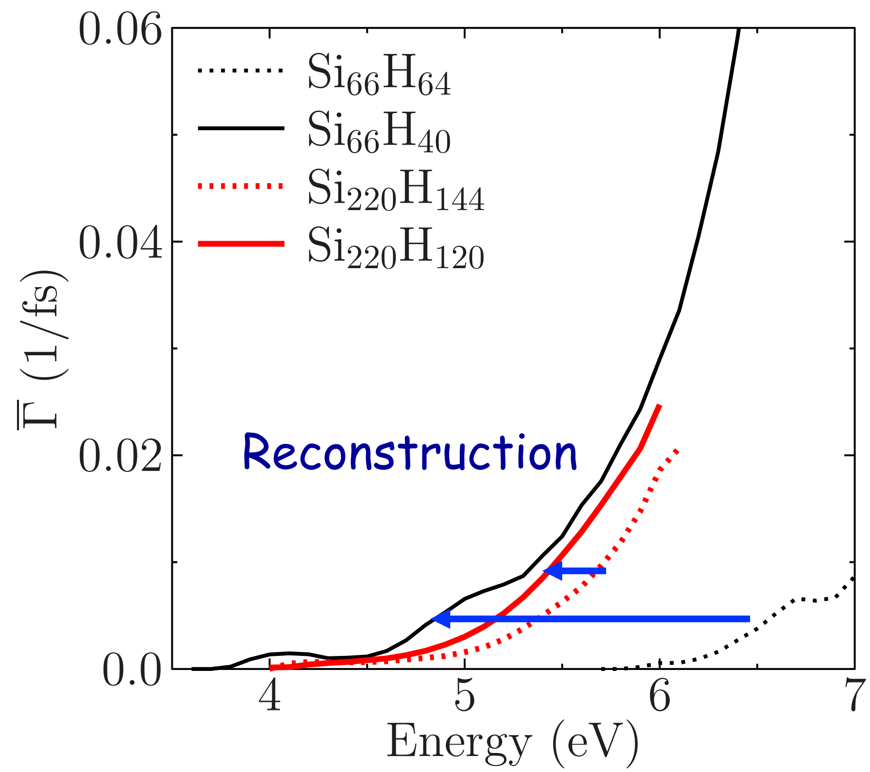


Surface reconstruction reduces gap by >10%

NanoLetters 2009

Transcendence: Reconstruction compensates gap-enhancement, preserves enhanced Coulomb strength





Quantum confinement enhances the gap in unreconstructed NPs

Reconstruction
- compensates gap enhancement
- preserves enhanced Coulomb/MEG

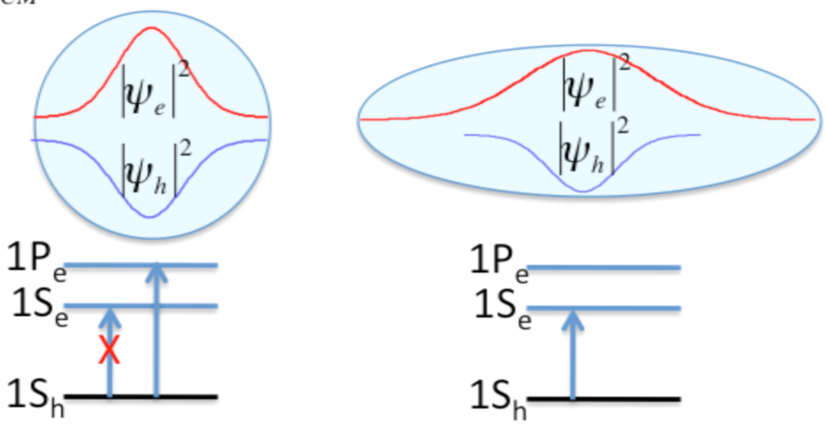
Phys. Rev. B, 2013

2. Shape engineering

- *Enhanced Coulomb interactions due to "breaking" local charge neutrality*

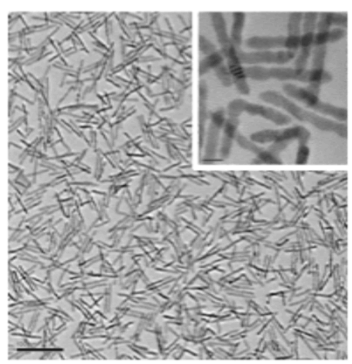
$e^*_{hot} \Leftrightarrow e + h$

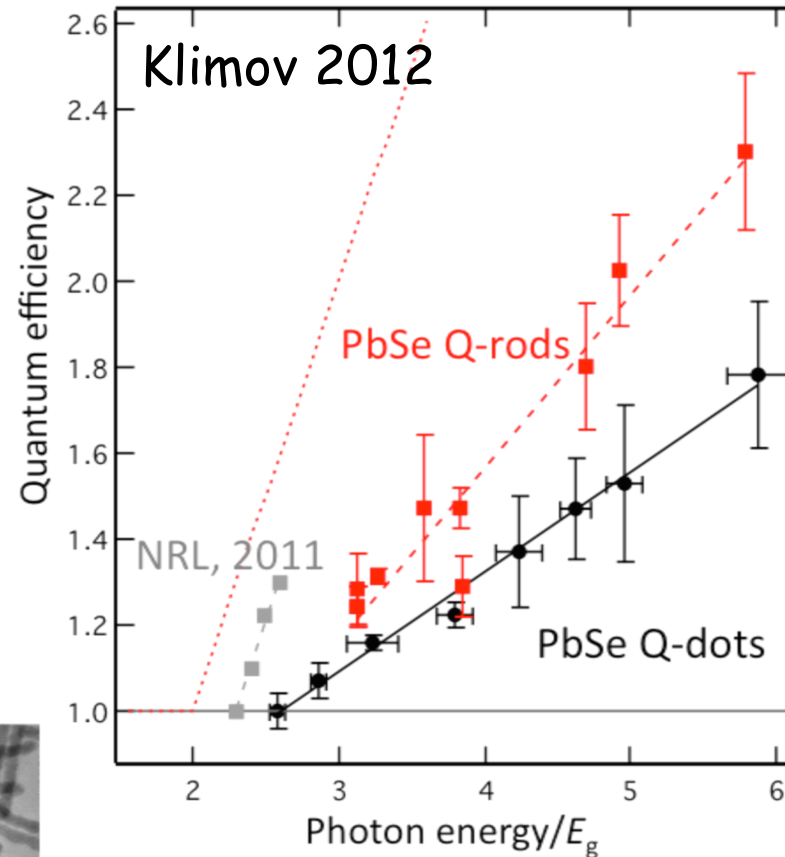
$$\frac{1}{\tau_{CM}} \propto |U_c|^2 \propto \int \rho_{e*}\rho_{eh}\,dV = \int |\psi_{e*}|^2\left(|\psi_e|^2 - |\psi_h|^2\right)dV$$



Comparative study: PbSe Dots vs. Rods

L. Padilha, J. Stewart, R. Sandberg, Wan-Ki Bae et al., to appear in *Acc. Chem. Res.* 2012



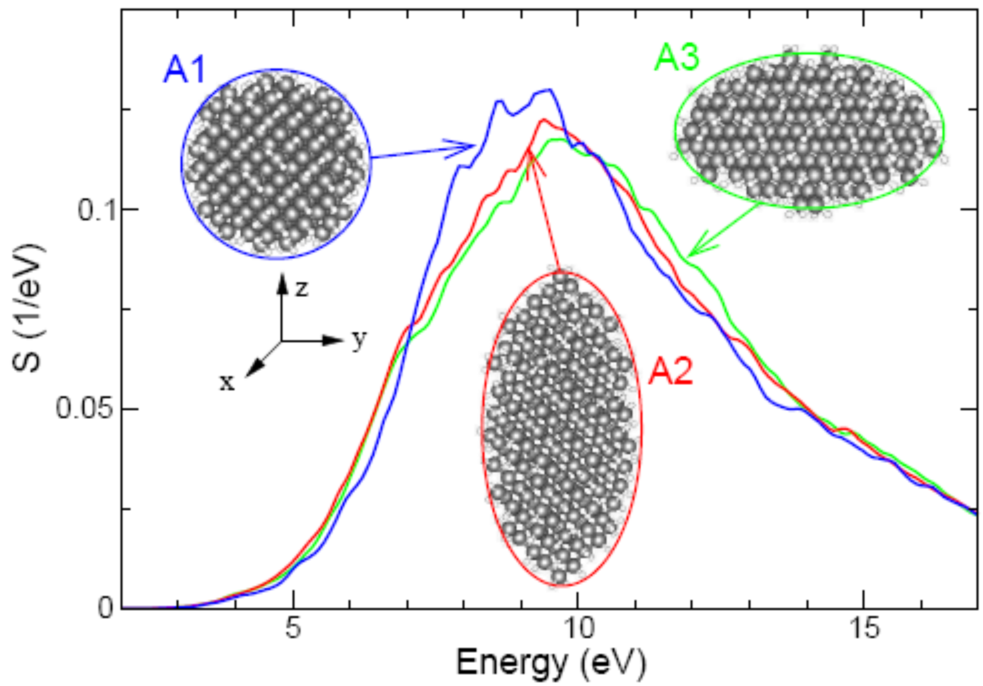


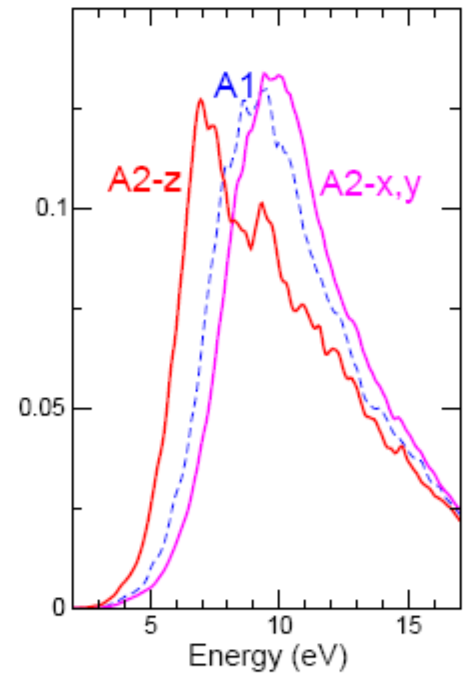
Multiexciton yield: η = QE - 1

η(rods) ≈ 1.8η(dots)

ε_{eh}(rods) ≈ 0.6ε_{eh}(dots)

2. Lowering Shape Symmetry Reduces the Gap



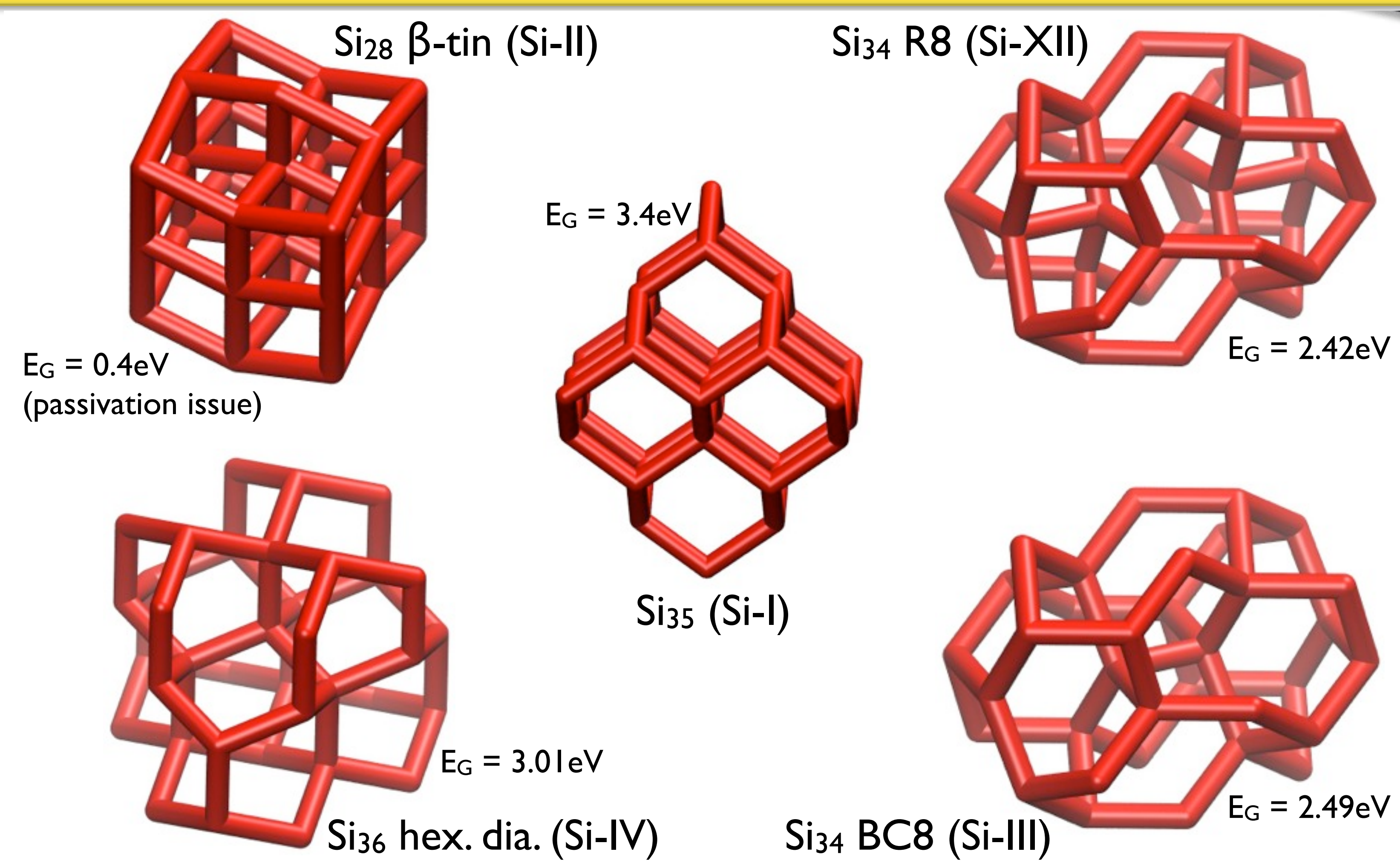


Lots of transitions are forbidden by symmetry-driven selection rules

Lowering symmetry of nanoparticles allows more transitions: nanorods show MEG at lower energies

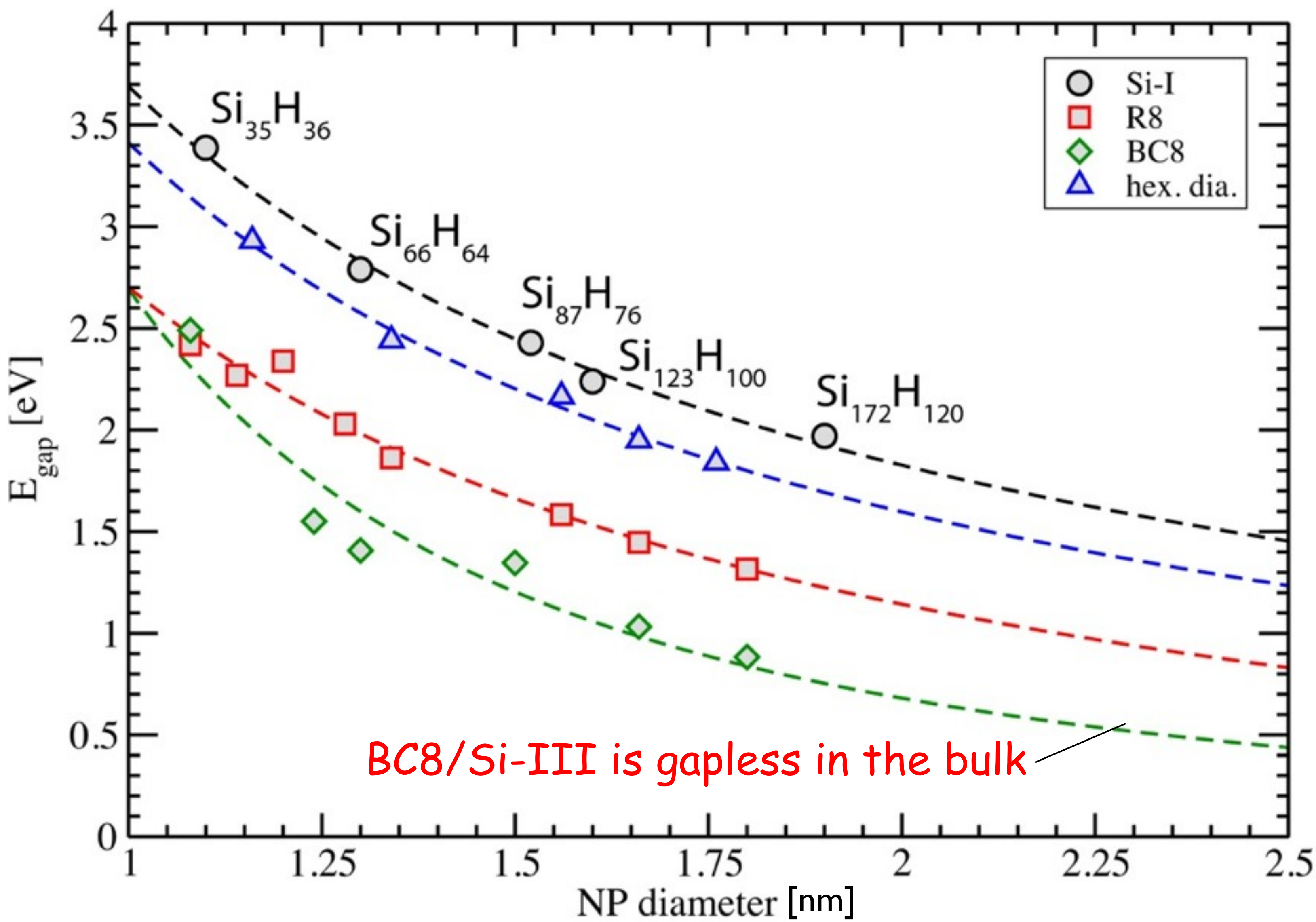
Gali, Kaxiras, Zimanyi, Meng, Phys. Rev. B 2010

3. Exotic Core Phase Si/Ge NPs:
3.1. Reduce Gap by using Bulk-Gapless Phases

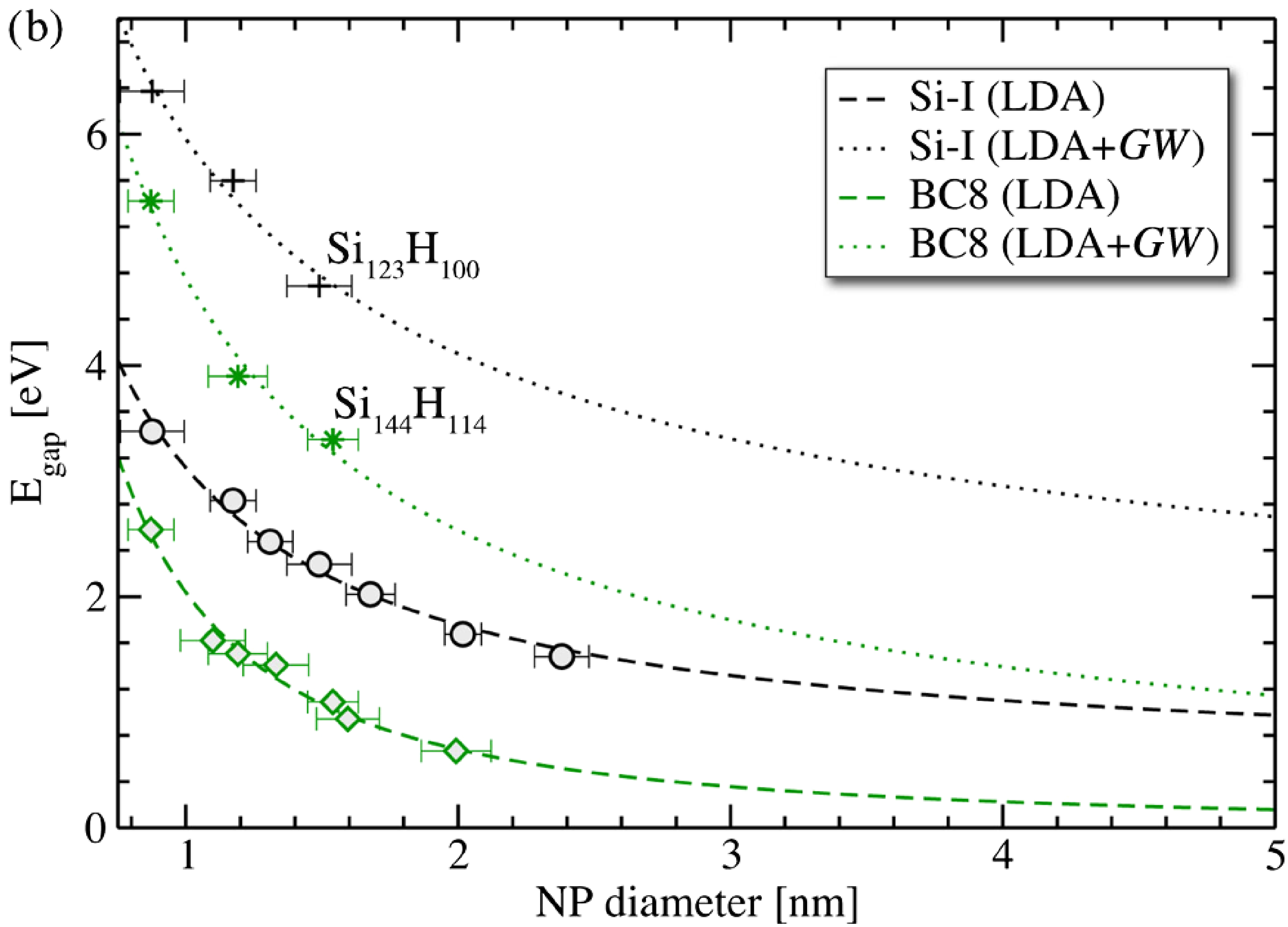


Wippermann, Voros, Gali, Rocca, Zimanyi, Galli Phys. Rev. Lett. **110**, 046804 (2013)

3.1. Gap reduction in BC8/Si-III

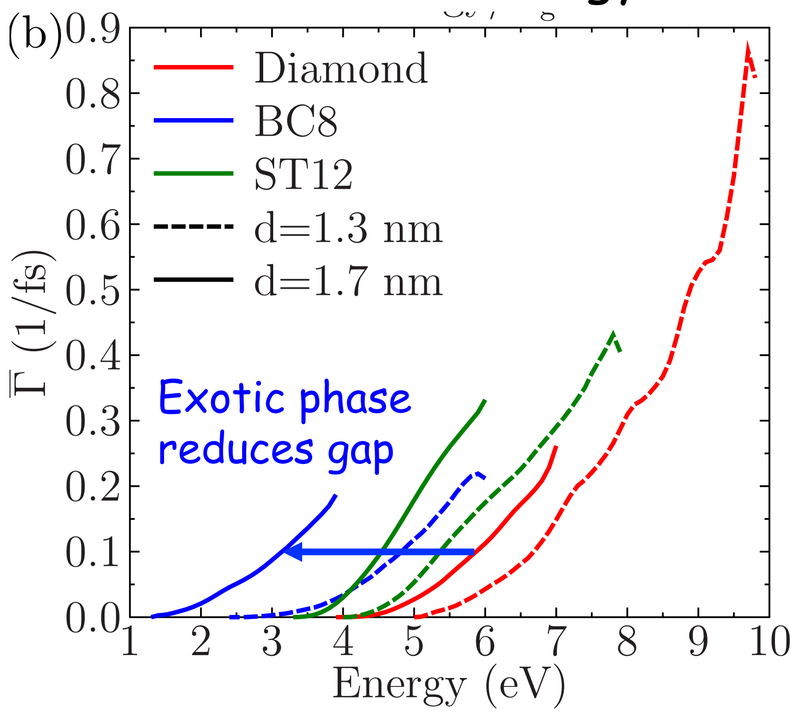


3.1. Comparison of LDA and GW

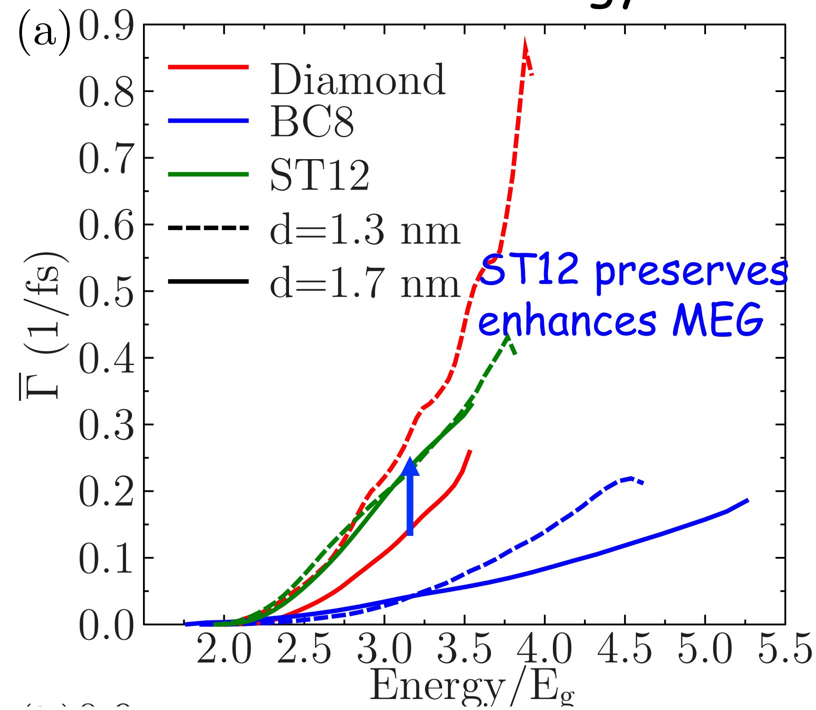


3.2. Transcendence: Exotic phases reduce gap in Ge nanoparticles, while preserving enhanced MEG

absolute energy



relative energy



Exotic core phase NPs:
Gap/MEG onset reduced in BC8 and ST12 relative to diamond

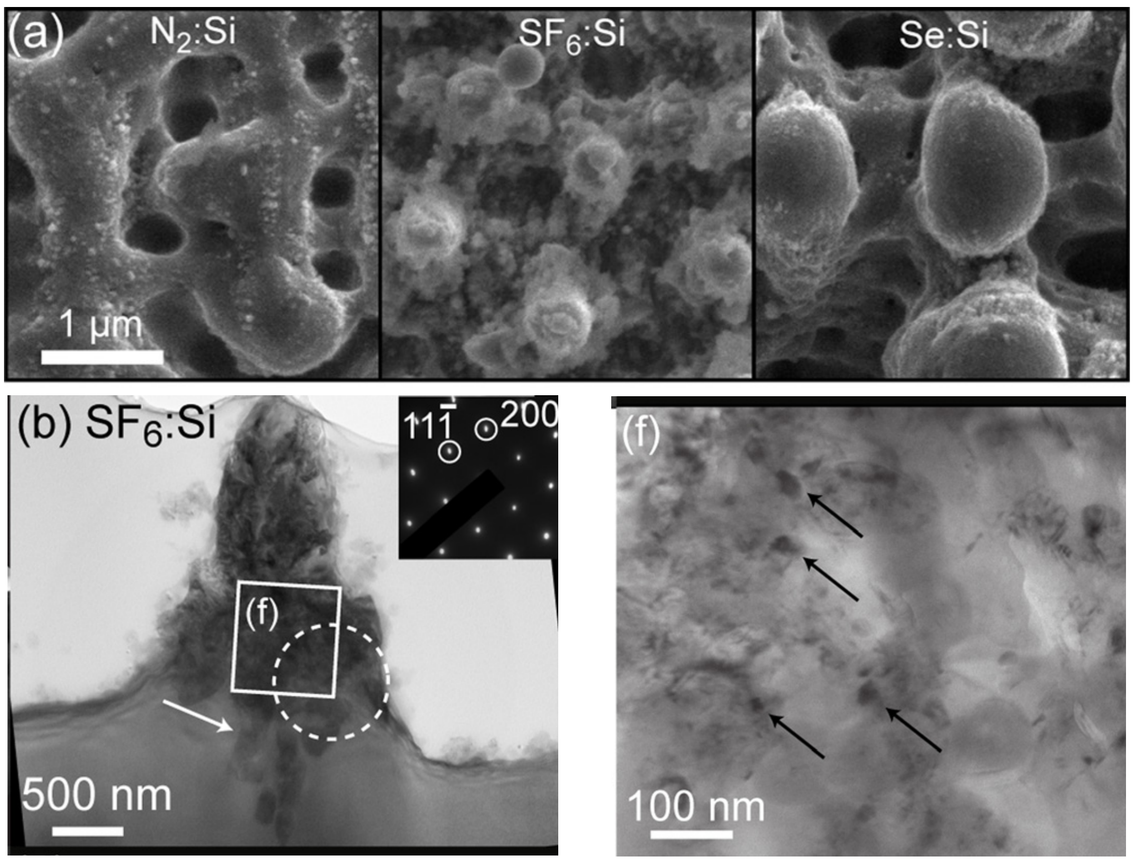
Exotic core phase NPs:
Coulomb/MEG enhancement preserved in ST12, when gap scaled out by switching to relative energy scales E/Eg

3.3. High Pressure Polymorphs in Black Si: Mazur/Gradecak

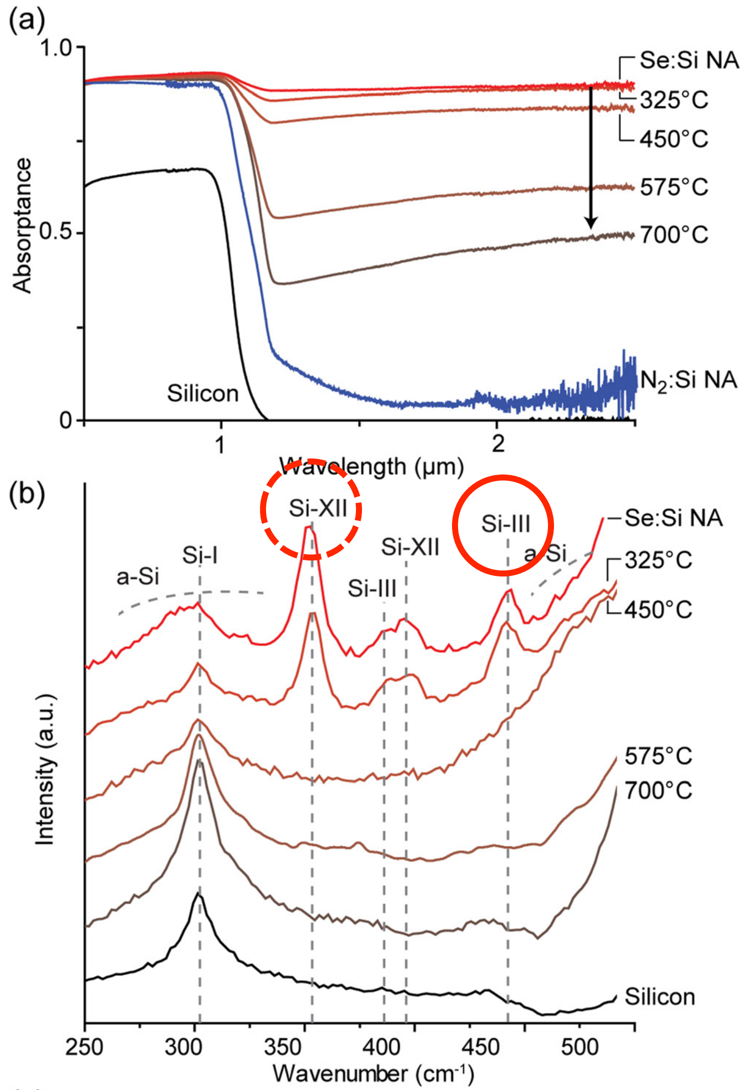
JOURNAL OF APPLIED PHYSICS **110**, 053524 (2011)

Pressure-induced phase transformations during femtosecond-laser doping of silicon

Matthew J. Smith,[1] Yu-Ting Lin,[2] Meng-Ju Sher,[3] Mark T. Winkler,[3] Eric Mazur,[2,3] and Silvija Gradečak[1,a)]



3.3. High Pressure Polymorphs in Black Si



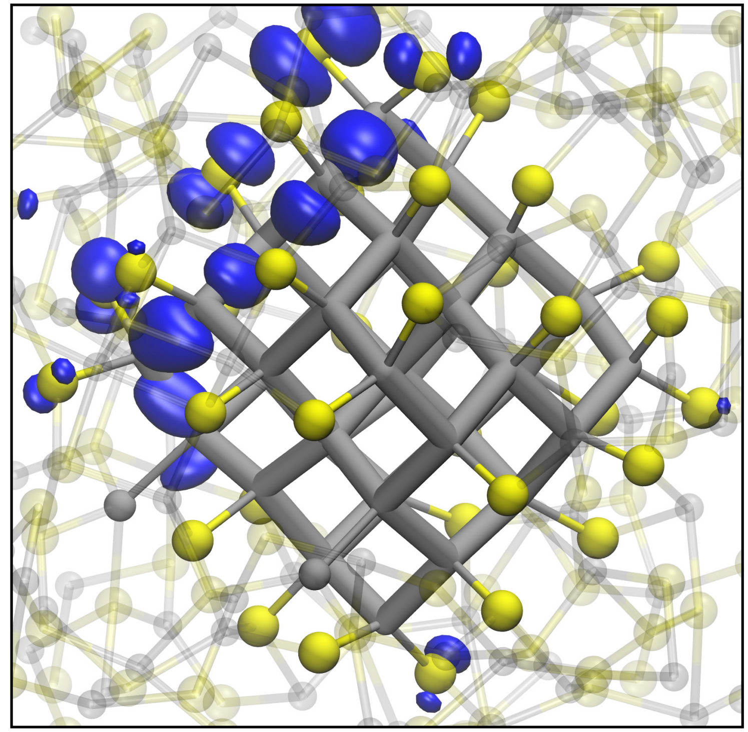
1. The presence of BC8/Si-III phase confirmed by Raman scattering

2. In some samples, when BC8/Si-III phase is annealed away, subgap absorptance is greatly reduced

Alternative explanations focus on defect sites

To shed further light, we have synthesized Ge ST12 NPs, presently fabricating PV cells

4. Charge Separation and Extraction:
4.1. Si NP in ZnS



1. Create ZnS matrix with 512 atoms
2. Replace 35-172 Zn/S atoms
   with Si atoms
3. Calculate energy
4. Calculate forces on ions
5. Relax structure with Qbox Molecular
   Dynamics at T(anneal) up to 1,000K

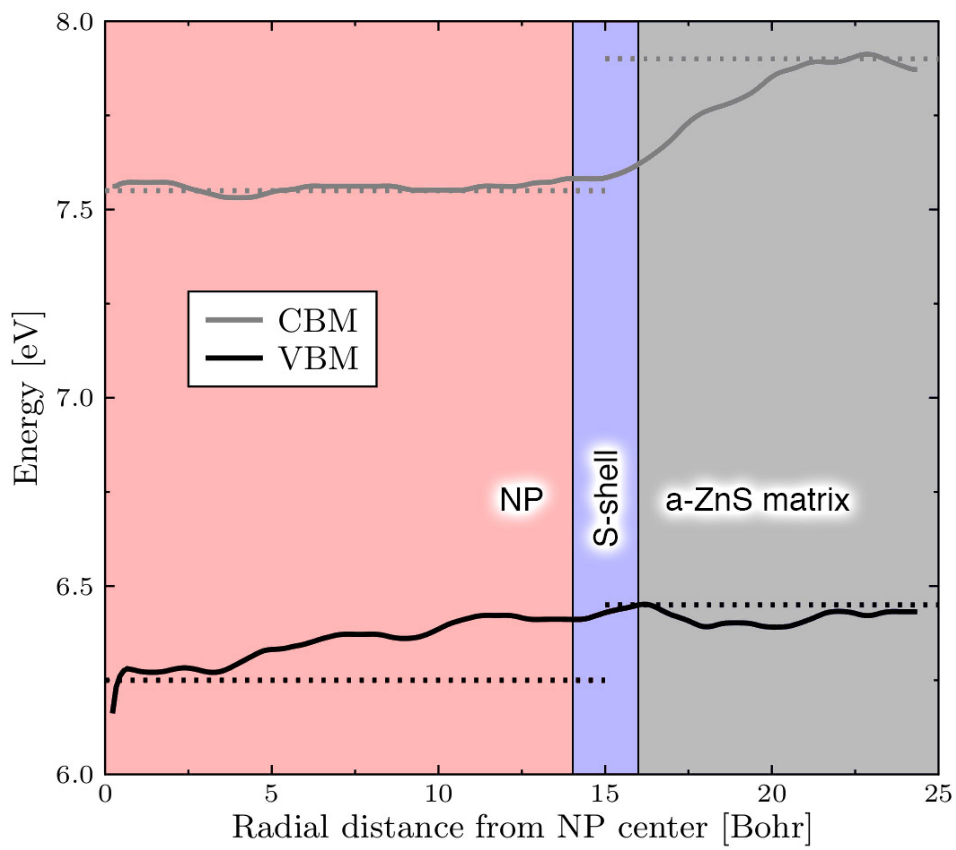
1. Observed formation of S shell around NP
2. Determined S stoichiometry optimal for clean gap

Wippermann, Voros, Gali, Gygi, Zimanyi, Galli Phys. Rev. Lett. **112**, accepted (2014)

4.2. Band Alignment

Spatially varying DOS and gap

$$D(\epsilon, r) = 2 \sum_n \overline{|\psi_n(\mathbf{r})|^2}(r)\delta(\epsilon - \epsilon_n)$$



Interface:

Bulk: type I

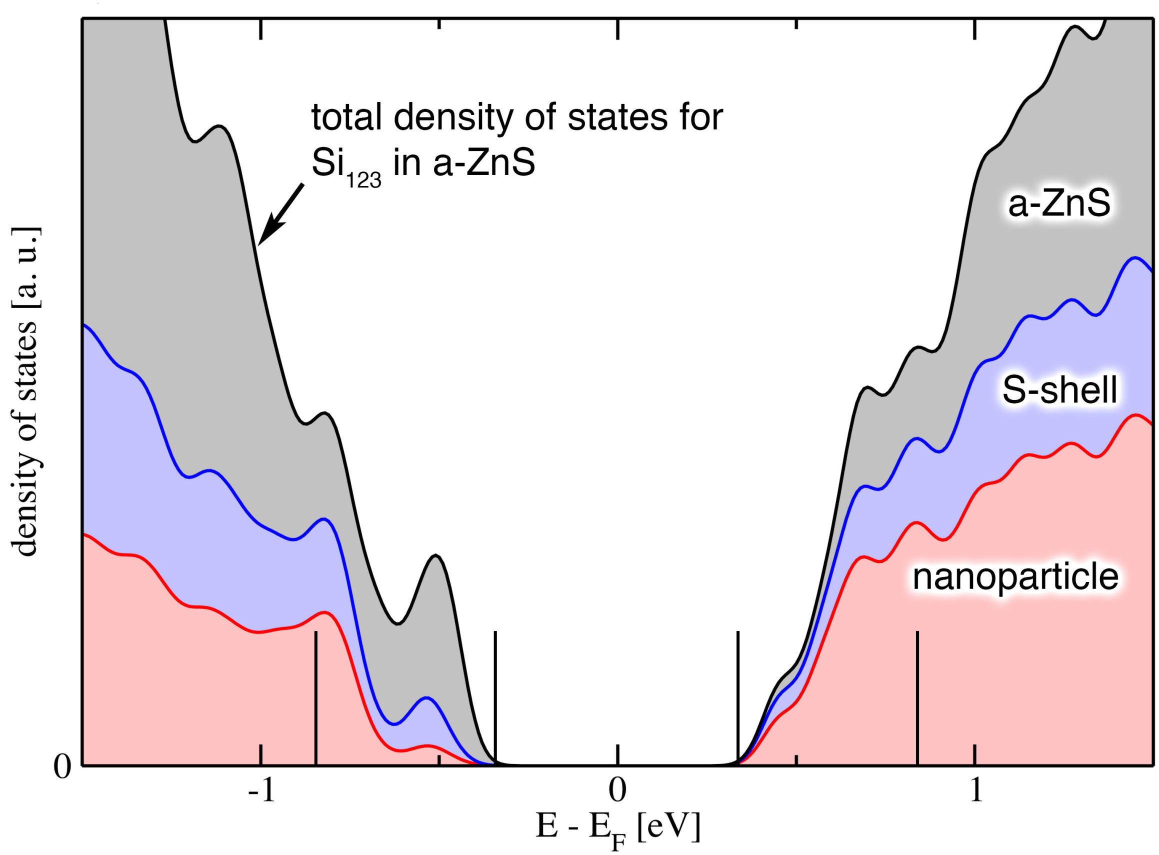
NP in matrix: changes to type II

This is favorable for charge separation

4.3. Projected DOS

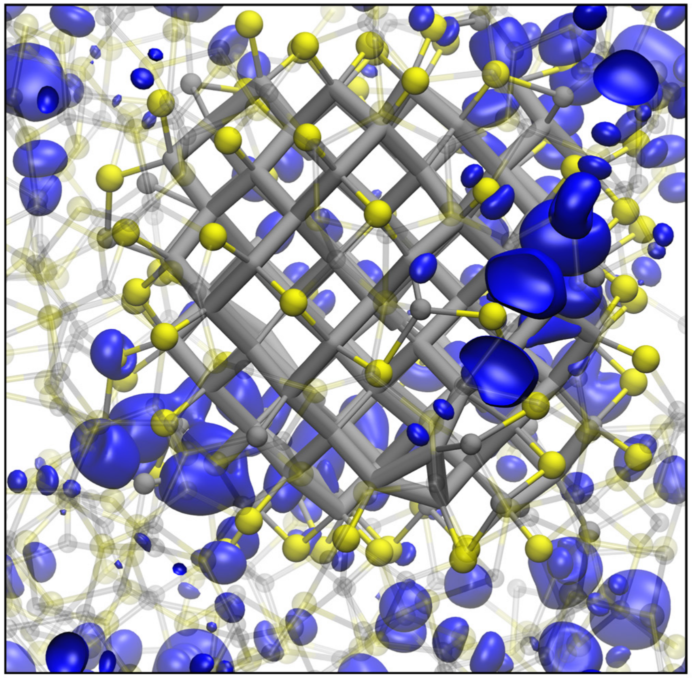
Projected states to atomic orbitals to determine character of states

$$EDOS_{\text{region}}(E) = \sum_j \sum_{i \in \text{region}} |\langle \phi_i | \psi_j \rangle|^2 \, \delta(E_j - E)$$



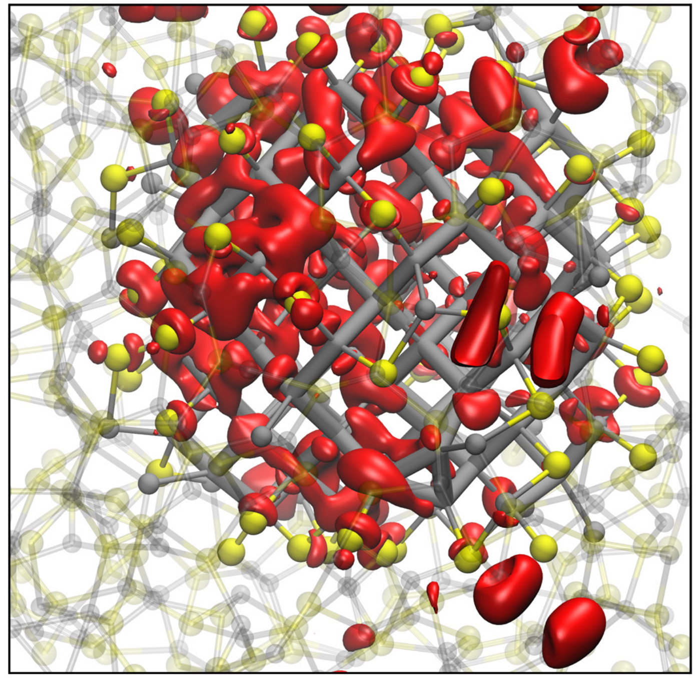
4.4. Transcending QCD impeding transport: Complementary Charge Transport Channels

Holes localized in host



Hole transport in host

Electrons localized in NPs



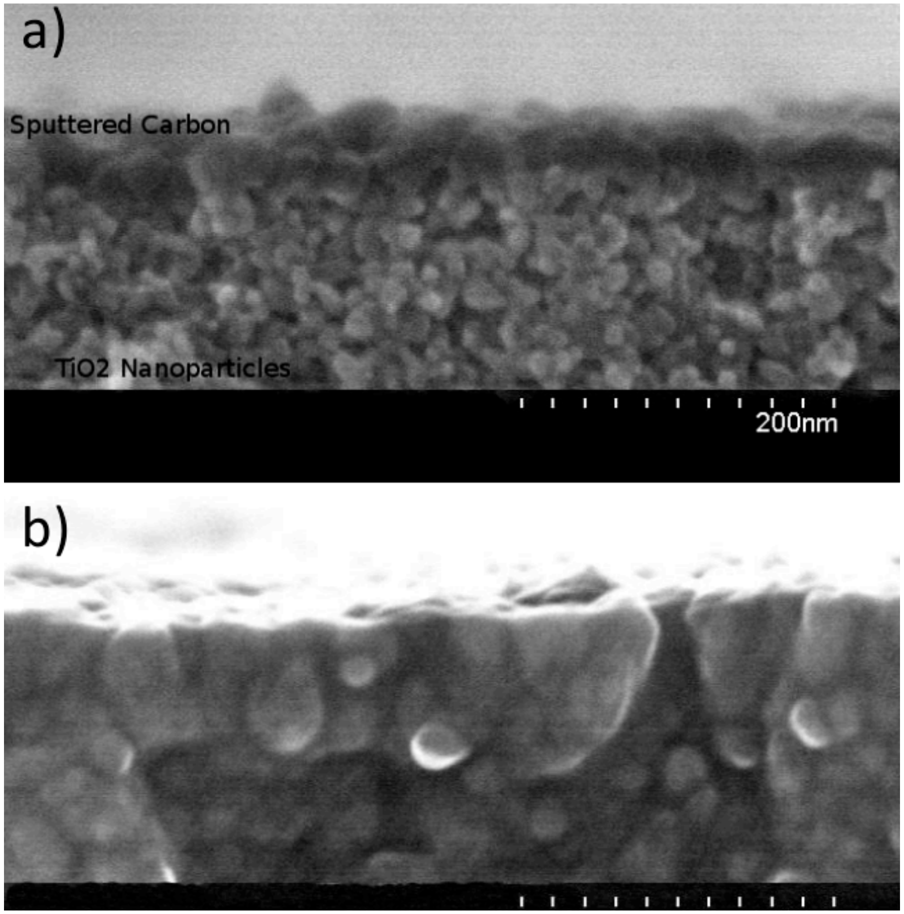
Electron transport: NP->NP

Complementary charge transport channels are formed

Quantum Confinement impeding transport: **transcended by complementary channels reducing recombination**

4.5. Towards Atomic Layer Deposition of ZnS on Ge films

Carter Lab:



Summary

Multiple Exciton Generation is a promising solar paradigm

Quantum Confinement Dilemma: QC enhances Coulomb/MEG, but enhances the gap and makes charge extraction harder

Transcending QCD is possible:

1. Surface reconstruction of NPs: decreases gap, preserves MEG

2. Shape engineering of NPs (from dots to rods): decreases gap, increases number of allowed transitions

3. Exotic core phase NPs: decreases gap, increases Coulomb/MEG

4. Embedding NPs in host matrix: interface changes type I -> type II: complementary charge transport channels form, reduce recombination

Theory Infrastructure

Structure → One particle energies → Optical absorption → Multiple Exciton Generation

- Si and Ge nanoparticles
- Hydrogen terminated surfaces
- Sizes: up to $Si_{220}H_{144}$ (~d=2.0nm)
- Up to 1.3nm vacuum around nanoparticle
- Energy of nanoparticle for an ion structure calculated in LDA
- Forces on ions calculated
- Ion structure relaxed by Qbox Molecular Dynamics

Theory Infrastructure

Structure → One particle energies → Optical absorption → Multiple Exciton Generation

- LDA
- Norm-conserving pseudopotentials, e.g. PBE
- 35 Ry (Si) – 80 Ry (Ge) cutoff
- Quantum Espresso package
- Quasi particle energies: GW
    - project to occupied states
    - avoid inversion of dielectric matrices (Galli)

Theory Infrastructure

Structure → One particle energies → Optical absorption → Multiple Exciton Generation

- TDDFT
- LDA for states
- Dielectric matrix $\varepsilon(k,k',\omega)$ in Random Phase Approximation (RPA)
- Liouville-Lanczos approach:
  - frequency dependence of ε from continued fractions

Theory Infrastructure

Structure → One particle energies → Optical absorption → Multiple Exciton Generation

- Exciton states: Slater determinants, built form DFT orbitals
- Transition rate: Fermi Golden rule

$$\Gamma_i = 2\pi \sum_f |\langle X_i | W | XX_f \rangle|^2 \delta(E_i - E_f)$$

- W in RPA approximation