Hierarchical Transport Modeling in Nanoparticle Solar Cells

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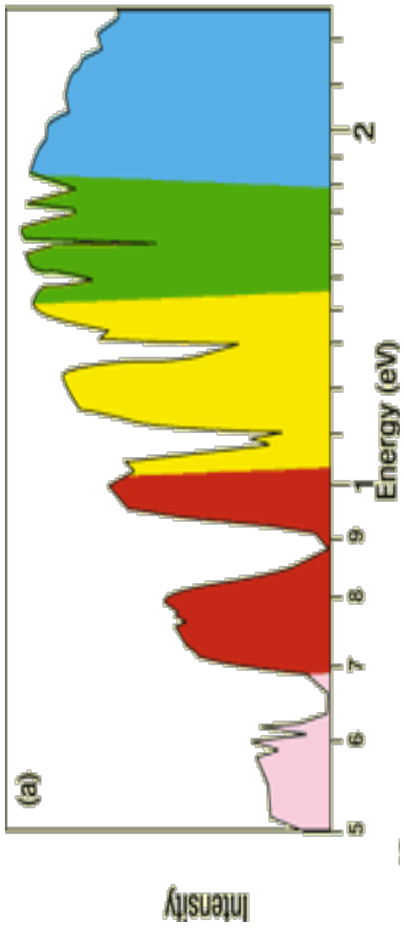
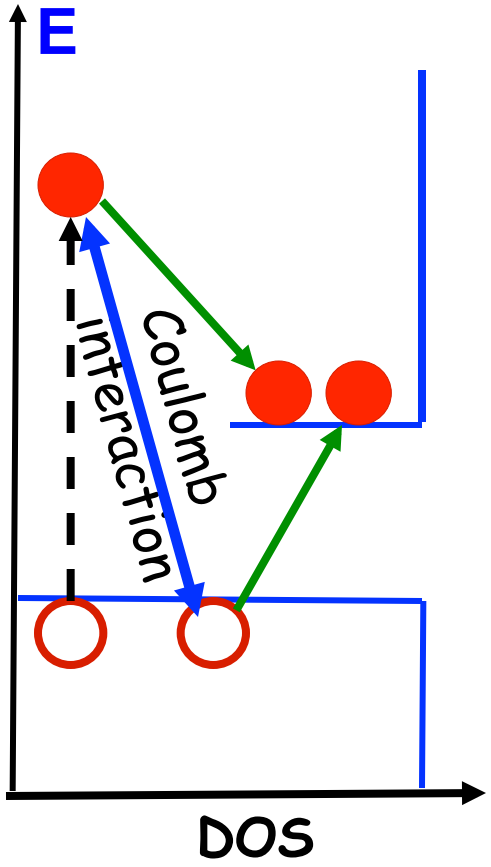
To improve conversion efficiency: Relaxation by excitons





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:

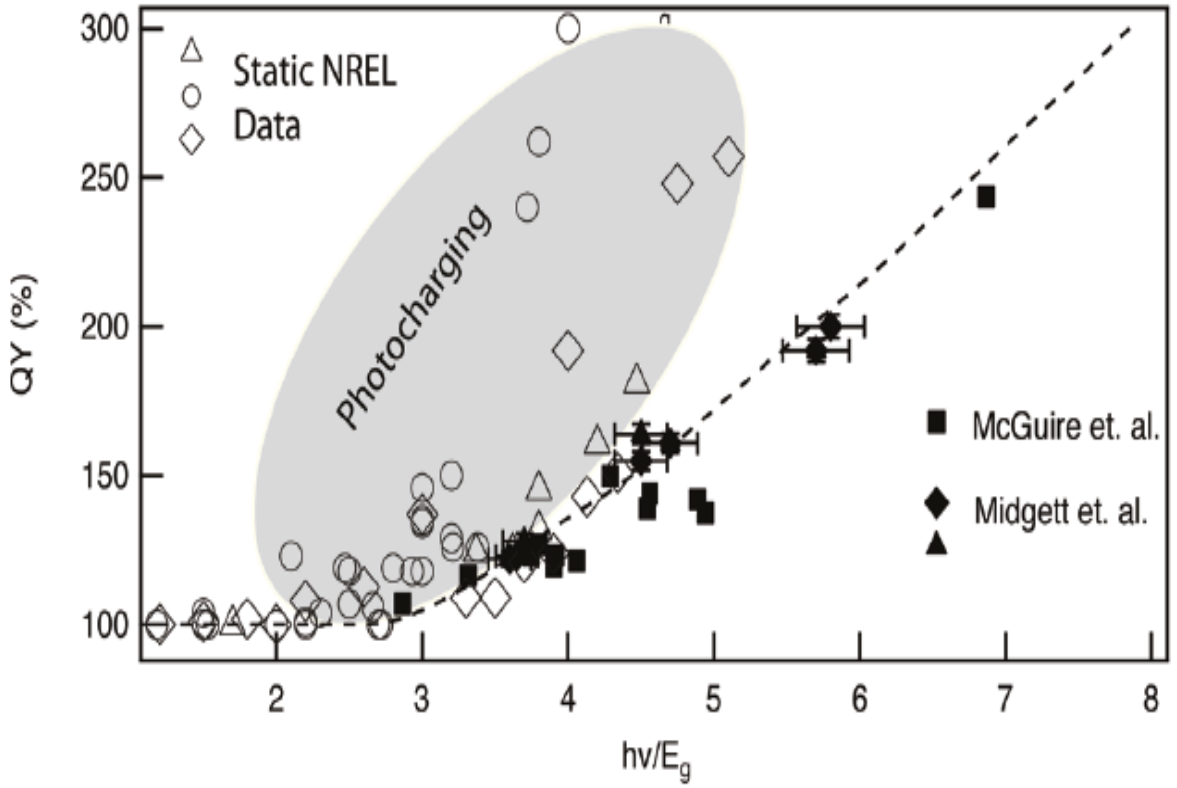
"We're going to need a bigger Coulomb interaction"

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)

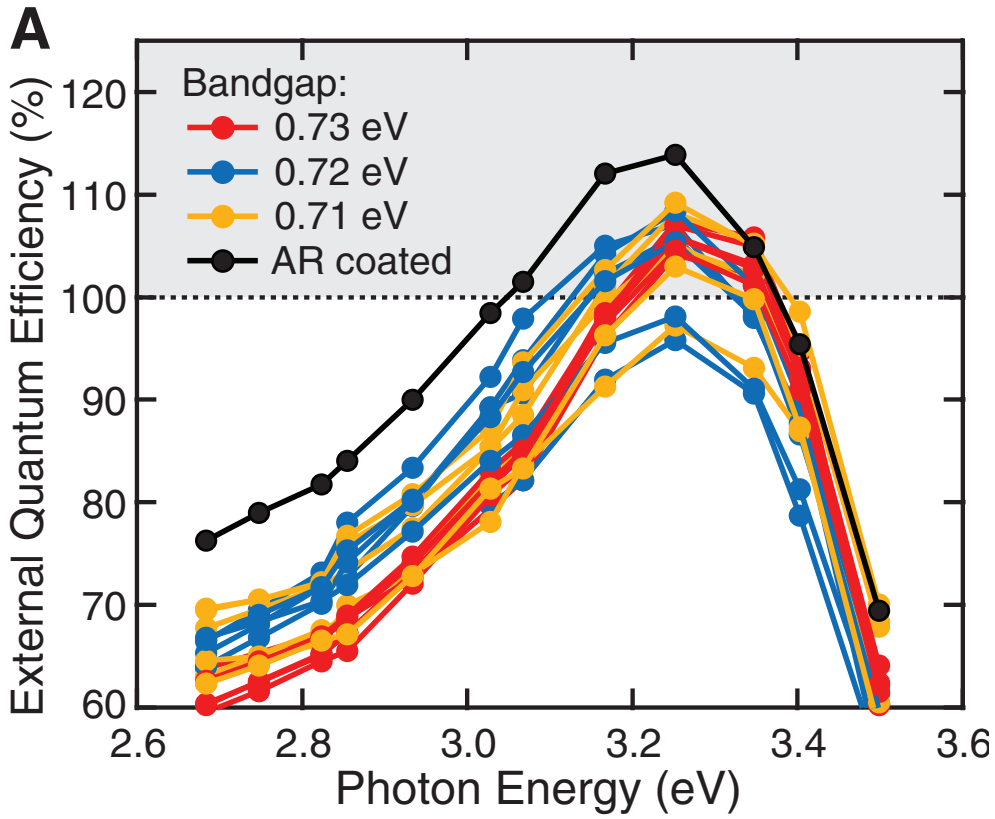
MEG is certainly present in NPs, even after charging is removed



MEG first implemented in working solar cell: Dec. 2011

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

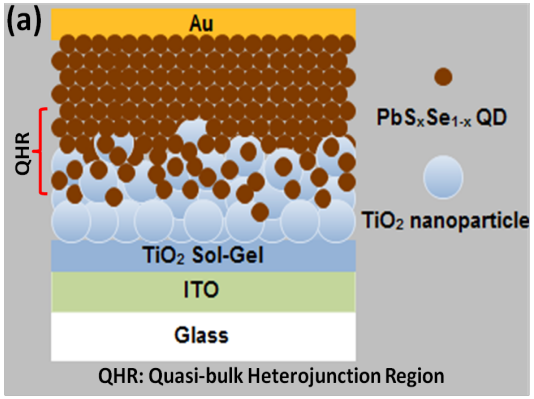
Octavi E. Semonin,[1,2] Joseph M. Luther,[1] Sukgeun Choi,[1] Hsiang-Yu Chen,[1] Jianbo Gao,[1,3] Arthur J. Nozik,[1,4]* Matthew C. Beard[1]*

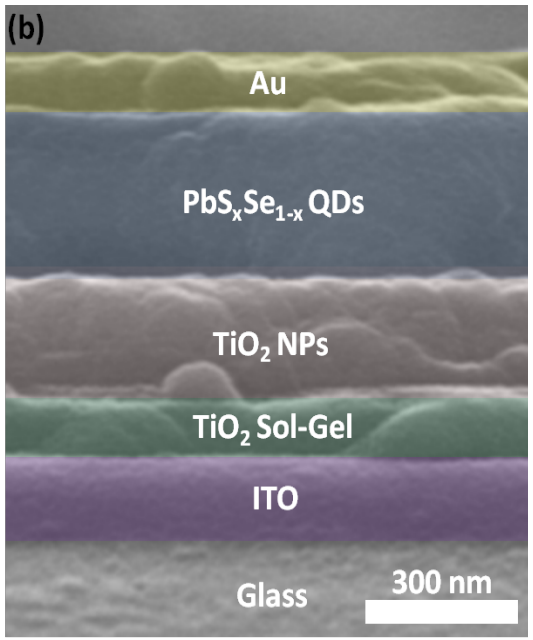


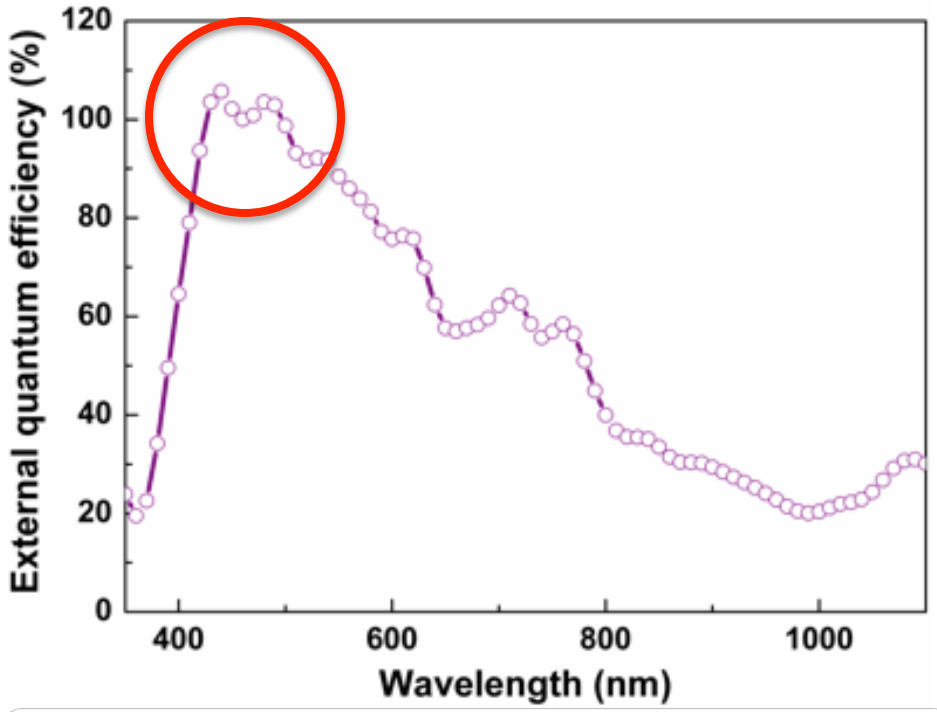
EQE > 100%:

Good

MEG implemented in working solar cell, II.







Carter lab: EQE>100%

Optimized cell performance by varying the composition PbS_xSe_{1-x}

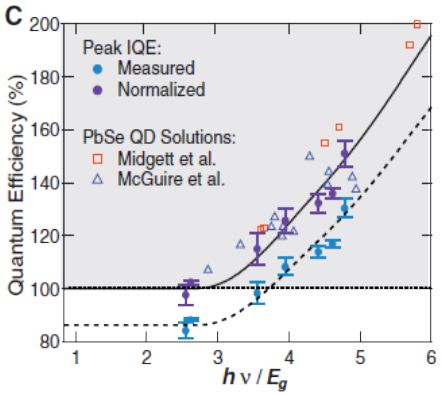
The Quantum Confinement Dilemma (QCD) in Nanostructured Solar Cells

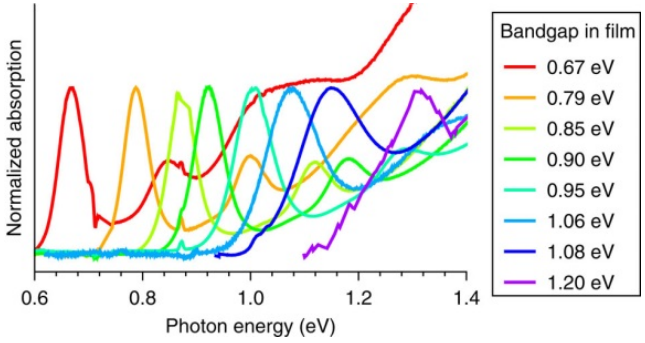
Quantum Confinement Dilemma

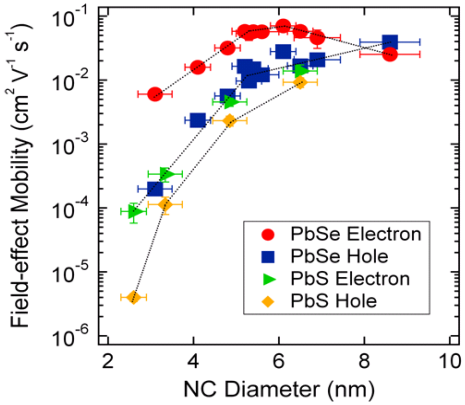
Enhances Coulomb interaction: Enhances MEG

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
Voros et al, Phys. Rev. B87, 155402 (2013)

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

3. Si nanoparticles with high-pressure low gap core structures
Wippermann et al, Phys. Rev. Lett. 110, 046804 (2013)

In collaboration with Stefan Wippermann, Marton Vörös, Adam Gali, Dario Rocca, and Giulia Galli

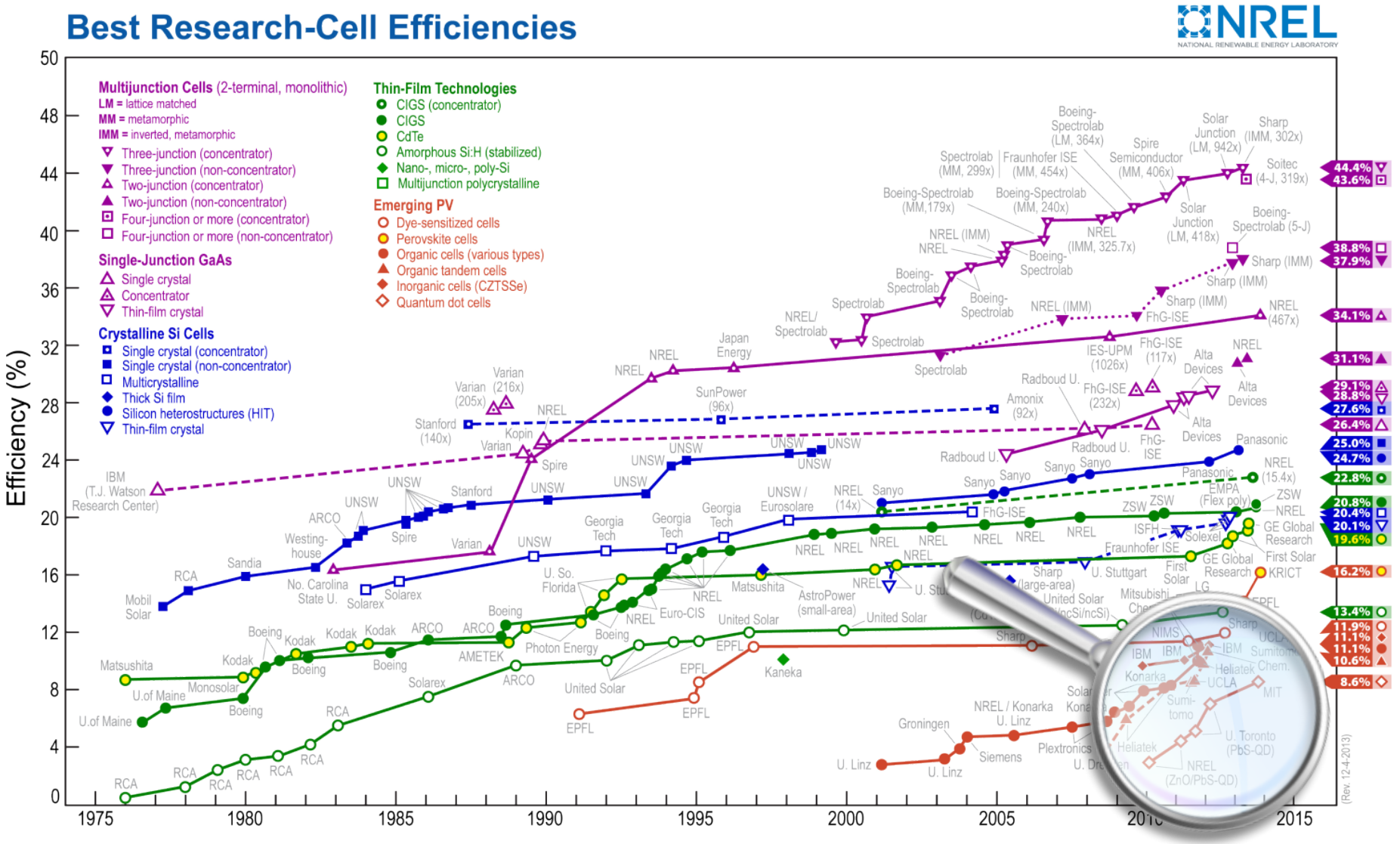
Transcending QCD: Transport boosting strategies

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)

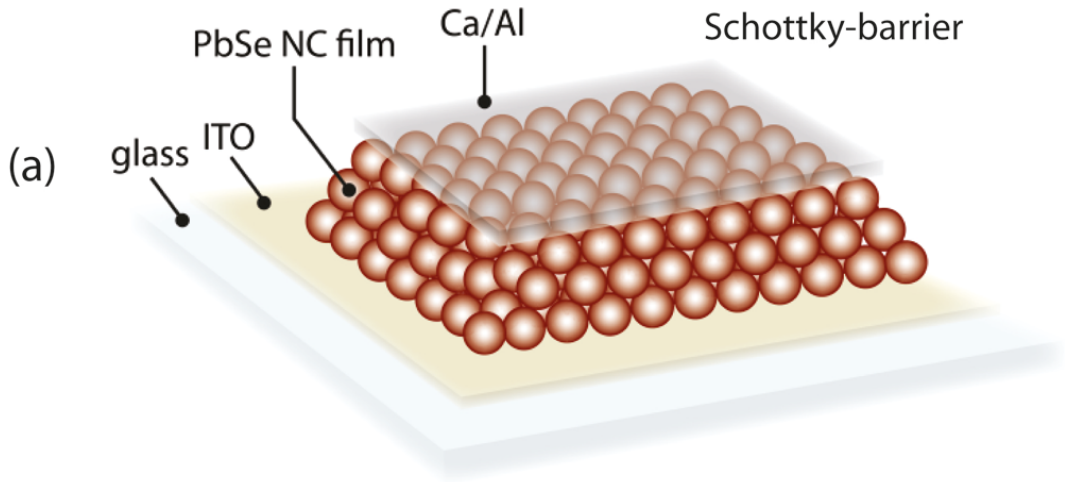
TALK OF STEFAN WIPPERMANN
M24.00003, Wednesday 12.03

In collaboration with Stefan Wippermann, Marton Vörös, Adam Gali, Francois Gygi, Dario Rocca, and Giulia Galli

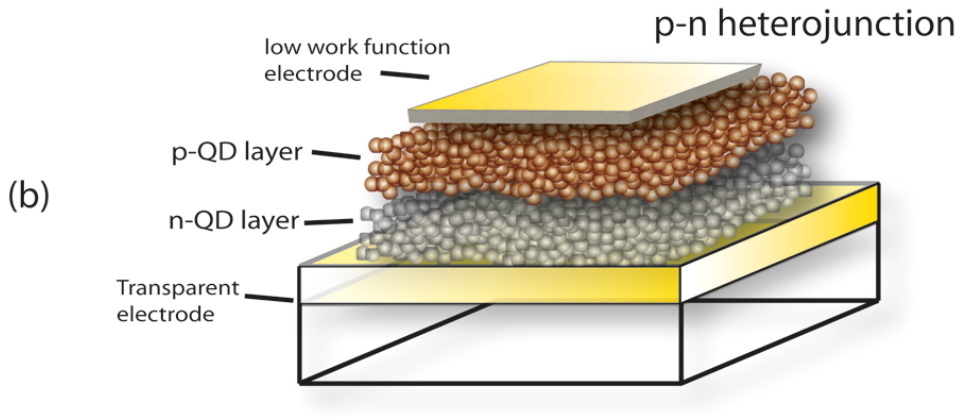
Nanoparticle solar cells appeared on the NREL efficiency chart



Nanoparticle solar cells

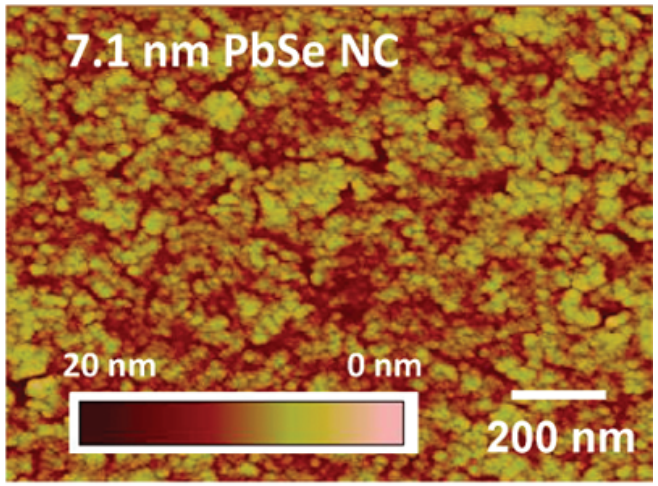


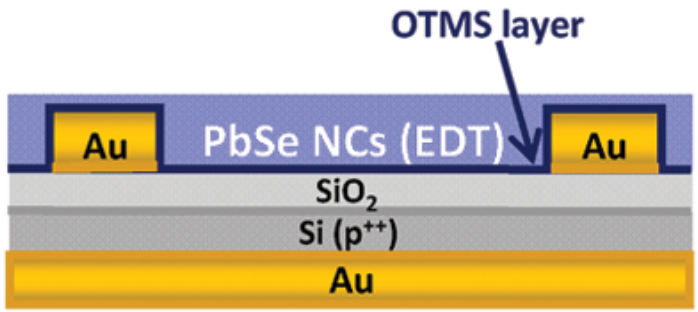
Built-in field generated by difference in electrode work functions



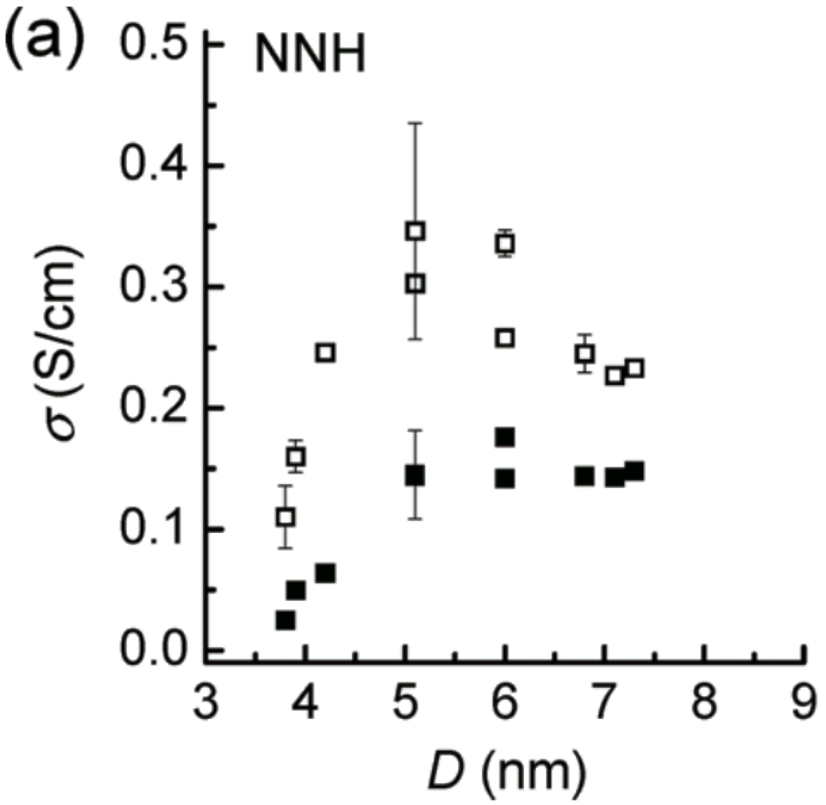
Built-in field generated by forming p- and n-doped nanoparticle layers

FET mobility in PbSe Nanoparticle films



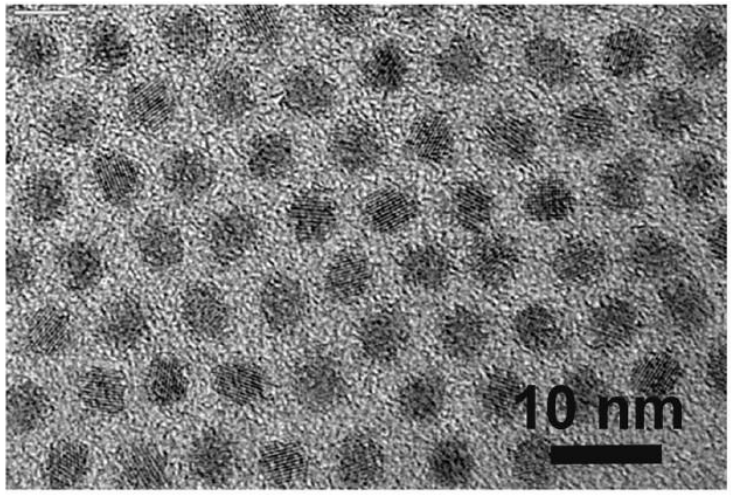


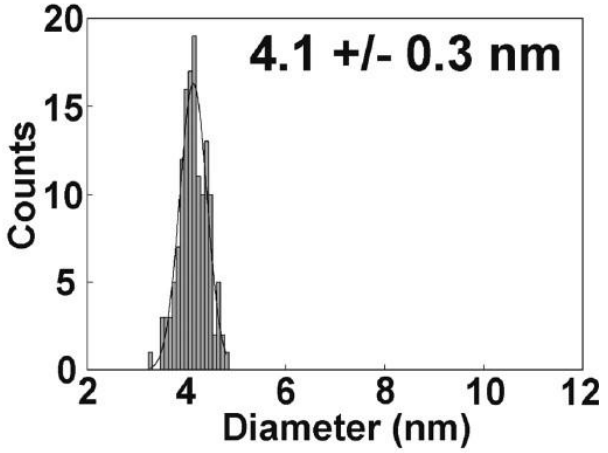
Kang, et al. Nano Lett. **11**, 3887 (2011)



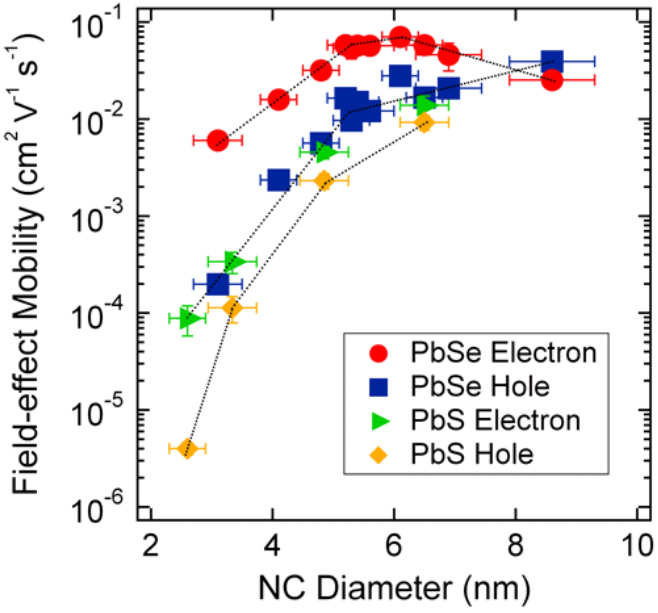
Mobility as fc. of diameter D:
Small D: steep rise
Large D: plateau/decrease

FET mobility in PbS and PbSe Nanoparticle films





M. Law group
Nano Lett.,
10, 1960 (2010)

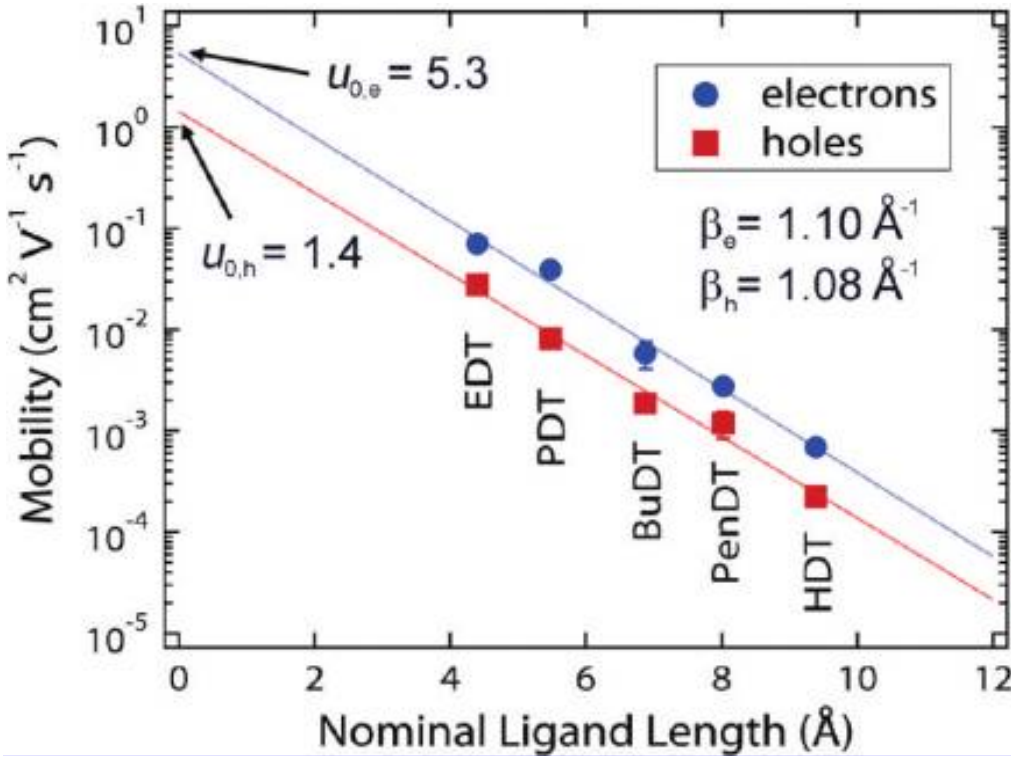


1. Mobility as fc. of diameter D:
Small D: steep rise
Large D: plateau/decrease

Mobility low: μ~10^{-3}-10^{-2} vs. 1000 cm^2/Vs for bulk Si

Hopping type seeT dependence

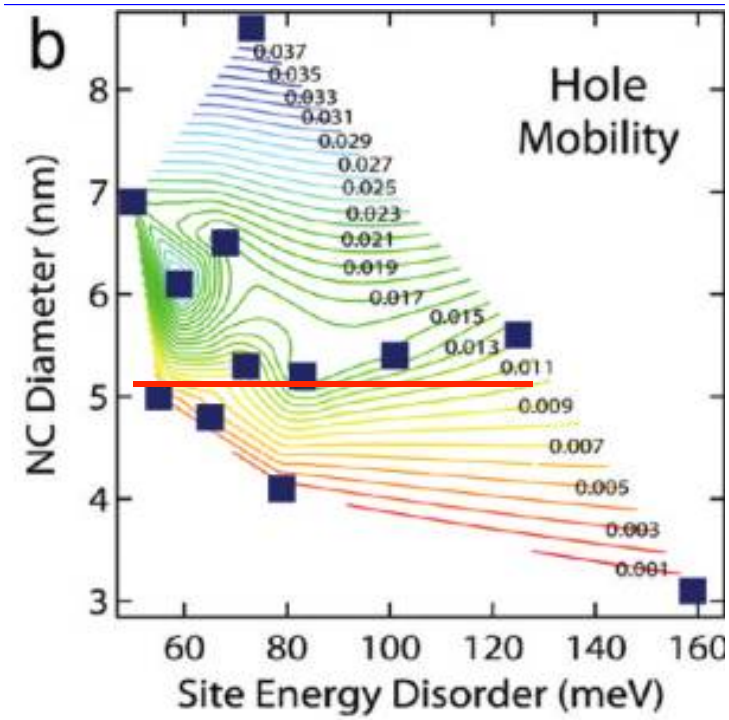
FET mobility in PbS and PbSe NP films

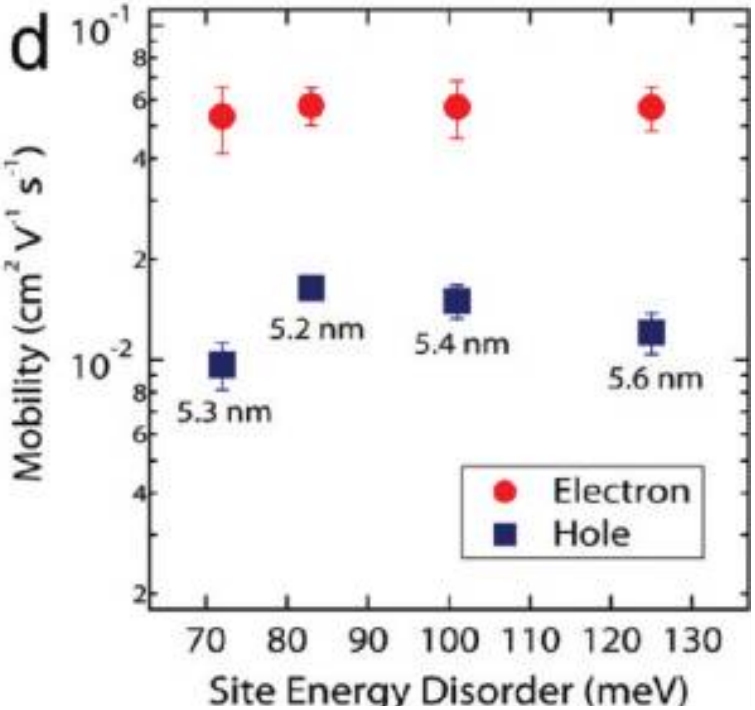


2. Mobility as funtion of ligand length: Monotonic exponential decay

M. Law group
Nano Lett.,
10, 1960 (2010)

FET mobility in PbS and PbSe NP films

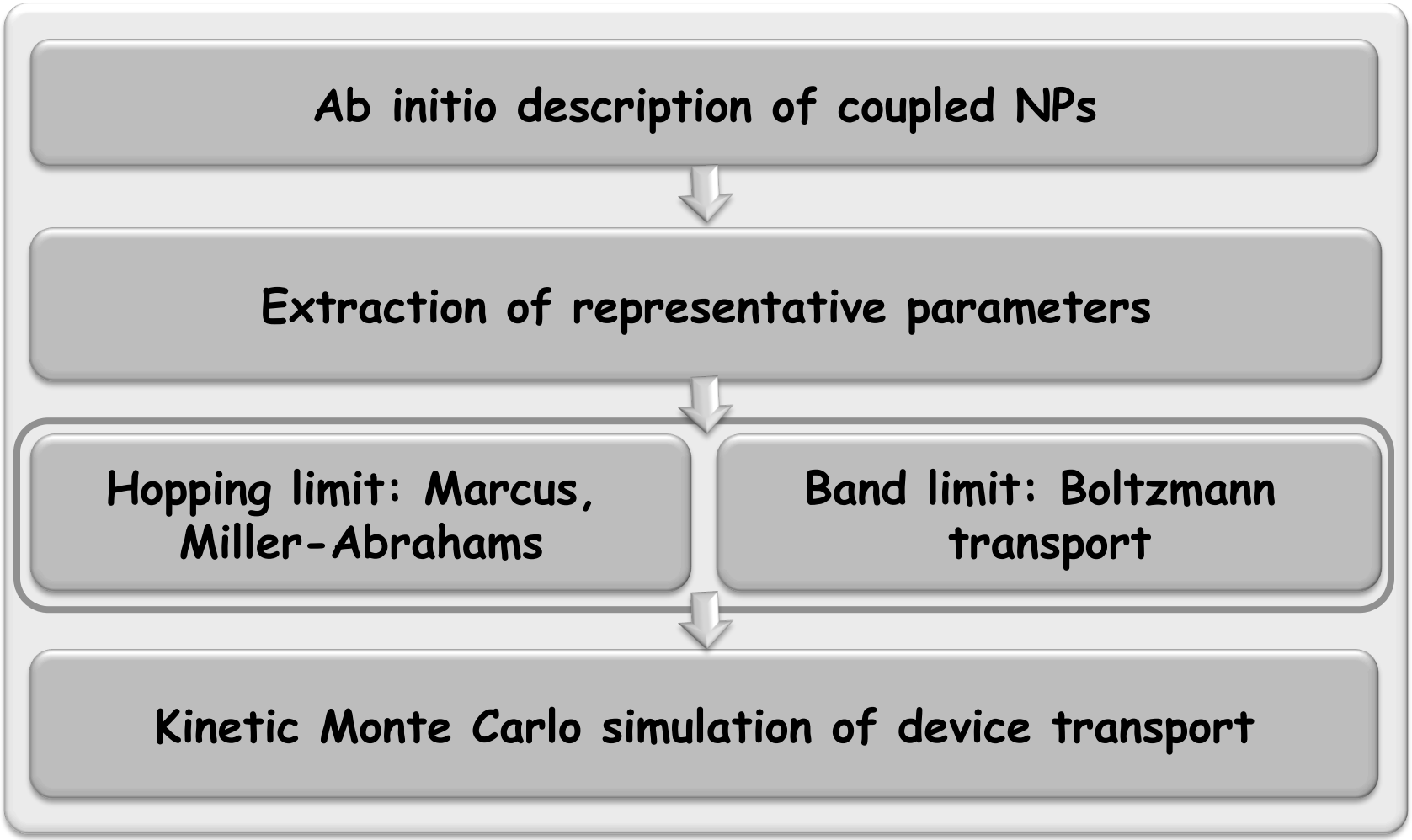




3. Mobility as function of disorder:
Strong effect at small disorder
Weak at large disorder

M. Law group
Nano Lett.,
10, 1960 (2010)

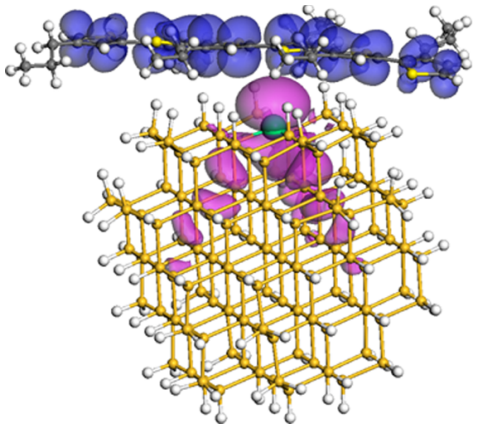
Transcending QCD on device level: ab-initio-based hierarchical transport studies

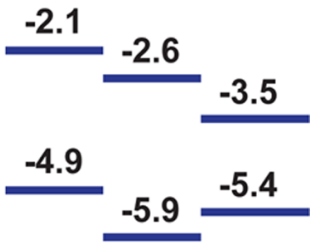


Marcus theory with ab initio parameters for nanostructures

$$k_{\mathrm{MJL}} = \frac{2\pi}{\hbar}|V_{\mathrm{DA}}|^2 \sqrt{\frac{1}{4\pi k_{\mathrm{B}} T \lambda_s}} \sum_{\nu=0}^{\infty} \mathrm{e}^{-S} \frac{S^{\nu}}{\nu!}$$

$$\exp\left\{-\frac{(\Delta G + \lambda_s + \nu\hbar\omega_{\mathrm{eff}})^2}{4\lambda_s k_{\mathrm{B}} T}\right\}$$





$$\mu = \frac{e}{k_{\mathrm{B}} T} \frac{1}{2N} r^2 k_{\mathrm{EH}}$$

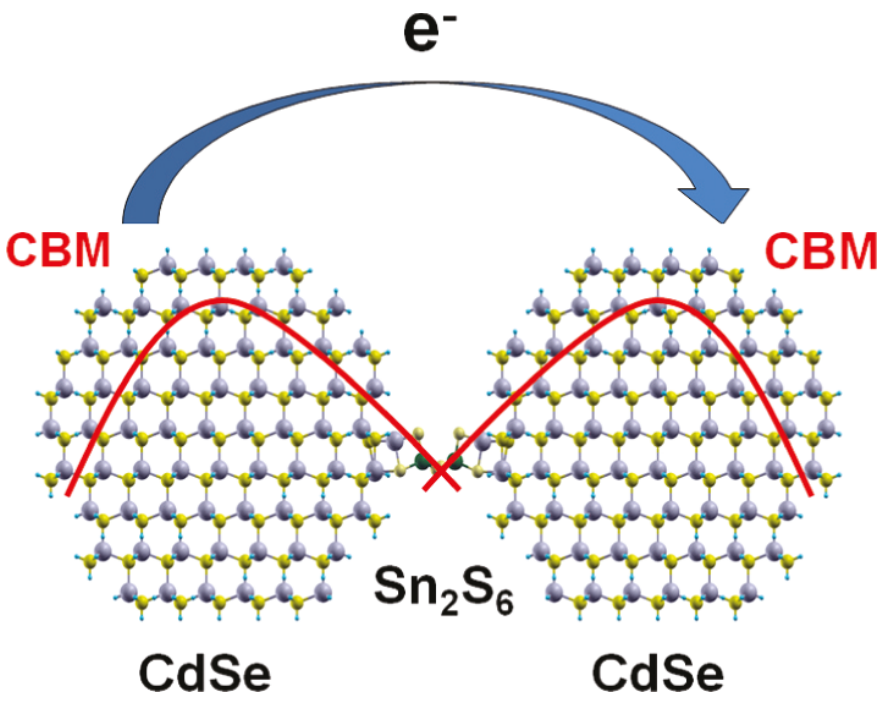
H. Li, Z. Wu, M. Lusk, J. Phys. Chem. C **18**, 46 (2014)

Liu et al., J. Phys. Chem. C **115**, 240 (2011) for organic systems

Individual nanostructures

Marcus theory with ab initio parameters for nanostructures

CdSe NPs,
5% size fluctation
two NPs coupled

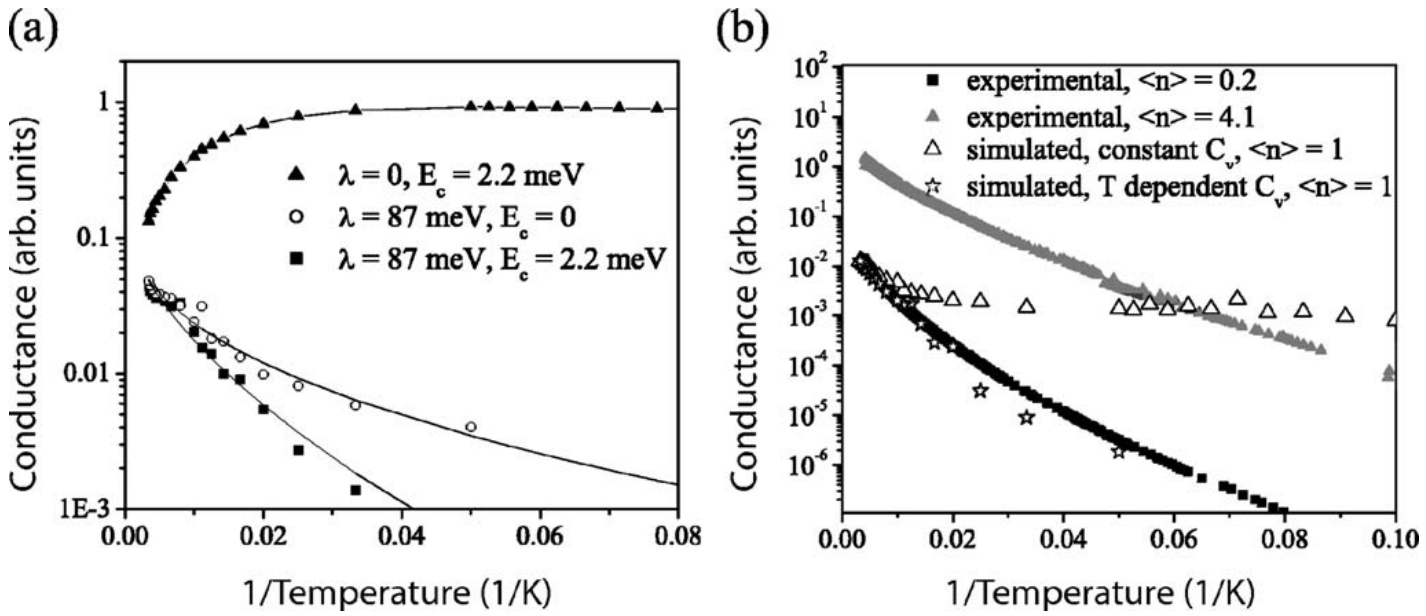


Iek-Heng Chu et al., J. Phys. Chem. C **115**, 21409 (2011)

Monte Carlo methods

ZnO nanocrystals
Continuous time random walk
Nearest neighbor hopping
Disorder effects

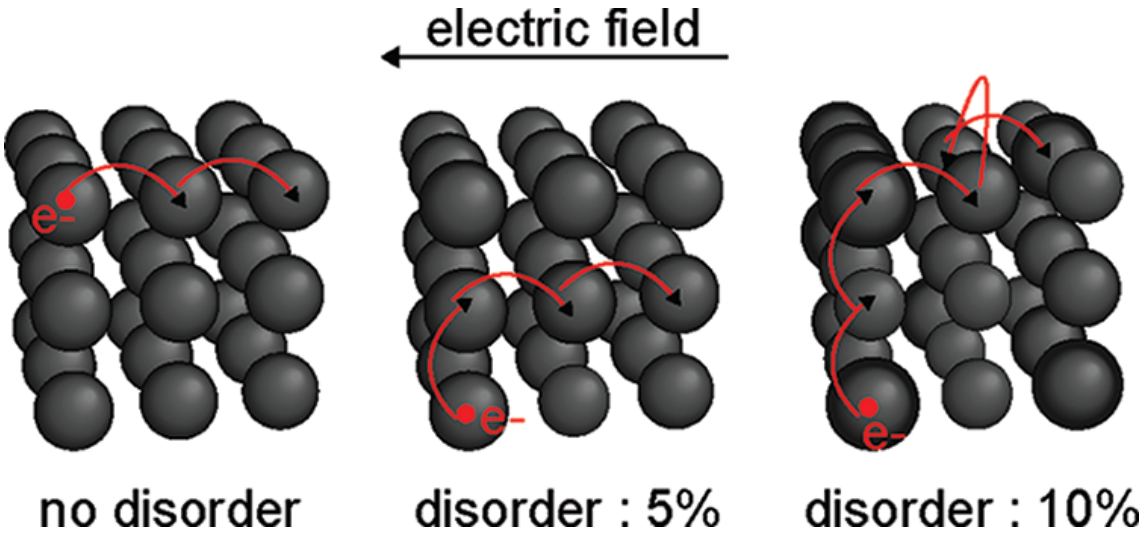
3x3x3 network
Large number of parameters

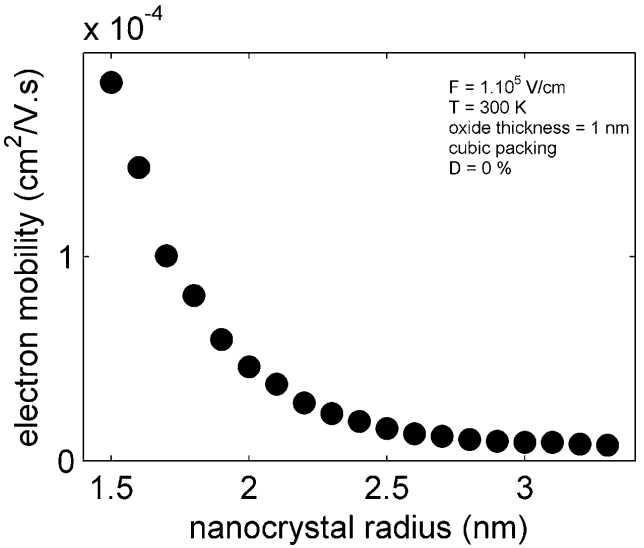


Chandler & Nelson Phys. Rev. B **75**, 085325 (2007)

Monte Carlo methods

Si NPs in SiO_2



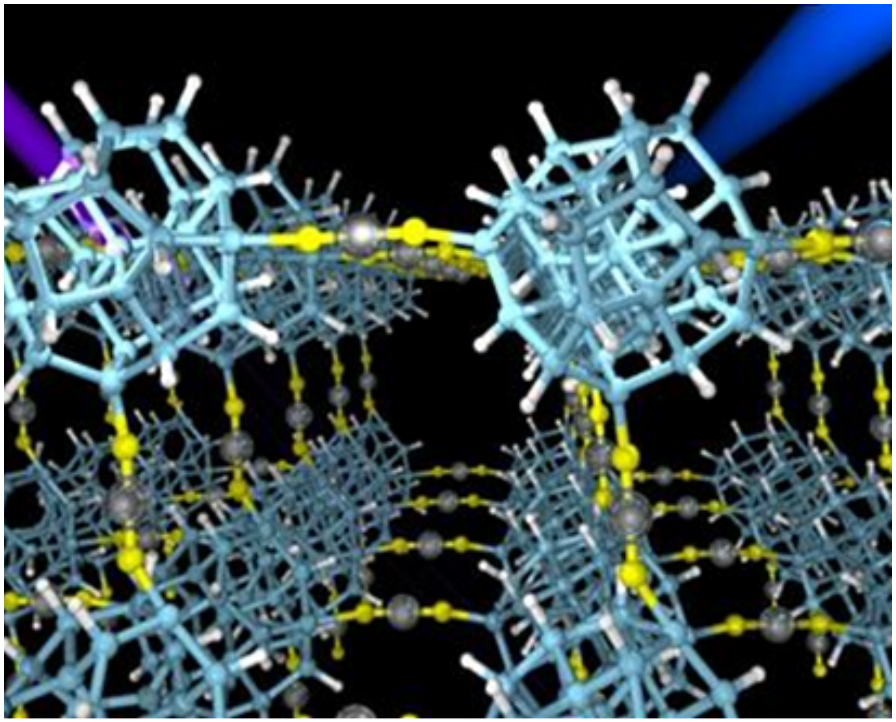


Hadrien Lepage et al., J. Phys. Chem. C **116**, 10873 (2012)

Hierarchical Transport Modeling: ab initio based Kinetic Monte Carlo

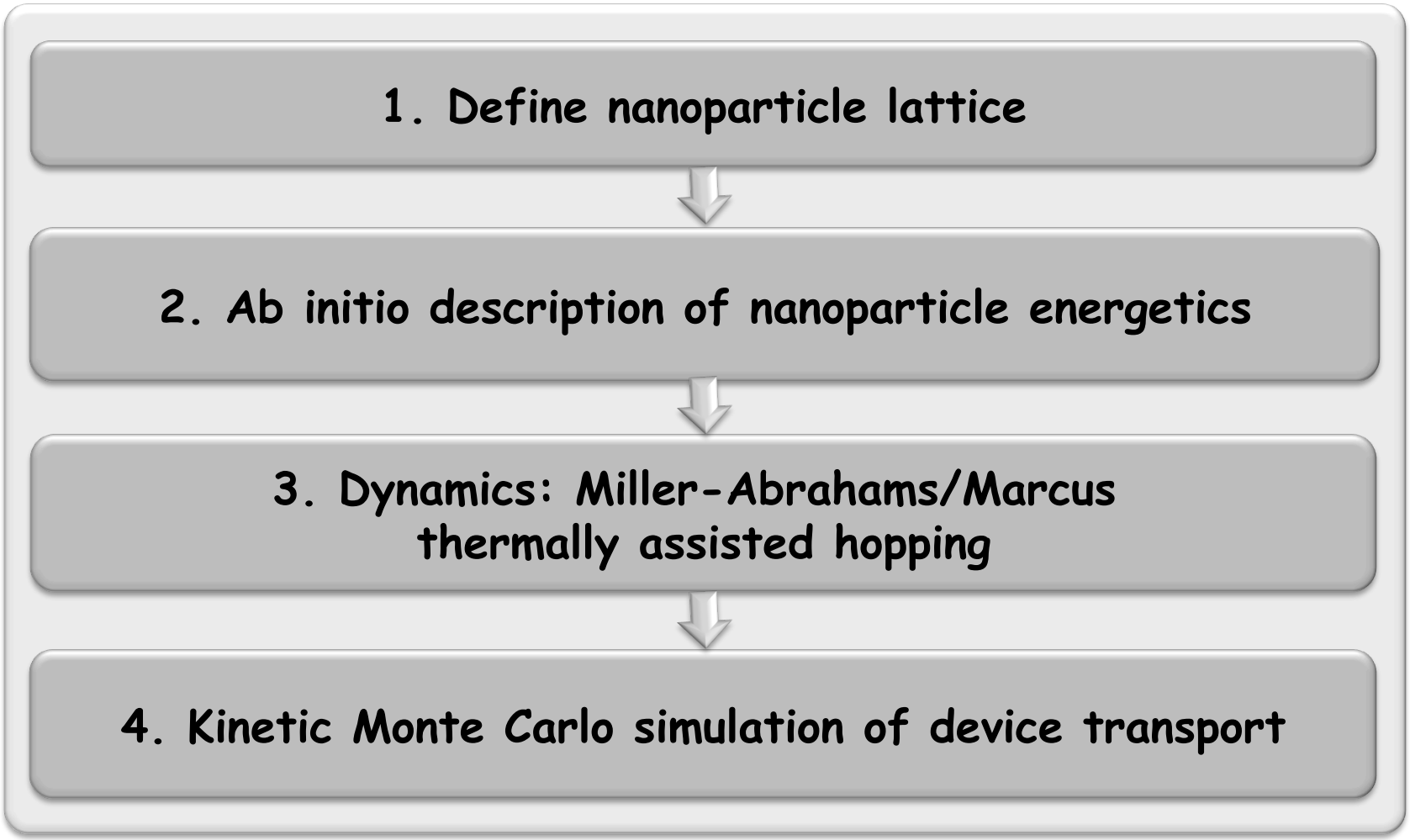
- I. Carbone, S. Carter and GTZ
  J. Appl. Phys. 114, 193709 (2013)

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



Galli et al.

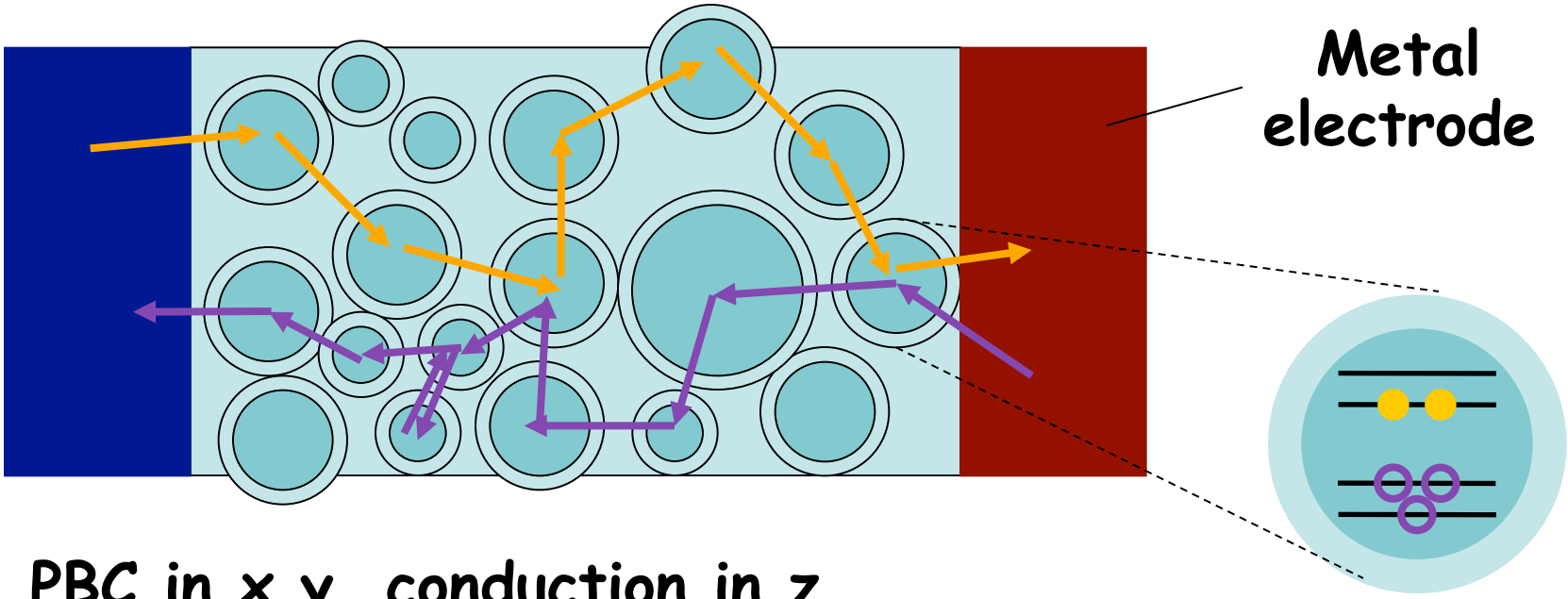
Hierarchical Transport Modeling: ab initio based Kinetic Monte Carlo



1. Define nanoparticle lattice

1. Topology of lattice retained, only size disorder

2. Remove lattice, size and positional disorder



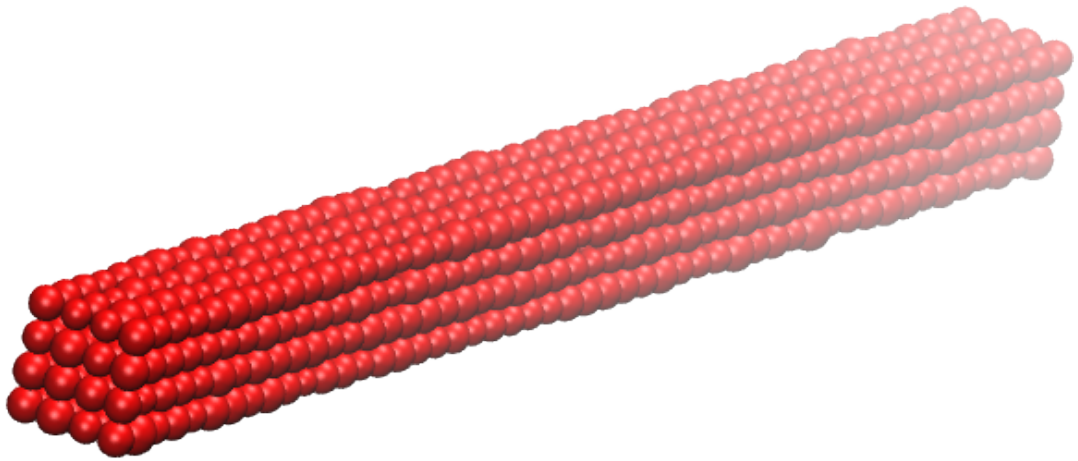
- PBC in x,y, conduction in z
- Nanoparticles enveloped by ligands
- Network can be infilled

1. Define nanoparticle lattice: Size disorder only

Fixed hopping distance „d"

Nanoparticle radius selected with Gaussian distribution

Always six nearest neighbors, packing density ~ ρ=0.52



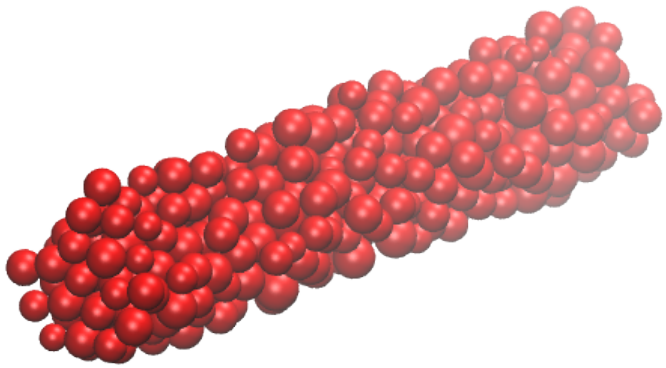
Closest packing of mono-disperse spheres is not the cubic but hexagonal close pack with 12 nearest neighbors: ρ=0.74

1. Define nanoparticle lattice: Size and positional disorder

PackLSD (collision driven molecular dynamics):

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

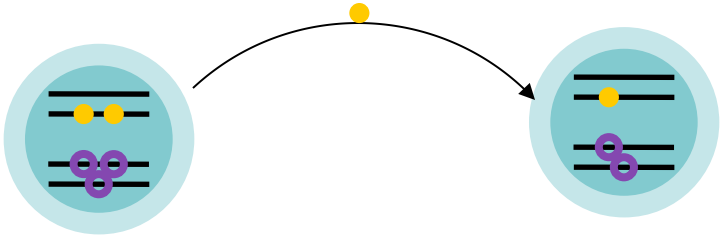
A. Donev, F. H. Stillinger, and S. Torquato, J. Comp. Phys, 202: 737 (2005)



2. Towards ab initio nanoparticle energetics

Input to transport: energy differences

n_a before
n_a-1 after



n_b before
n_b+1 after

$$\Delta E_{ab} = \Delta E^{kin}_{ab} + \Delta E^{C}_{ab} + \Delta E^{V}_{ab}$$

Confined kinetic energy (~1/R²)

$$\Delta E^{kin}_{ab} = E^{kin}_{b} - E^{kin}_{a}$$

Long range Coulomb interaction (~1/d)

Coulomb

$$\Delta E^{C}_{ab} = \Sigma_b + n_b E^{e-e}_{b} - (\Sigma_a + (n_a - 1)E^{e-e}_{a}) + \frac{1}{2}V_{ab}$$

External field

$$\Delta E^{V}_{ab} = q\frac{V}{L_z}(z_b - z_a)$$

On-site Coulomb (~1/R)

2. Towards ab initio nanoparticle energetics

1. Kinetic energy E^{kin} Kang and Wise J. Opt. Soc. Am. B, **14**, 1632 (1997)

2. On-site Coulomb E^{C} self-polarization Lannoo, Delerue, Allan, PRL **74**, 3415 (1995)

Loading first charge

$$\Sigma(R) = \frac{q^2}{8\pi\epsilon_0 R}\left(\frac{1}{\epsilon_{out}} - \frac{1}{\epsilon_{in}}\right) + 0.47\frac{q^2}{4\pi\epsilon_0\epsilon_{in}R}\left(\frac{\epsilon_{in}-\epsilon_{out}}{\epsilon_{in}+\epsilon_{out}}\right)$$

Loading additional charges $E^{e-e}(R) = \frac{q^2}{4\pi\epsilon_0 R}\left(\frac{1}{\epsilon_{out}} + 0.79\frac{1}{\epsilon_{in}}\right)$

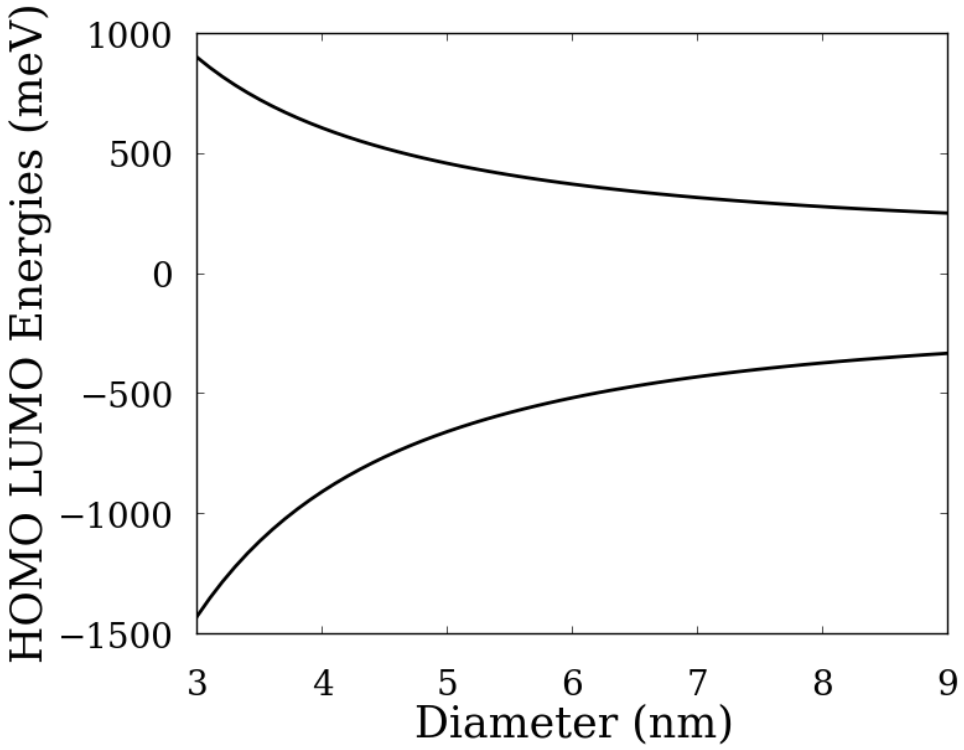
Alt. 1: Configuration interaction from pseudopotentials
An, Franceschetti, Zunger, PRB 76, 045401 (2007)

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^{kin} Sophisticated k.p calculation

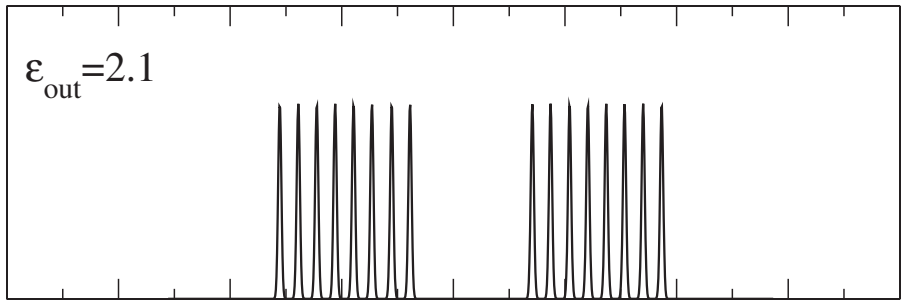
Kang and Wise **J. Opt. Soc. Am. B, 14**, 1632 (1997)

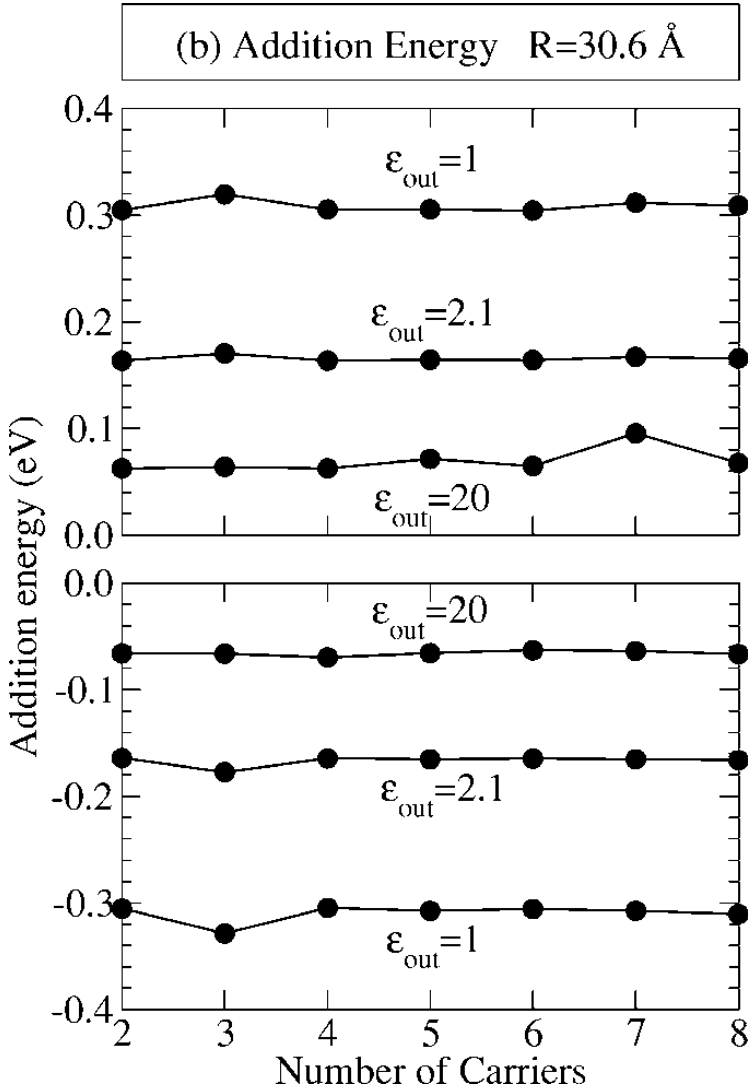


2. Towards ab initio nanoparticle energetics

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

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





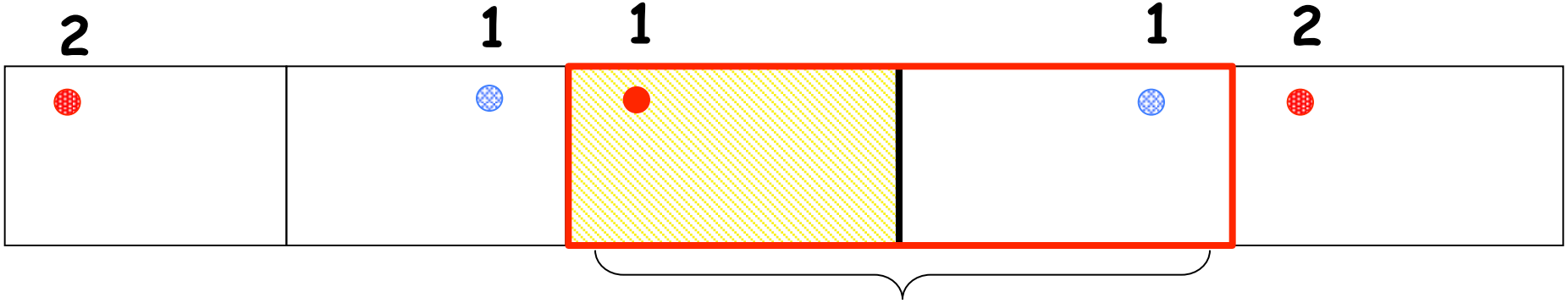
2. Coulomb energetics

3. Nearest neighbor Coulomb

4. Ewald summation for the long-range Coulomb portion

$$V_b^a = \frac{q}{4\pi\epsilon_{out}\epsilon_0}\left[\sum_R \frac{\mathrm{erfc}(\beta|r_{ab}+R|)}{|r_{ab}+R|} + \frac{4\pi}{\Omega}\sum_{k\neq 0}\frac{1}{|k|^2}\exp(\frac{-|k|^2}{4\beta^2})\cos(k.r_{ab})\right]$$

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



2. Electron-hole interaction

Solar photons generate electrons and holes

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

$$\Delta E^C_{ab} = \Sigma_b + n_b E^{e-e}_b - (\Sigma_a + (n_a - 1)E^{e-e}_a) + \frac{1}{2}V_{ab}$$
$$-n^{\mathrm{exc}}_b E^{e-h}_b + n^{\mathrm{exc}}_a E^{e-h}_a$$

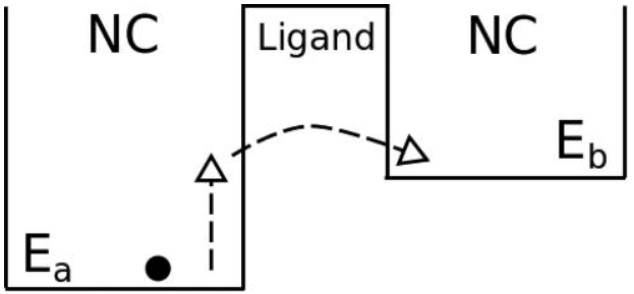
Now including holes

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

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

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

Marcus: high T "multi phonon"/polaronic

$$\Gamma_{a\to b} = \frac{2\pi}{\hbar}|H_{ab}|^2 \frac{1}{\sqrt{4\pi\lambda_{ab}kT}} \exp -\frac{(\lambda_{ab} + E_b - E_a)^2}{4\lambda_{ab}kT}$$

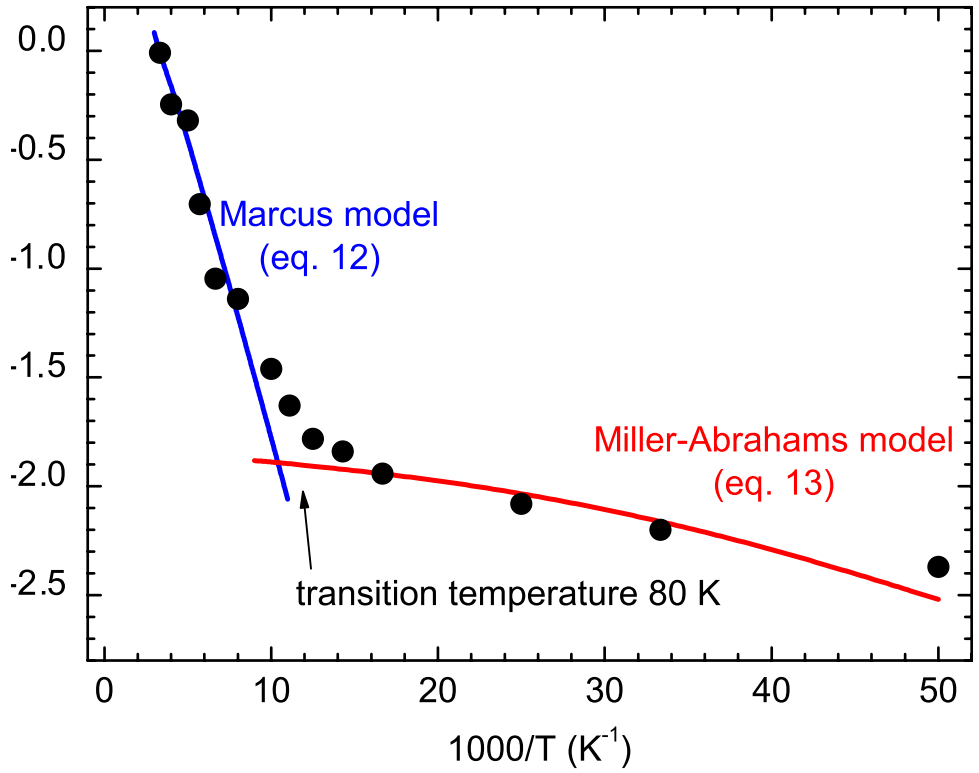
$$|H_{ab}|^2 \approx |H_0|^2 \exp(-2\beta\Delta x)$$

λ: 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]

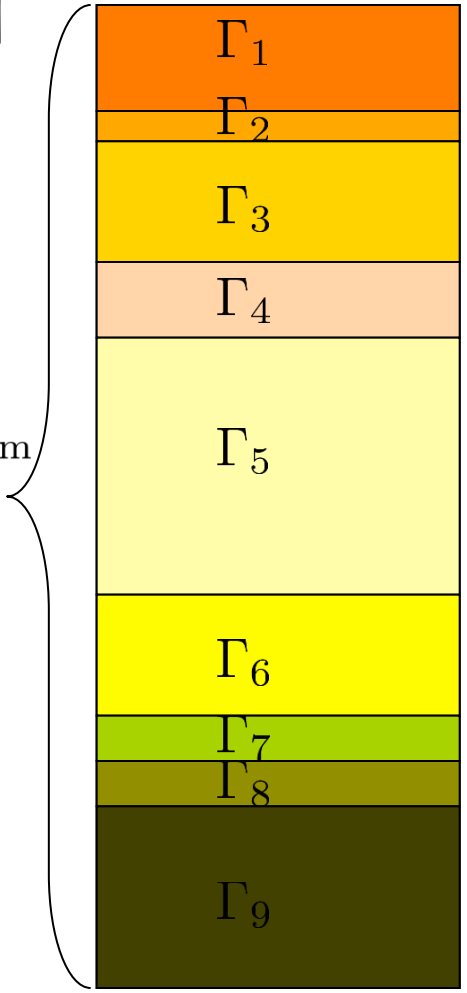
1. Calculate all hopping rates Γ_i
2. Draw a uniform random number r_1
3. Identify hop j for which:

$$\sum_{i=1}^{j-1} \Gamma_i < r_1 \Gamma_{\text{sum}} < \sum_{i=j+1}^{N} \Gamma_i$$

4. Execute hop j
5. Advance simulation time using second random number r_2

$$\Delta t = -\frac{\ln r_2}{\Gamma_{\text{sum}}}$$

$$\sum \Gamma_i = \Gamma_{\text{sum}}$$

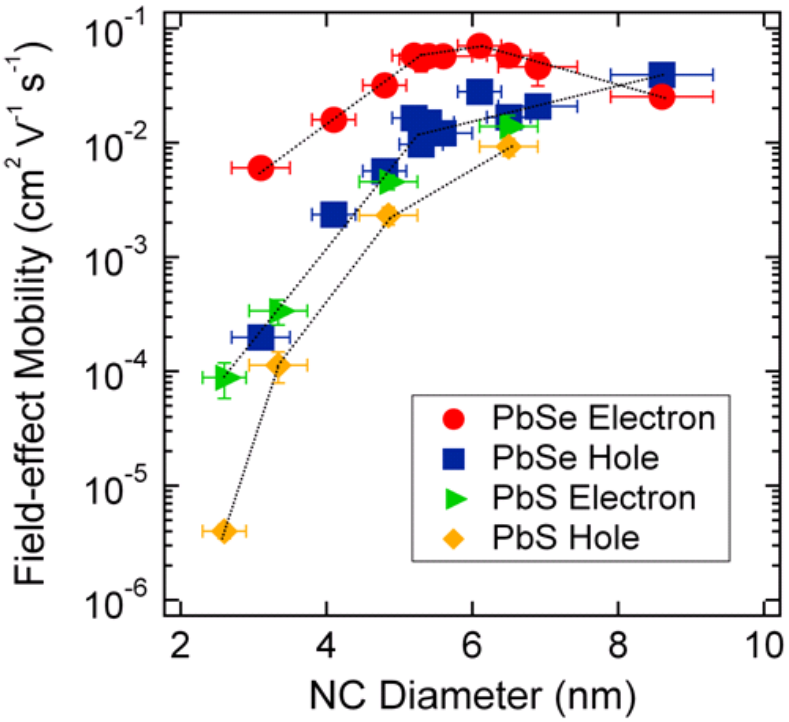


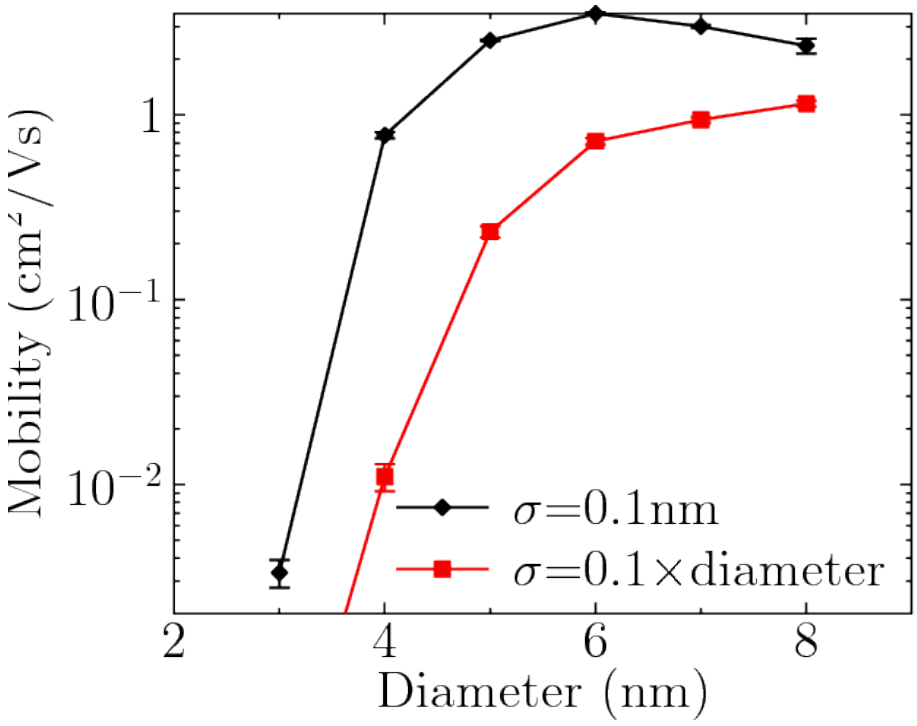
4. Kinetic Monte Carlo: Measuring the mobility

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

$$\mu_e = \frac{\text{harvested charges} \times Z}{\text{t} \times \text{total number of carriers} \times F_{\text{ext}}}$$

RESULTS: 1.Diameter dependence of μ





Small D: steep rise

Large D: plateau/decrease

Exp: larger the diameter,
harder to control the size distribution:
Possible σ=0.1*diameter

RESULTS: 1.Diameter dependence of μ: Physics

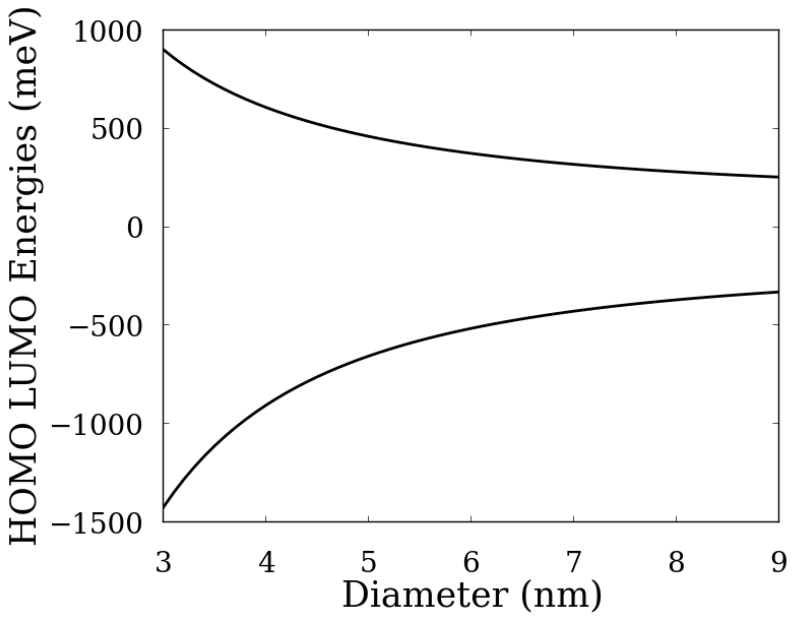
Small D: steep rise

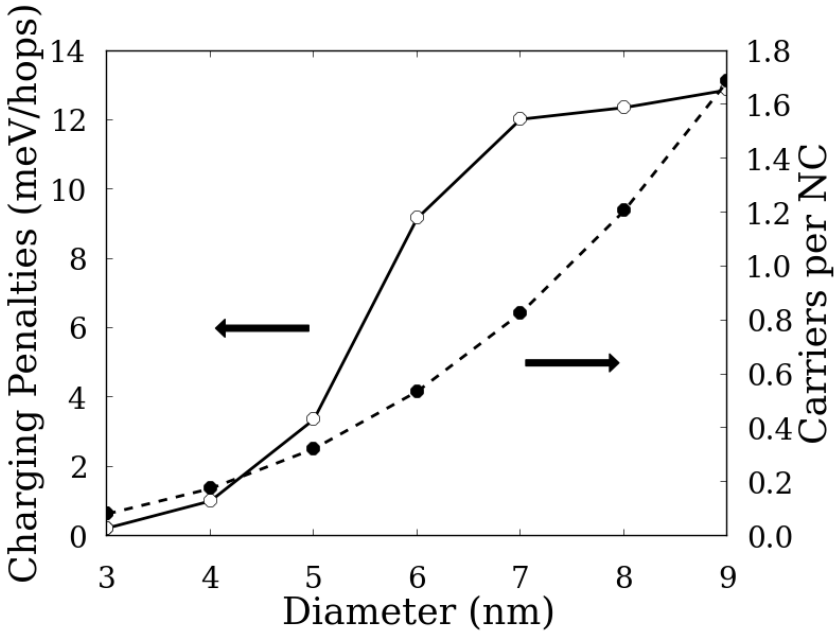
1. For increasing D less hops are enough to cross sample

2. $E^{kin}(D)$ less steep for increasing D, reduces energy disorder

Large D: plateau/decrease

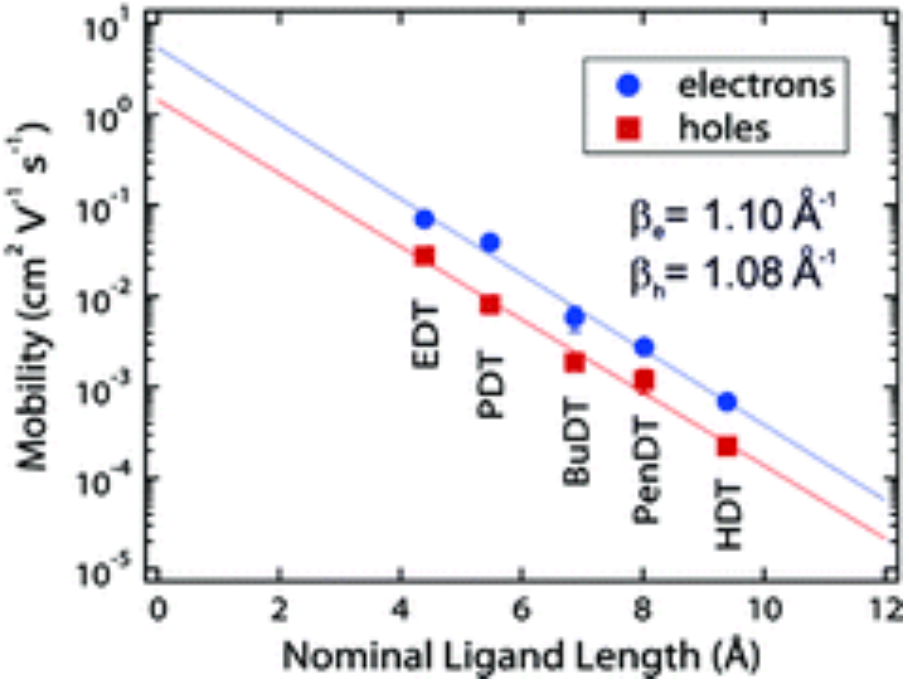
As the electron density (#/unit volume) is kept constant, for increasing D the electron #/ nanoparticle increases, causing increasing transport blockade by charging energy E^C

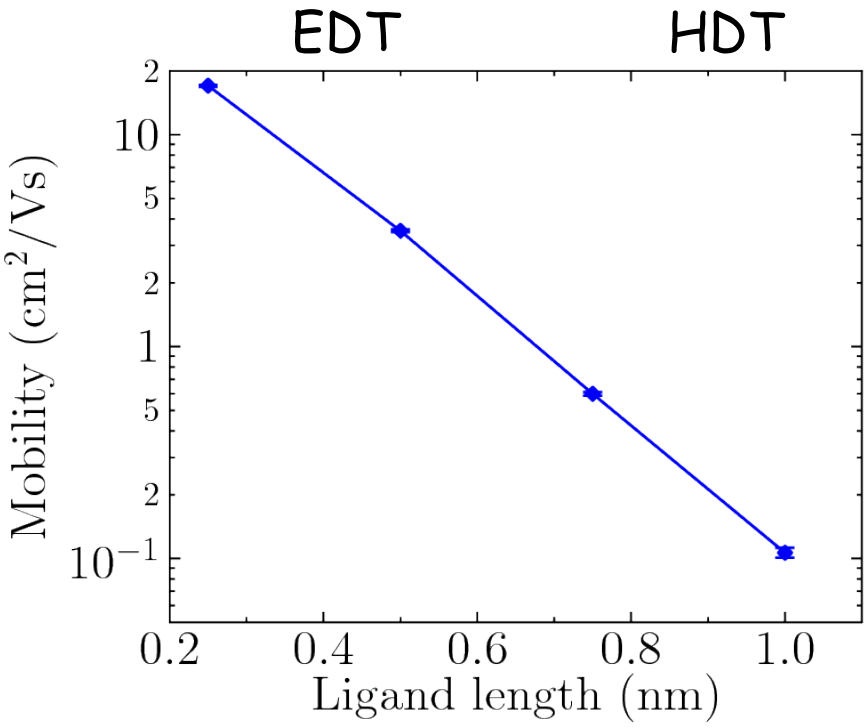




RESULTS: 2. Ligand length dependence of μ

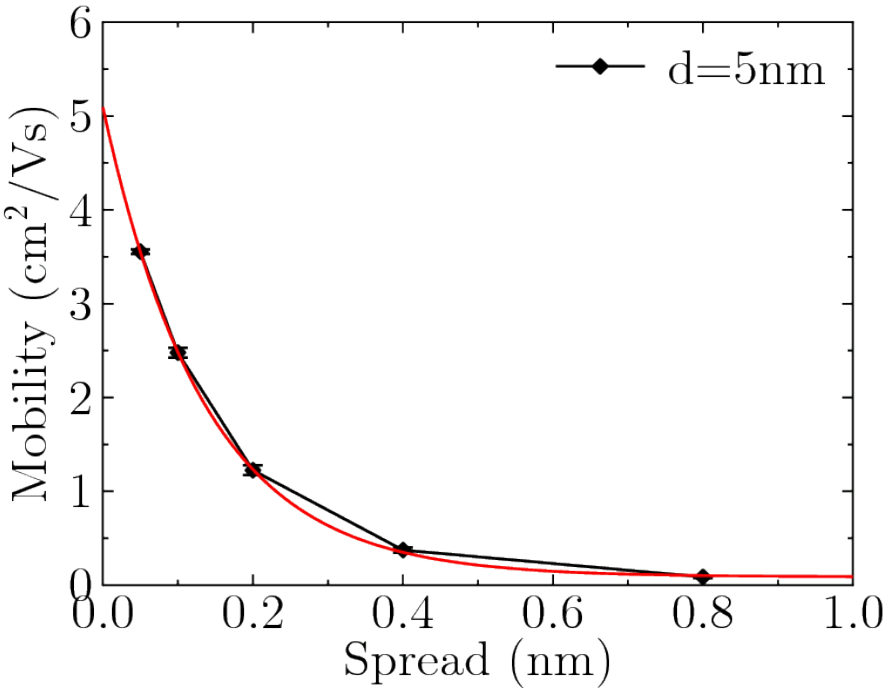
Longer the ligand, wider the hopping barrier, lower the mobility

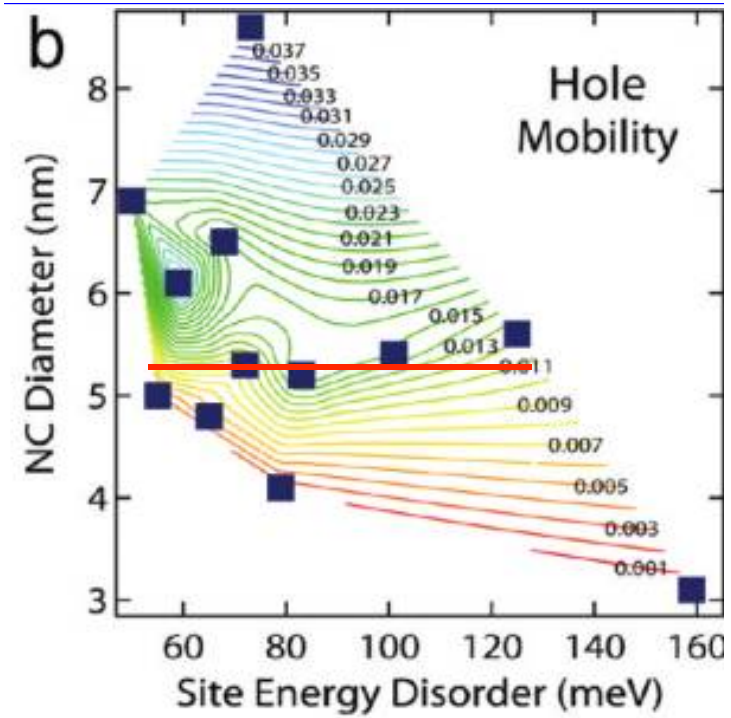




RESULTS: 3. Size disorder dependence of μ

Nanoparticle diameter=5nm±spread
Exponential decrease of μ with spread

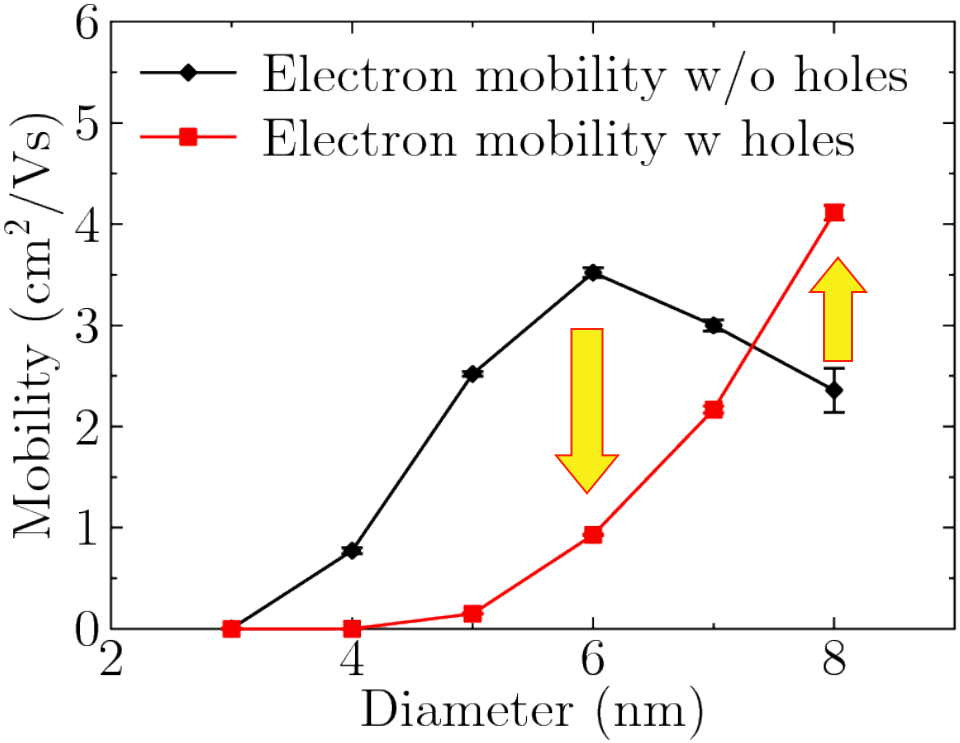




μ decreases in simulation, **increases in experiment**

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



SUMMARY

- 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