Hierarchical Transport Modeling in Nanoparticle Solar Cells

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To improve conversion efficiency: Relaxation by excitons

Keep energy of high frequency 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

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: Consensus Status (in solutions)

Discovery: Schaller, Klimov (2004)  
Consensus status: Beard (2011)

MEG is certainly present in NPs, even after charging is removed.
MEG first implemented in working solar cell: Dec. 2011

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

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Bandgap:
- 0.73 eV
- 0.72 eV
- 0.71 eV
- AR coated

External Quantum Efficiency (%)

External Quantum Efficiency

Photon Energy (eV)

EQE > 100%:
Good
MEG implemented in working solar cell, II.

Carter lab: EQE > 100%

Optimized cell performance by varying the composition PbS$_x$Se$_{1-x}$
The Quantum Confinement Dilemma (QCD) in Nanostructured Solar Cells

Quantum Confinement Dilemma

Enhances Coulomb interaction: Enhances MEG

Widens gap: Absorption is pushed out of solar spectrum

Localizes charges: Hinders transport
Transcending QCD: Gap reduction strategies

1. Engineering surface reconstruction can lower gap while preserving MEG, Si nanoparticles

2. Engineering core structures in Ge nanoparticles
   Voros et al, submitted

3. Si nanoparticles with high-pressure low gap core structures

In collaboration with Stefan Wippermann, Marton Vörös, Adam Gali, Dario Rocca, and Giulia Galli
Transcending QCD: Transport boosting strategies

1. Embedding nanoparticles into suitable host forms complementary charge transport pathways for electrons and holes: Si nanoparticles embedded in ZnS
Wippermann et al, accepted in PRL (2014)

TALK OF STEFAN WIPPERMANN
M24.00003, Wednesday 12.03

In collaboration with Stefan Wippermann, Marton Vörös, Adam Gali, Francois Gygi, Dario Rocca, and Giulia Galli
Nanoparticle solar cells appeared on the NREL efficiency chart
Nanoparticle solar cells

Built-in field generated by difference in electrode work functions

Built-in field generated by forming p- and n-doped nanoparticle layers
FET mobility in PbSe Nanoparticle films


Mobility as fuc. of diameter D:
Small D: steep rise
Large D: plateau/decrease
FET mobility in PbS and PbSe Nanoparticle films

1. Mobility as function of diameter D:
   - Small D: steep rise
   - Large D: plateau/decrease

Mobility low: \( \mu \approx 10^{-3} - 10^{-2} \) vs. 1000 \( \text{cm}^2/\text{Vs} \) for bulk Si

Hopping type see \( T \) dependence

M. Law group
FET mobility in PbS and PbSe NP films

2. Mobility as function of ligand length: Monotonic exponential decay

M. Law group
The charging energy, site energy disorder, and carrier mobility on different days over the course of several months. Channel dimensions: length and polydispersity of the samples. Many error bars are smaller than the data markers. Each marker represents the average of 6 blue markers. (c) The dependence of mobility on NC size. Arrows denote four NC samples of nearly equal energy disorder (indicated in Table 1), showing that mobility depends on NC size rather than the size distribution. Lines serve as guides to the eye. (d) Mobility plotted against site energy disorder (indicated in Table 1), emphasizing that mobility is independent of the site energy disorder. Strong effect at small disorder. Weak at large disorder.

M. Law group
Transcending QCD on device level: ab-initio-based hierarchical transport studies

Ab initio description of coupled NPs

Extraction of representative parameters

Hopping limit: Marcus, Miller-Abrahams
Band limit: Boltzmann transport

Kinetic Monte Carlo simulation of device transport
Marcus theory with ab initio parameters for nanostructures

\[
k_{\text{MJL}} = \frac{2\pi}{\hbar} |V_{DA}|^2 \sqrt{\frac{1}{4\pi k_B T \lambda_s}} \sum_{\nu=0}^{\infty} e^{-s} \frac{S^\nu}{\nu!}
\]

\[
\exp \left\{ - \frac{(\Delta G + \lambda_s + \nu \hbar \omega_{\text{eff}})^2}{4\lambda_s k_B T} \right\}
\]

\[
\mu = \frac{e}{k_B T} \frac{1}{2N} \frac{1}{r^2 k_{\text{EH}}}
\]


Individual nanostructures
Marcus theory with ab initio parameters for nanostructures

CdSe NPs, 5% size fluctation
two NPs coupled

Monte Carlo methods

ZnO nanocrystals
Continuous time random walk
Nearest neighbor hopping
Disorder effects

3x3x3 network
Large number of parameters

Monte Carlo methods

Si NPs in SiO$_2$

Hierarchical Transport Modeling: ab initio based Kinetic Monte Carlo

- I. Carbone, S. Carter and GTZ

- M. Voros, I. Carbone, S. Carter, G. Galli and GTZ
  in progress

Galli et al.
Hierarchical Transport Modeling: ab initio based Kinetic Monte Carlo

1. Define nanoparticle lattice

2. Ab initio description of nanoparticle energetics

3. Dynamics: Miller-Abrahams/Marcus thermally assisted hopping

4. Kinetic Monte Carlo simulation of device transport
1. Define nanoparticle lattice

1. Topology of lattice retained, only size disorder

2. Remove lattice, size and positional disorder

- PBC in x,y, conduction in z
- Nanoparticles enveloped by ligands
- Network can be infilled
1. Define nanoparticle lattice: Size disorder only

Fixed hopping distance „d”

Nanoparticle radius selected with Gaussian distribution

Always six nearest neighbors, packing density \( \rho = 0.52 \)

Closest packing of mono-disperse spheres is not the cubic but hexagonal close pack with 12 nearest neighbors: \( \rho = 0.74 \)
1. Define nanoparticle lattice: Size and positional disorder

PackLSD (collision driven molecular dynamics):

Generate disordered jammed packing,
density: $\rho=0.62-0.63$ (monodisperse max.: $\rho=0.634$)

2. Towards ab initio nanoparticle energetics

Input to transport: energy differences

\[ \Delta E_{ab} = \Delta E_{kin}^{ab} + \Delta E_{ab}^{C} + \Delta E_{ab}^{V} \]

- **Confined kinetic energy** (~\(1/R^2\))
  \[ \Delta E_{kin}^{ab} = E_{b}^{kin} - E_{a}^{kin} \]
- **Coulomb**
  \[ \Delta E_{ab}^{C} = \Sigma_{b} + n_{b}E_{b}^{e-e} - (\Sigma_{a} + (n_{a} - 1)E_{a}^{e-e}) + \frac{1}{2}V_{ab} \]
- **External field**
  \[ \Delta E_{ab}^{V} = q \frac{V}{L_{z}} (z_{b} - z_{a}) \]
- **Long range Coulomb interaction** (~\(1/d\))
- **On-site Coulomb** (~\(1/R\))
2. Towards ab initio nanoparticle energetics


Loading first charge

$$\Sigma(R) = \frac{q^2}{8\pi\varepsilon_0 R} \left( \frac{1}{\varepsilon_{\text{out}}} - \frac{1}{\varepsilon_{\text{in}}} \right) + 0.47 \frac{q^2}{4\pi\varepsilon_0 \varepsilon_{\text{in}} R} \left( \frac{\varepsilon_{\text{in}} - \varepsilon_{\text{out}}}{\varepsilon_{\text{in}} + \varepsilon_{\text{out}}} \right)$$

Loading additional charges $E^{\text{e-e}}(R) = \frac{q^2}{4\pi\varepsilon_0 R} \left( \frac{1}{\varepsilon_{\text{out}}} + 0.79 \frac{1}{\varepsilon_{\text{in}}} \right)$

Alt. 1: Configuration interaction from pseudopotentials

An, Franceschetti, Zunger, PRB 76, 045401 (2007)

Alt. 2: True ab initio: $GW$ using Density Functional Perturbation Theory

Galli group, PRB 85, 081101 (2012)
2. Towards ab initio nanoparticle energetics

1. Kinetic energy $E^{\text{kin}}$ Sophisticated k.p calculation


Site Energies $E_a$ and $E_b$ in Equation 2 are determined by the nanocrystal sizes assigned to each location in the simulation lattice. For the simulation of films of mean crystal size, $d_{\text{crystal}}$, we distribute the crystal sizes according to a Gaussian distribution of mean, $d_{\text{crystal}}$, and standard deviation, $s(d_{\text{crystal}})$. Colloidal nanocrystal size generally becomes more difficult to control as crystal size increases. 1,7,23 This is captured by using a standard deviation that increases with diameter:

$$s(d_{\text{crystal}}) = s_0 d_{\text{crystal}},$$

where $s_0$ is a parameter constant across all crystal sizes.

The site energies, given by the LUMO energy levels for electron carriers, and the HOMO levels for hole carriers, were calculated by Kang and Wise for a range of nanocrystal diameters. 3 We assign site energies to each site by adopting the Kang-Wise values corresponding to their designated sizes. Figure 3 shows the HOMO and LUMO levels used in our simulation.

Figure 3: HOMO and LUMO energies for PbSe used in hopping simulations. Values were calculated by Kang and Wise.

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\[ \text{HOMO LUMO Energies (meV)} \]

\[ \text{Diameter (nm)} \]
2. Towards ab initio nanoparticle energetics

2. On site charging energy $E^C$ from Configuration interaction with pseudopotentials

An, Franceschetti, Zunger, PRB 76, 045401 (2007)
3. Nearest neighbor Coulomb

4. Ewald summation for the long-range Coulomb portion

\[ V_{b}^{a} = \frac{q}{4\pi \epsilon_{\text{out}} \epsilon_{0}} \left[ \sum_{R} \frac{\text{erfc}(\beta |r_{ab} + R|)}{|r_{ab} + R|} + \frac{4\pi}{\Omega} \sum_{k \neq 0} \frac{1}{|k|^2} \exp\left(\frac{-|k|^2}{4\beta^2}\right) \cos(k.r_{ab}) \right] \]

Nanoparticle layer sandwiched between two semi infinite metallic electrodes: mirror images

new (neutral) unit cell: 2L
2. Electron-hole interaction

Solar photons generate electrons and holes

Account for electrons and holes in on-site and long-range Coulomb interaction

\[
\Delta E_{ab}^C = \Sigma_b + n_b E_{b}^{e-e} - (\Sigma_a + (n_a - 1) E_{a}^{e-e}) + \frac{1}{2} V_{ab}
\]

Analogous equation for holes

Lannoo, Delerue, Allan, PRL 74, 3415 (1995)
An, Franceschetti, Zunger, PRB 76, 045401 (2007)
3. Dynamics: Transition rates

Thermally activated nearest-neighbor hopping

**Miller–Abrahams: low \( T \) single phonon**

\[
\Gamma_{a\rightarrow b} = \Gamma_0 \exp(-2\beta \Delta x) \begin{cases} 
\exp\left(-\frac{E_b - E_a}{kT}\right) & (E_b > E_a), \\
1 & (E_b \leq E_a).
\end{cases}
\]

\[
\beta = \sqrt{\frac{2m^*(E_{vac} - E_{barrier})}{\hbar^2}}
\]

**Marcus: high \( T \) “multi phonon”/polaronic**

\[
\Gamma_{a\rightarrow b} = \frac{2\pi}{\hbar} |H_{ab}|^2 \frac{1}{\sqrt{4\pi \lambda_{ab} kT}} \exp\left(-\frac{(\lambda_{ab} + E_b - E_a)^2}{4\lambda_{ab} kT}\right)
\]

\[
|H_{ab}|^2 \approx |H_0|^2 \exp(-2\beta \Delta x)
\]

\( \lambda \): reorganization energy

\( H \): “electronic coupling”
3. Dynamics: Transition rates

Transition between Miller-Abrahams and Marcus can be in experimentally relevant $T$ range

Polymer system: Fishchuck et al, PRB 78 (2008)
3. Dynamics: Solving rate equations with Monte Carlo: BKL method

BKL: *J. of Comp. Phys.* 17, 10 (1975) [analogue to Gillespie, N-fold way, residence time]

1. Calculate all hopping rates $\Gamma_i$
2. Draw a uniform random number $r_1$
3. Identify hop $j$ for which:
   \[
   \sum_{i=1}^{j-1} \Gamma_i < r_1 \Gamma_{\text{sum}} < \sum_{i=j+1}^{N} \Gamma_i
   \]
   \[
   \sum \Gamma_i = \Gamma_{\text{sum}}
   \]
4. Execute hop $j$
5. Advance simulation time using second random number $r_2$
   \[
   \Delta t = -\frac{\ln r_2}{\Gamma_{\text{sum}}}
   \]
4. Kinetic Monte Carlo: Measuring the mobility

1. Execute iterations
2. Check that steady state has been achieved
3. Statistical analysis with re-blocking
4. Electron mobility in (cm$^2$/Vs):

\[ \mu_e = \frac{\text{harvested charges } \times Z}{t \times \text{total number of carriers } \times F_{\text{ext}}} \]
RESULTS: 1. Diameter dependence of $\mu$

Small D: steep rise
Large D: plateau/decrease

Exp: larger the diameter, harder to control the size distribution:
Possible $\sigma=0.1 \times$ diameter
RESULTS: Diameter dependence of $\mu$: Physics

Small D: steep rise
1. For increasing D less hops are enough to cross sample
2. $E^{\text{kin}}(D)$ less steep for increasing D, reduces energy disorder

Large D: plateau/decrease
As the electron density (#/unit volume) is kept constant, for increasing D the electron #/nanoparticle increases, causing increasing transport blockade by charging energy $E^C$

![Diagram showing HOMO and LUMO energies vs. Diameter (nm)]

![Diagram showing Charging Penalties vs. Diameter (nm)]
RESULTS: 2. Ligand length dependence of $\mu$

Longer the ligand, wider the hopping barrier, lower the mobility

- $\beta_e = 1.10 \text{ Å}^{-1}$
- $\beta_h = 1.08 \text{ Å}^{-1}$
RESULTS: 3. Size disorder dependence of $\mu$

Nanoparticle diameter = 5nm ± spread
Exponential decrease of $\mu$ with spread

$\mu$ decreases in simulation, increases in experiment
RESULTS: 4. Electron-hole effects

Relevance of FET mobilities for solar cells?
Simulated equal electron and hole densities.

**Small D**: Electron-hole binding slows transport

**Larger D**: electron-hole attraction reduces charging barrier, boosts transport

![Graph showing electron mobility with and without holes vs diameter](image-url)
Developed hierarchical ab initio-based Kinetic Monte Carlo

Reproduced NP diameter dependence of mobility, explained physics of non-monotonic diameter dependence

Reproduced ligand length dependence of mobility

Called attention to electron-hole correlation effects

Disorder dependence requires further analysis

Framework for extensive method developments established