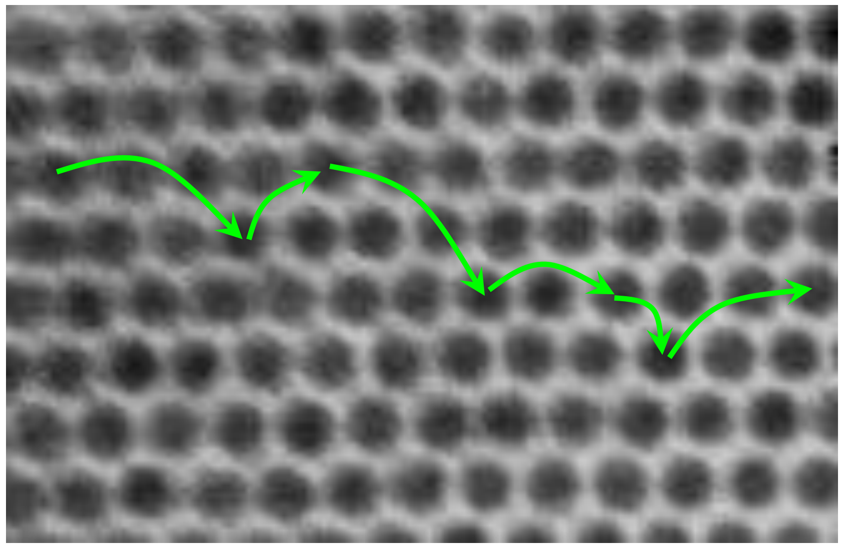
Theory of Hopping Transport in Arrays of Doped Semiconductor Nanocrystals



Brian Skinner, Tianran Chen, and B. I. Shklovskii
Fine Theoretical Physics Institute
University of Minnesota

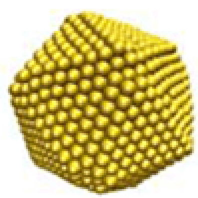
14 June 2013

UMN MRSEC

Ingredients in the design of NC arrays

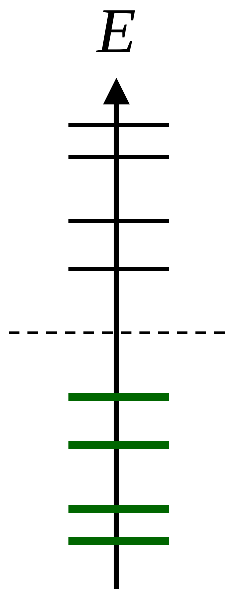
In NC arrays, an interplay between individual and collective properties

Energy spectrum of individual NCs

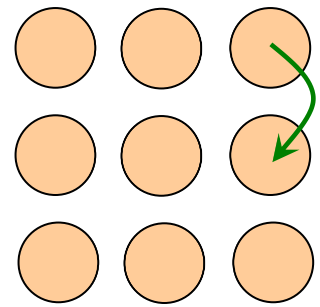


Tuned by:

- composition
- size
- shape
- surface
- magnetism
- superconductivity



Tunneling amplitude between NCs



Tuned by:

- spacing
- insulator material
- super-crystallinity

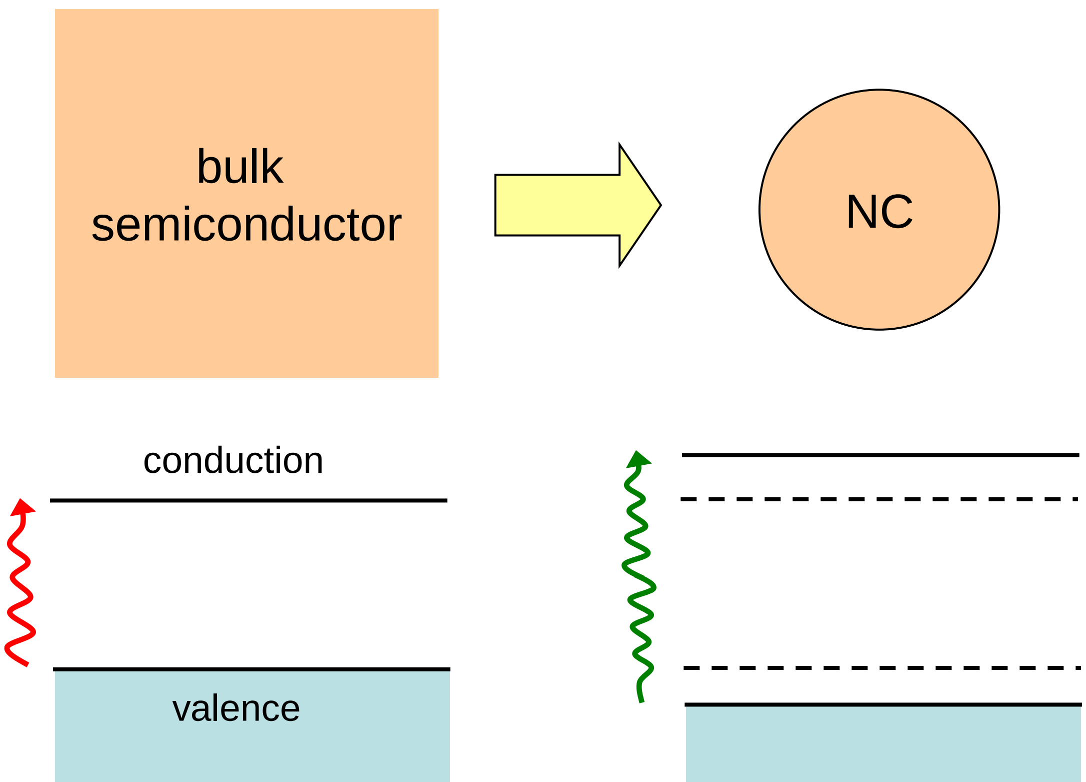
Overall doping level

Disorder

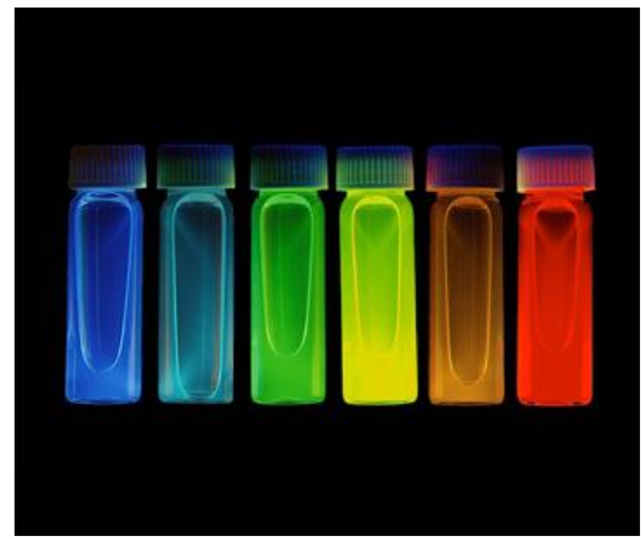
This interplay is reflected in the *T*-dependent conductivity.

Quantum confinement

For semiconductors, quantum confinement affects the spectrum when $D \lesssim a_B = 4\pi\varepsilon\hbar^2/m^* e^2$

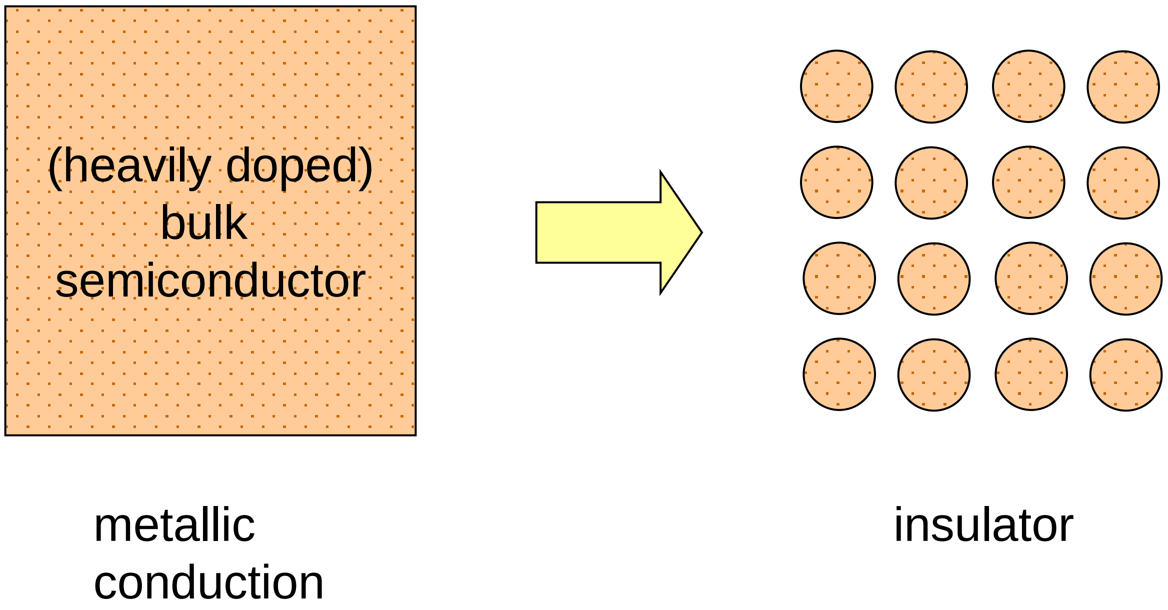


CdSe NCs, $D = 2\ \mathrm{nm} - 8\ \mathrm{nm}$ ($a_B \approx 5\ \mathrm{nm}$)



[Bawendi group, MIT]

Heavily doped and heavily insulating

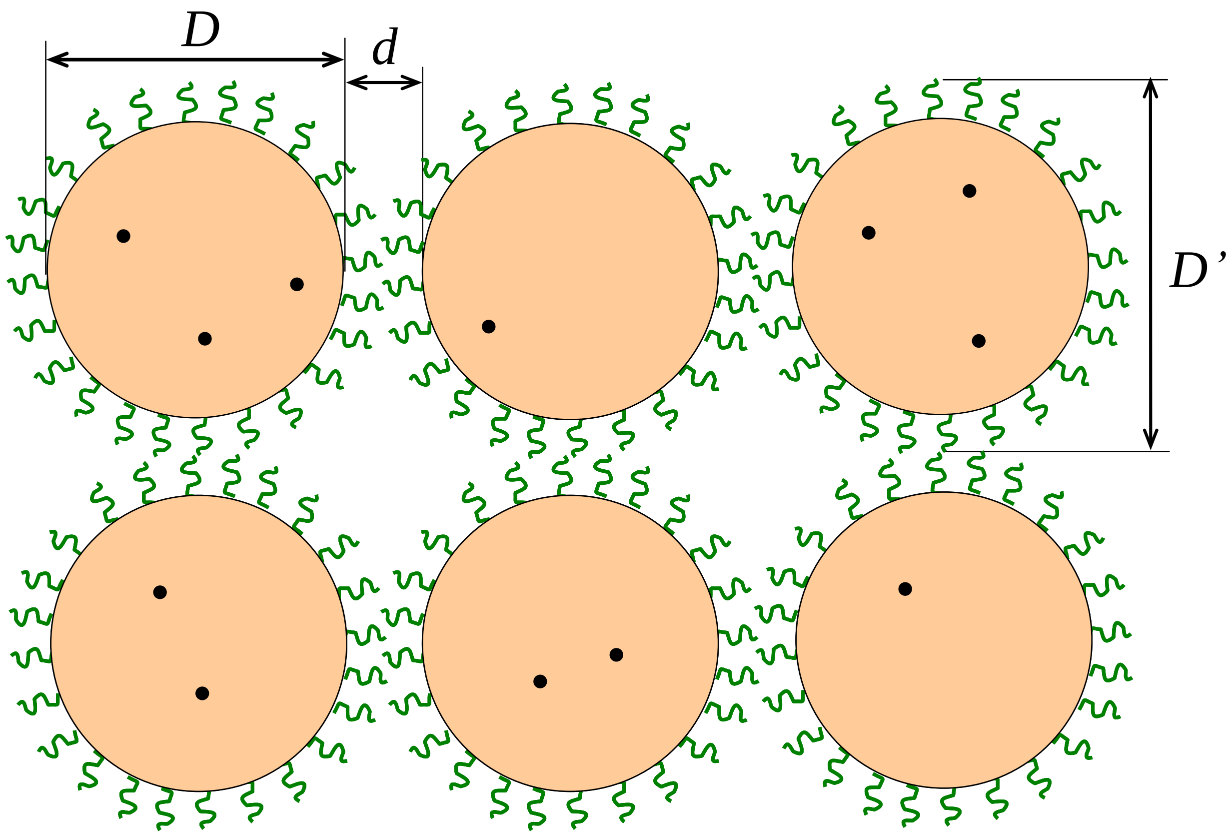


Our interest: "heavily-doped" NCs with ~1 dopant each

Focus: Theory of conductivity in the heavily-insulating limit.

σ as a function of temperature, doping, and NC size.

Model of randomly-doped NCs



Regular lattice of monodisperse semiconductor NCs

Donor number N_i is random:

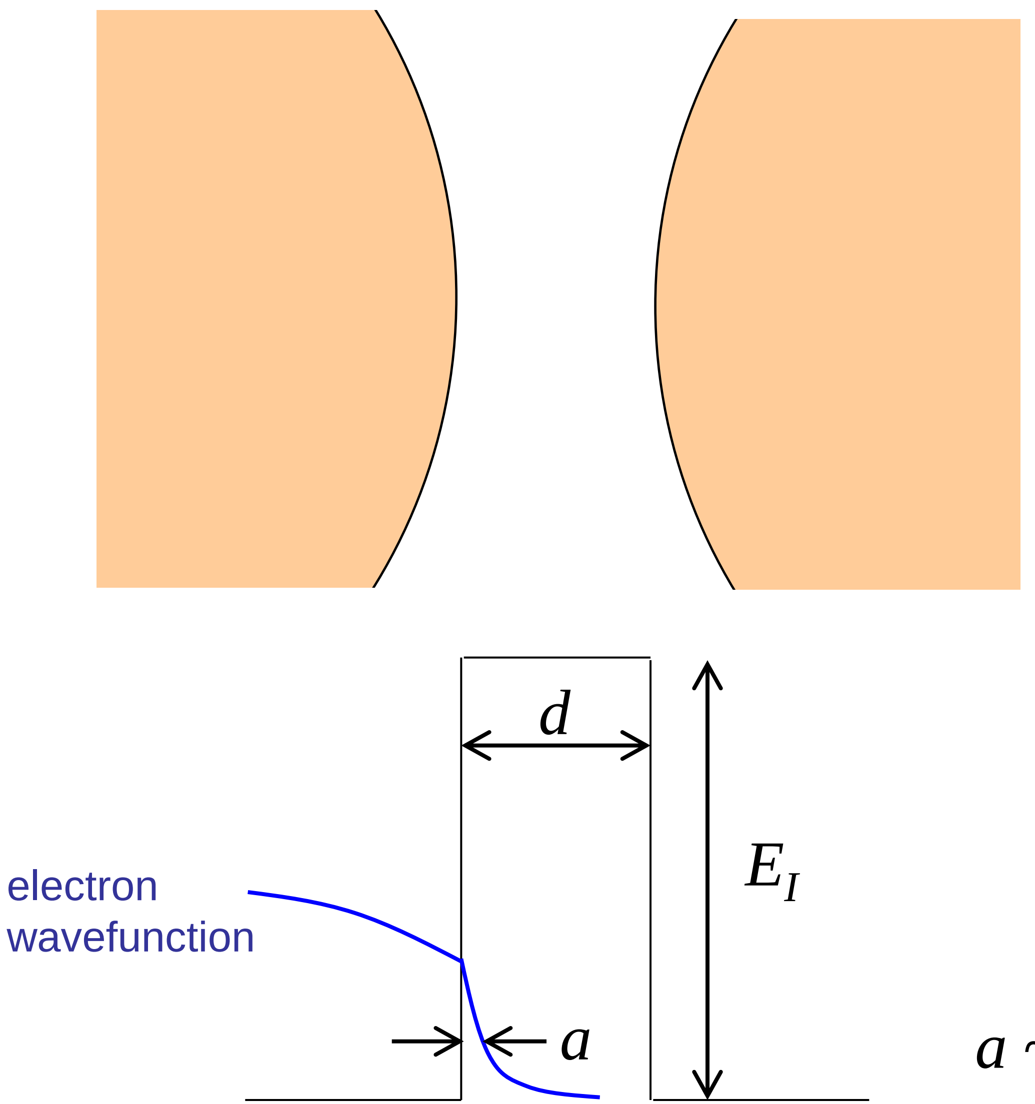
$$\langle N \rangle = \nu$$

$$P(N) = \frac{\nu^N}{N!} e^{-\nu}$$

No other source of disorder (for now).

(Intrinsic carriers are exponentially rare)

Inter-NC tunneling



High tunneling barriers

$$a << d$$

Tunneling between NCs is weak:

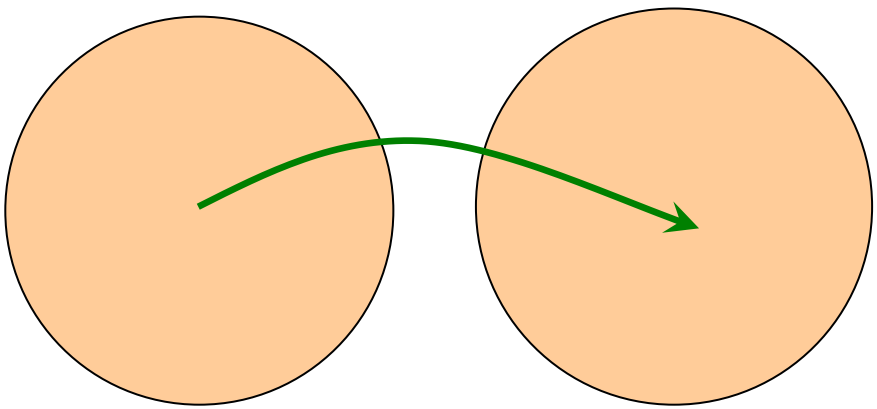
$$G/(e^2/h) << 1$$

Electron states are Anderson-localized by disorder.

$$h\,\Gamma << (\Delta E)_{\text{dis}}$$

$$a \sim \hbar / \sqrt{2mE_I}$$

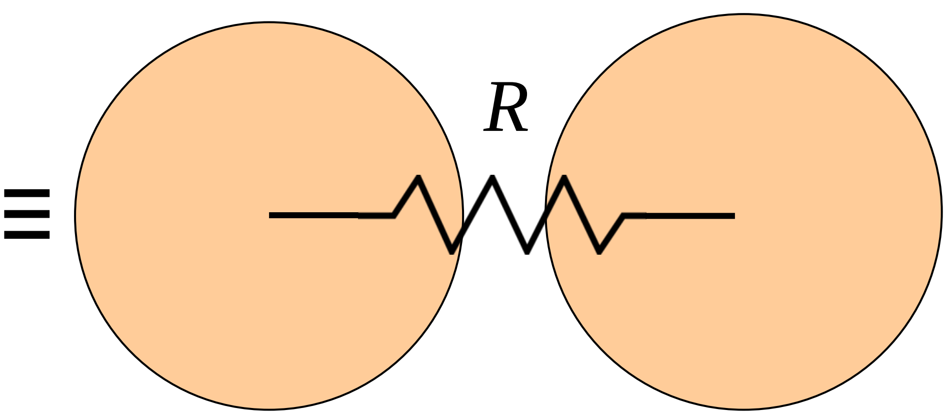
Nearest-neighbor hopping



tunneling rate:

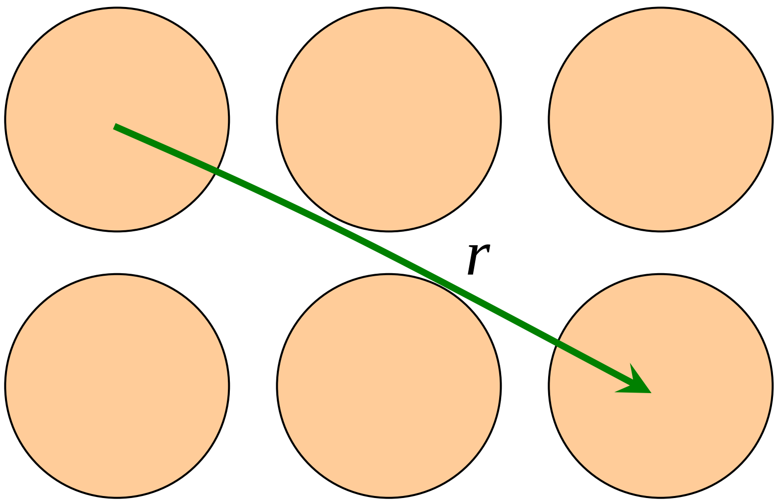
$$\Gamma \propto \exp\left[-\frac{2d}{a}-\frac{\Delta E}{k_B T}\right]$$

"phonon-assisted tunneling"



$$R \propto \exp\left[\frac{2d}{a}+\frac{\Delta E}{k_B T}\right]$$

Variable-range hopping

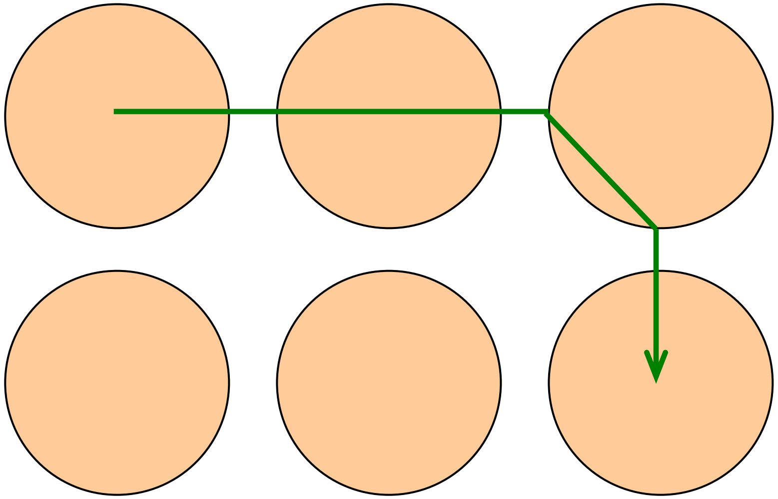


tunneling rate:

$$\Gamma \propto \exp\left[-\frac{2r}{\xi} - \frac{\Delta E}{k_B T}\right]$$

ξ = localization length

Variable-range hopping



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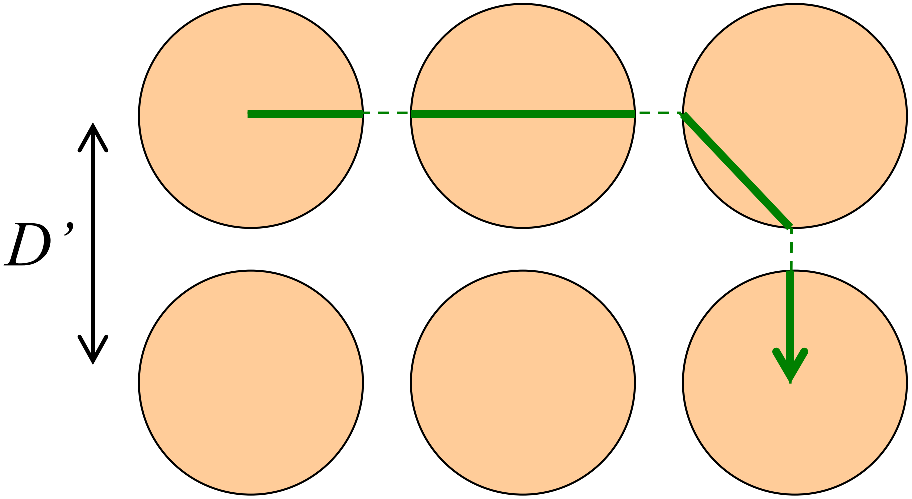

tunneling rate:

$$\Gamma \propto \exp\left[-\frac{2r}{\xi}-\frac{\Delta E}{k_B T}\right]$$

ξ = localization length

$\xi \sim a\, D'/d >> a$

Large localization length in the variable-range hopping regime

NANO LETTERS
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Dependence of Carrier Mobility on Nanocrystal Size and Ligand Length in PbSe Nanocrystal Solids

Yao Liu,[†] Markelle Gibbs,[†] James Puthussery,[†] Steven Gaik,[†] Rachelle Ihly,[†] Hugh W. Hillhouse,[‡] and Matt Law*[,†]

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“Linear fits to the data yield tunneling decay constants β of 1.10 and 1.08 $Å^{-1}$ for electron and hole transport.”

NANO LETTERS
LETTER
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Size- and Temperature-Dependent Charge Transport in PbSe Nanocrystal Thin Films

Moon Sung Kang,[†] Ayaskanta Sahu,[†,‡] David J. Norris,*[,‡] and C. Daniel Frisbie*[,†]

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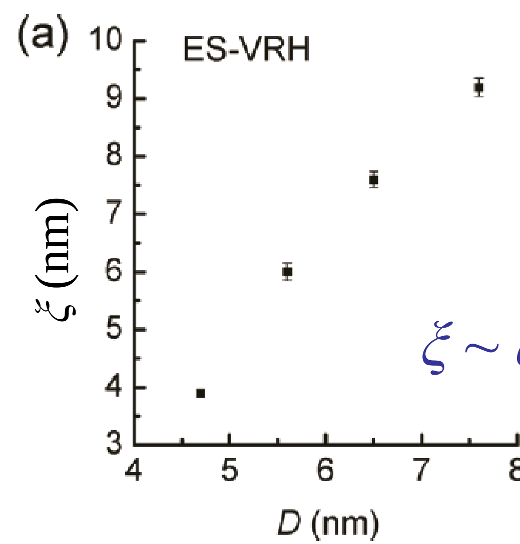
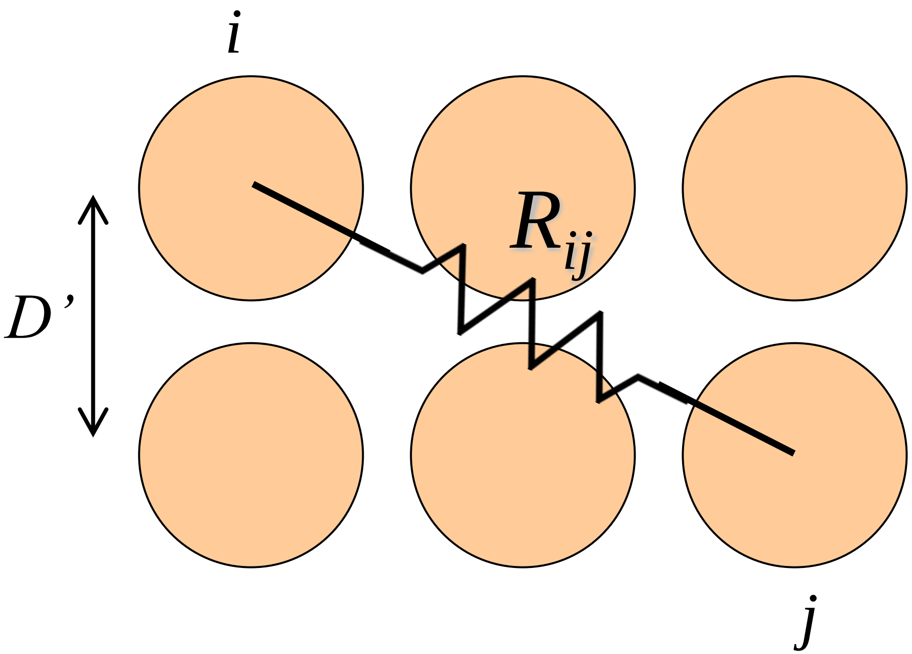


$\xi \sim a\, D'/d >> a$

Variable-range hopping



tunneling rate:

$$\Gamma \propto \exp\left[-\frac{2r}{\xi} - \frac{\Delta E}{k_B T}\right]$$

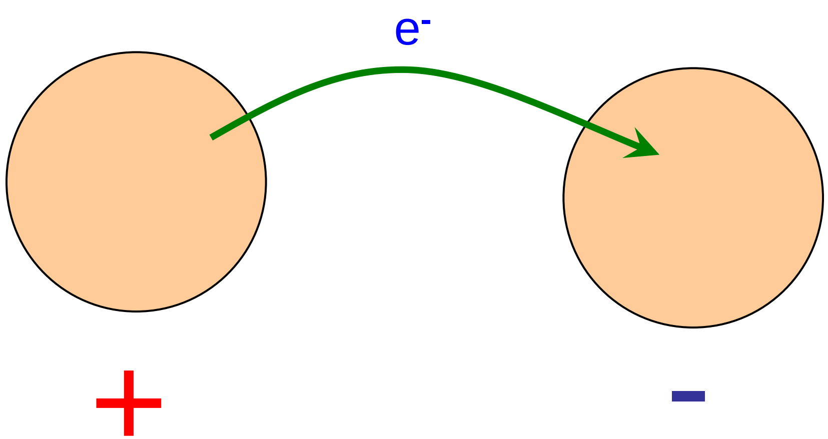
ξ = localization length

$$R_{ij} \propto \exp\left[\frac{2r}{\xi} + \frac{\Delta E_{ij}}{k_B T}\right]$$

$\xi \sim a\, D'/d >> a$

Importance of the charging energy

A single electron hop:



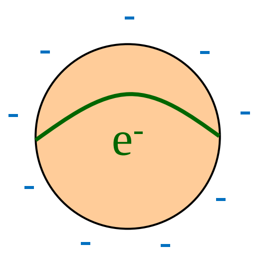
Coulomb self-energy:

$$E_c \sim e^2/2C_0$$

energy required for hop:

$$2E_c$$

When $\varepsilon_{NC} >> \varepsilon_I$:



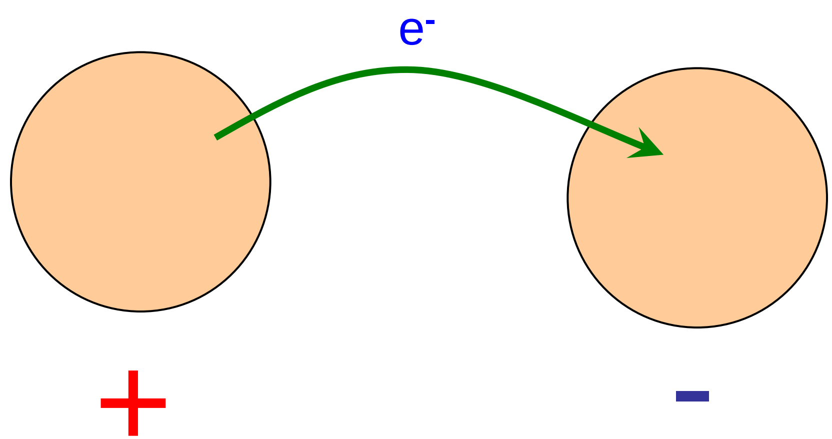
Fraction $\varepsilon_{NC}/(\varepsilon_{NC} + \varepsilon_I) \sim 1$ of negative electron charge is relayed to the surface

Coulomb self-energy

$$\sim E_c = e^2 / 4\pi\varepsilon_{\text{out}} D$$

Importance of the charging energy

A single electron hop:



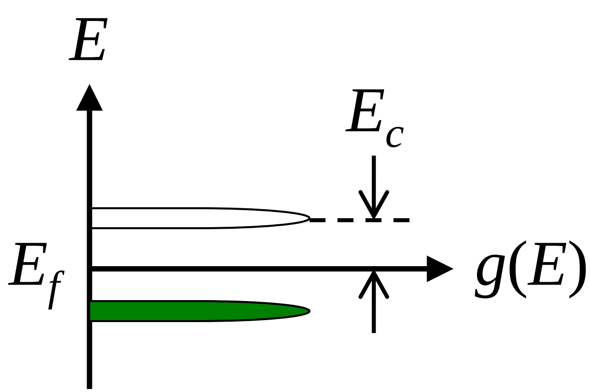
Coulomb self-energy:

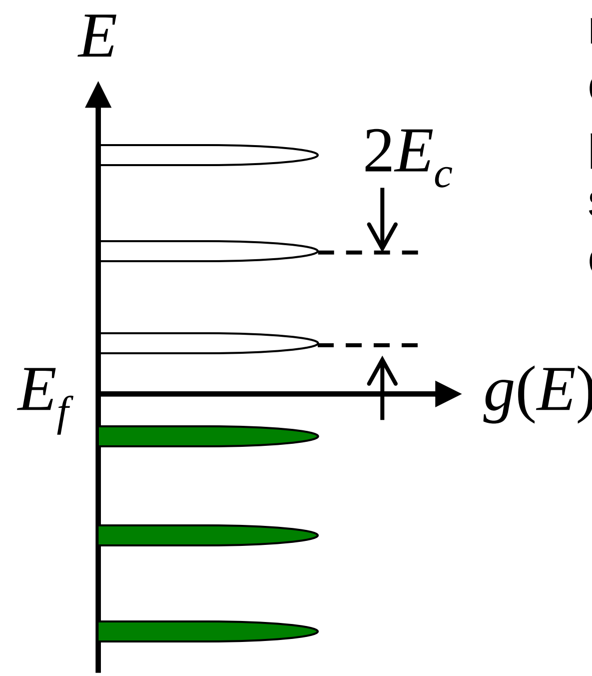
$$E_c \sim e^2/2C_0$$

energy required for hop:

$$2E_c$$

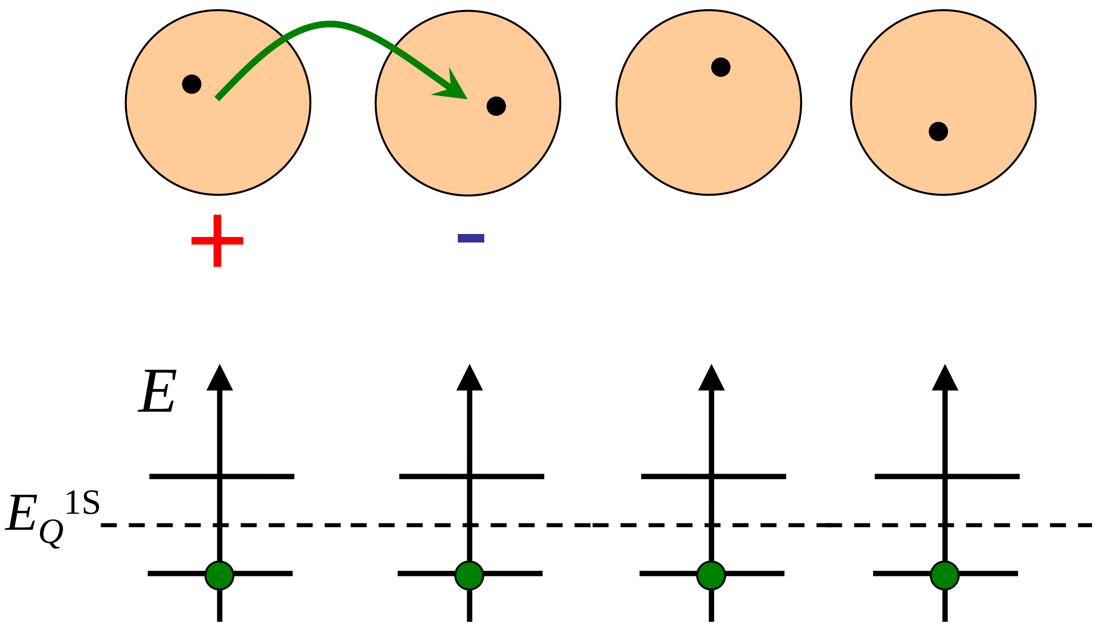
ground state energy levels:





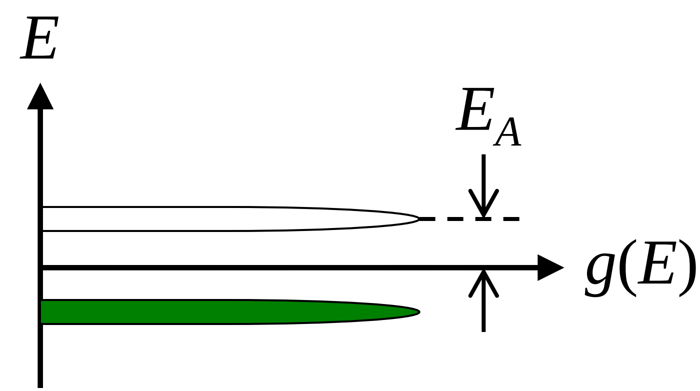
multiple charging: periodic spectrum of energy levels

Conduction with uniform doping



histogram of energy states

("density of ground states"):



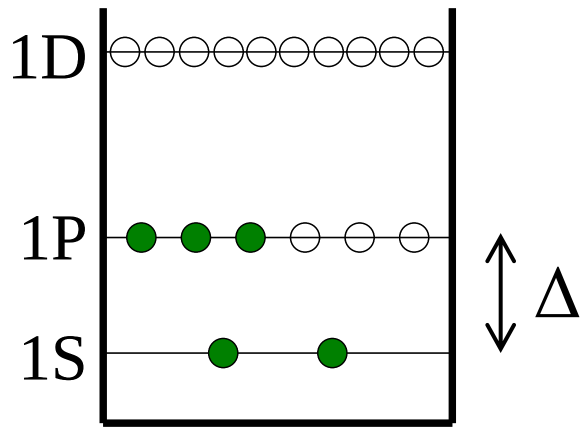
$$R \propto \exp\left[\frac{2d}{a} + \frac{E_c}{k_B T}\right]$$

Without fluctuations in doping, conduction is activated.

Quantum confinement energy

At small D/a_B, electron states are extended across the NC:

Energy levels of the 3D infinite potential well:

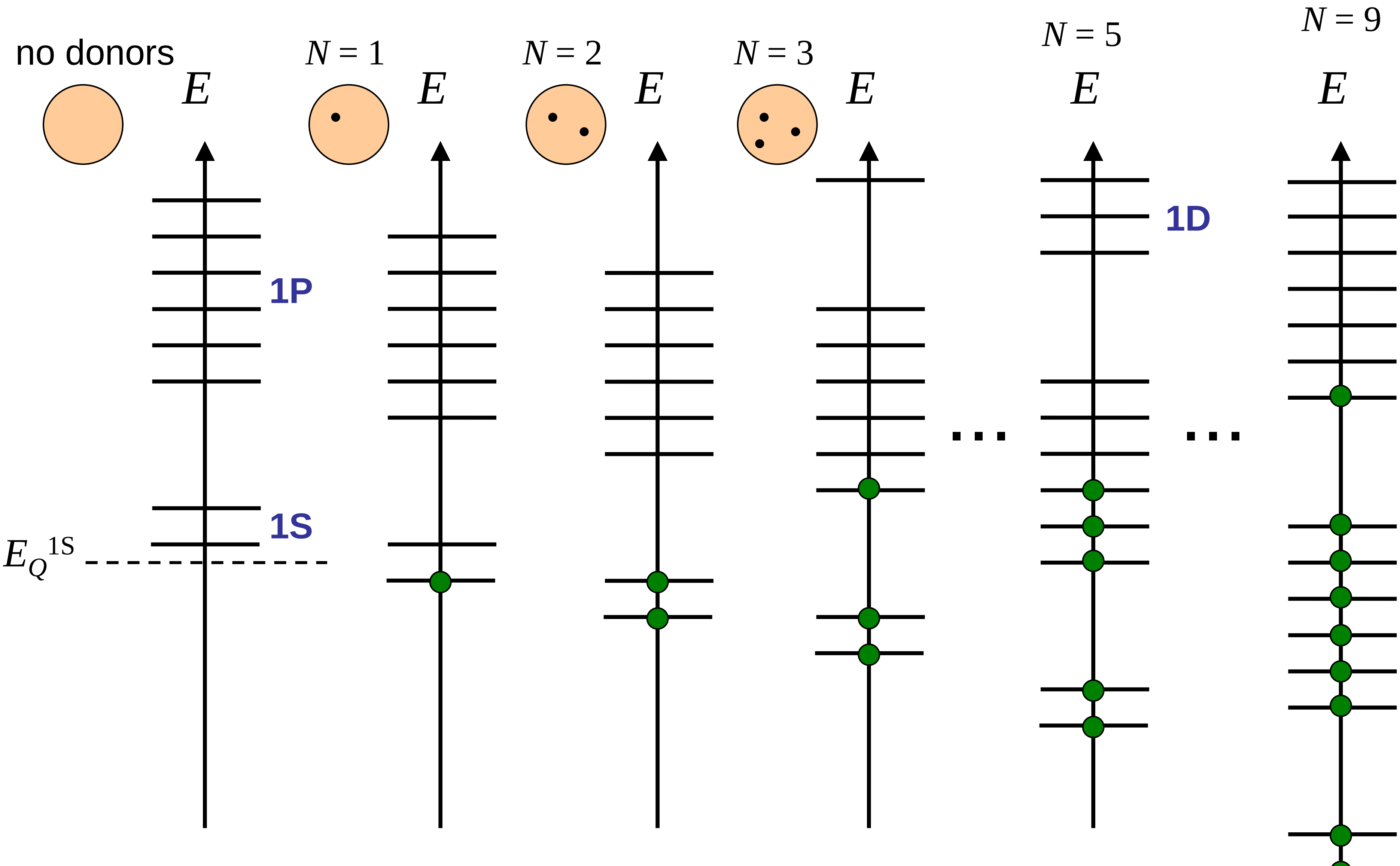


$(D/a_B \lesssim 6)$

$\boldsymbol{\Delta >> E_c}$

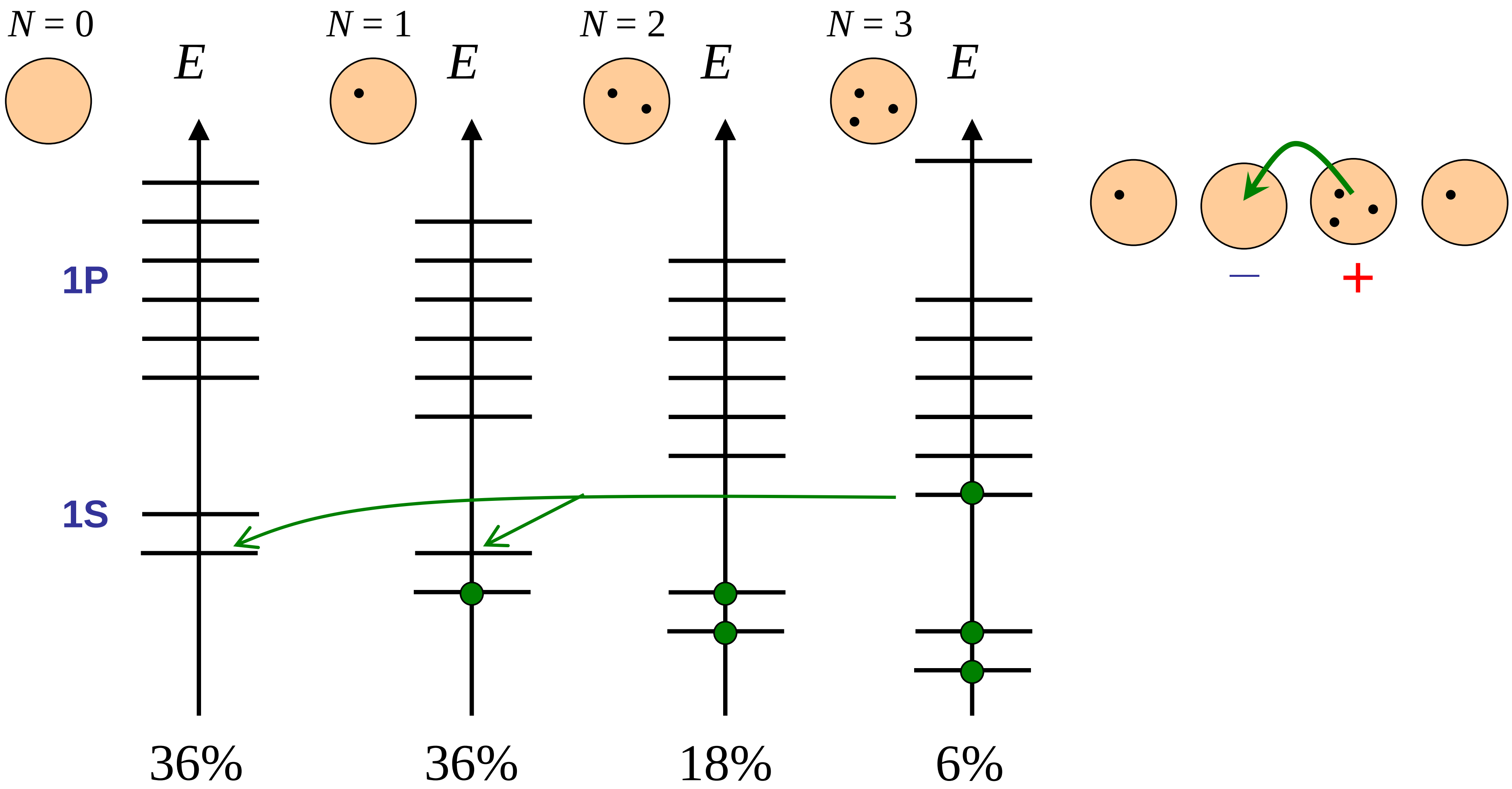
$$E_Q(n) = \frac{\hbar^2}{mD^2} \times \begin{cases} 19.74, & n = 1, 2 \\ 40.38, & 3 \le n \le 8 \\ 66.43, & 9 \le n \le 18 \end{cases}$$

Electron energy spectrum of a single nanocrystal

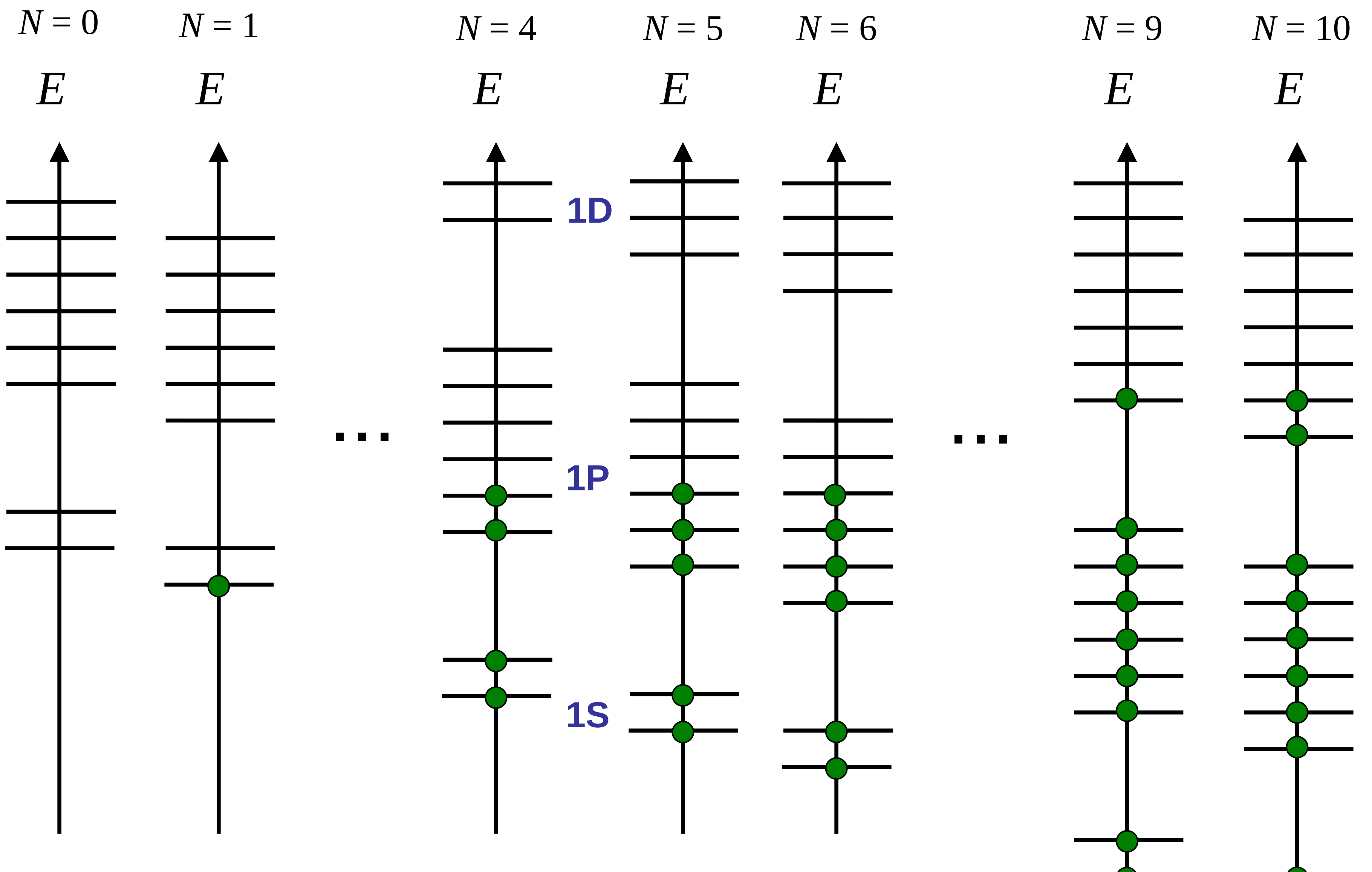


Random doping produces spontaneous charging

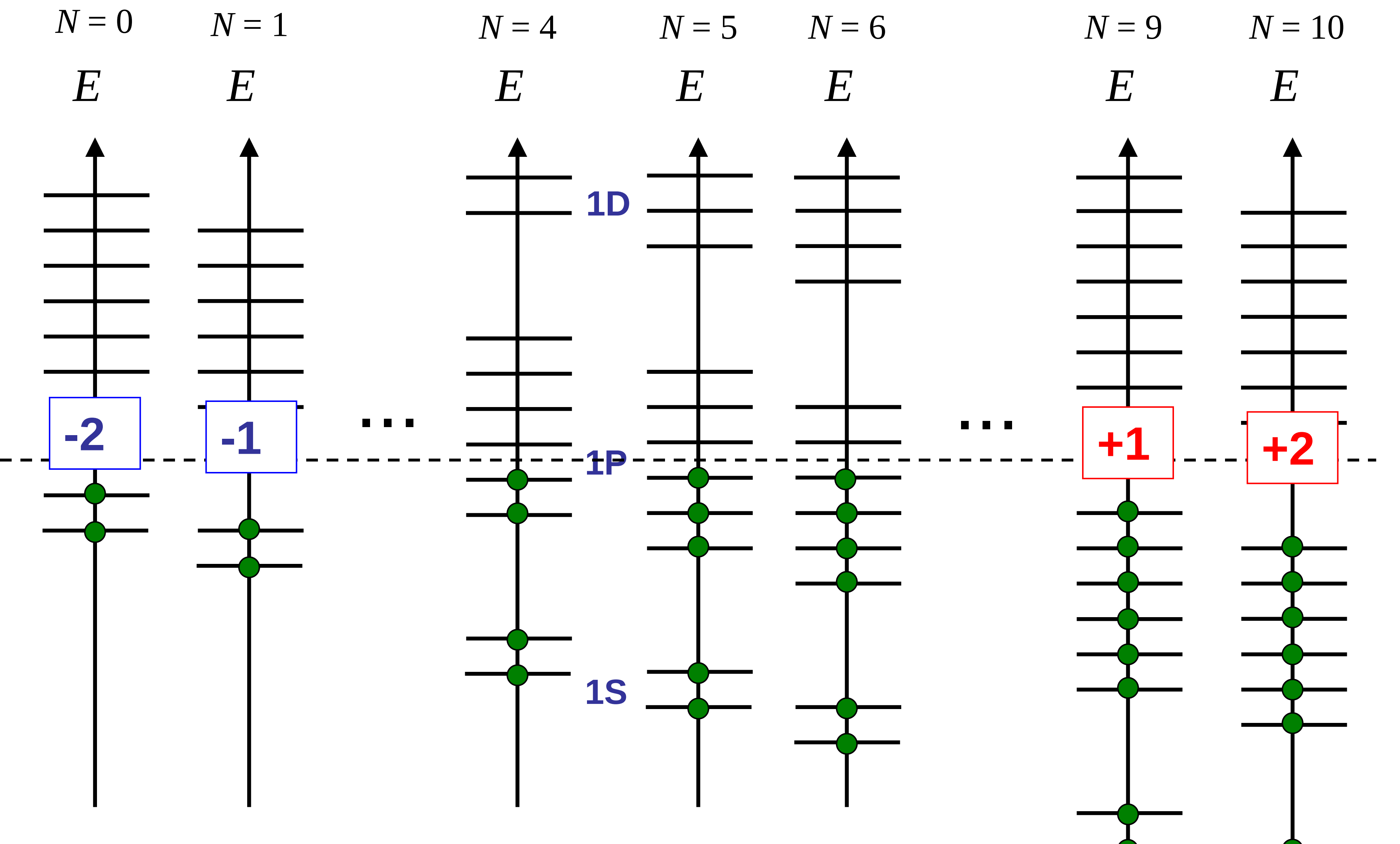
$\nu = 1,\ \Delta = 5\ e^2/\kappa D:$



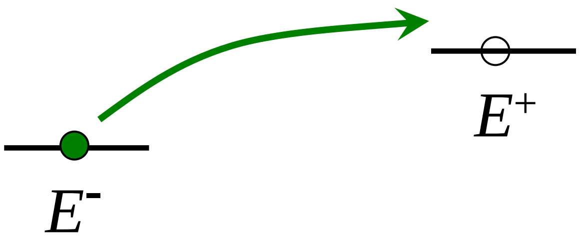
Typical case: $\nu = 5$, $\Delta = 5\ e^2/\kappa D$



Typical case: $\nu = 5$, $\Delta = 5\ e^2/\kappa D$



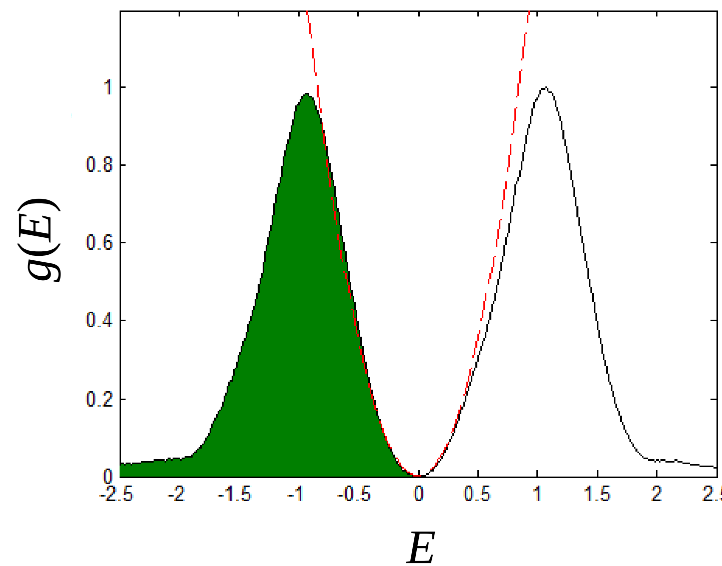
The Coulomb gap



$$E^- - \left(E^+ - \frac{e^2}{4\pi\varepsilon r}\right) > 0 \Rightarrow E^+ - E^- > \frac{e^2}{4\pi\varepsilon r}$$

$$g(E) \lesssim \frac{E^2}{\left(e^2/4\pi\varepsilon\right)^3} \qquad \text{(in 3D)}$$

Density of Ground States (DOGS):



Minimum resistance hopping paths:

$$r_{\text{hop}} \sim \left(\frac{4\pi\varepsilon\xi}{e^2 k_B T}\right)^{1/2} \Rightarrow$$

Efros-Shklovskii conductivity:

$$\rho \propto \exp\left[\left(\frac{T_{ES}}{T}\right)^{1/2}\right]$$

Hamiltonian and computer model

- Simulate a lattice of NCs with random donor numbers $\{N_i\}$
- Search for the electron occupation numbers $\{n_i\}$ that minimize the total energy

$$\boxed{H = \sum_i \left[\frac{e^2 (N_i - n_i)^2}{2C_0} + \sum_{k=0}^{n_i} E_Q(k) \right] + \sum_{\langle ij \rangle} \frac{e^2 (N_i - n_i)(N_j - n_j)}{4\pi\varepsilon r_{ij}}}$$

- Calculate conductivity as a function of ν, Δ, and *T* by mapping the ground state arrangement to a resistor network

- Analyze *T*-dependence:

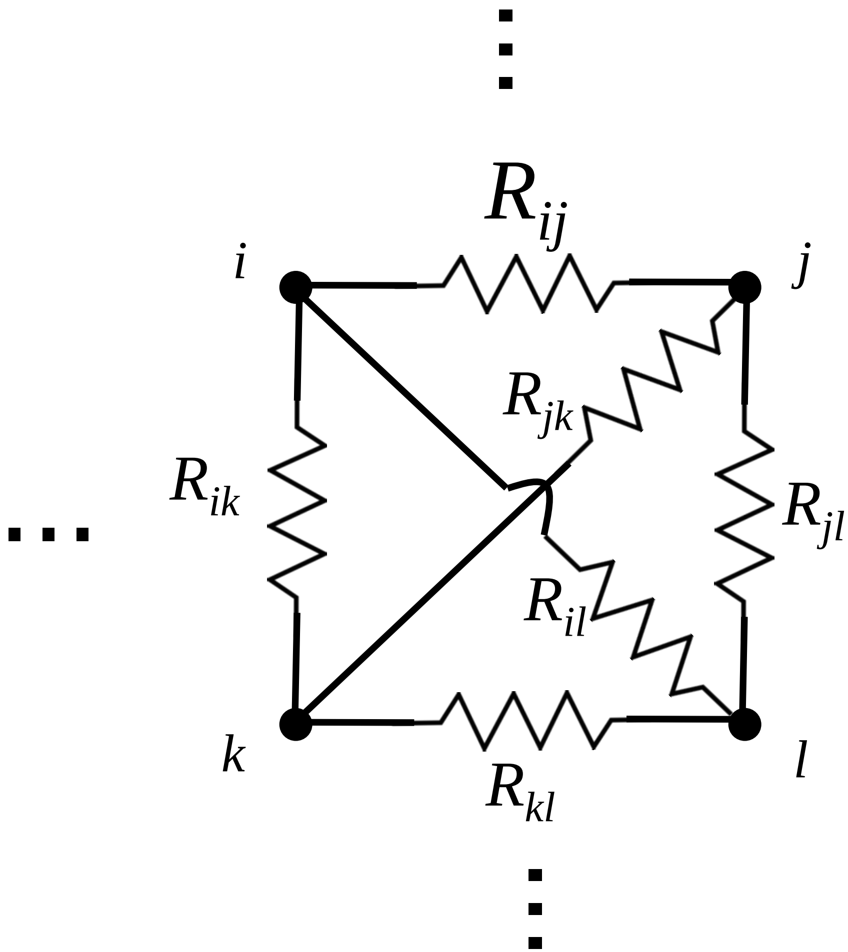
$$\ln \rho \propto T^{-\gamma} + \text{const.}$$

γ = 1 : Activated (Arrhenius)

γ = 1/2 : ES VRH

γ = 1/4 : Mott VRH

Miller-Abrahams resistor network

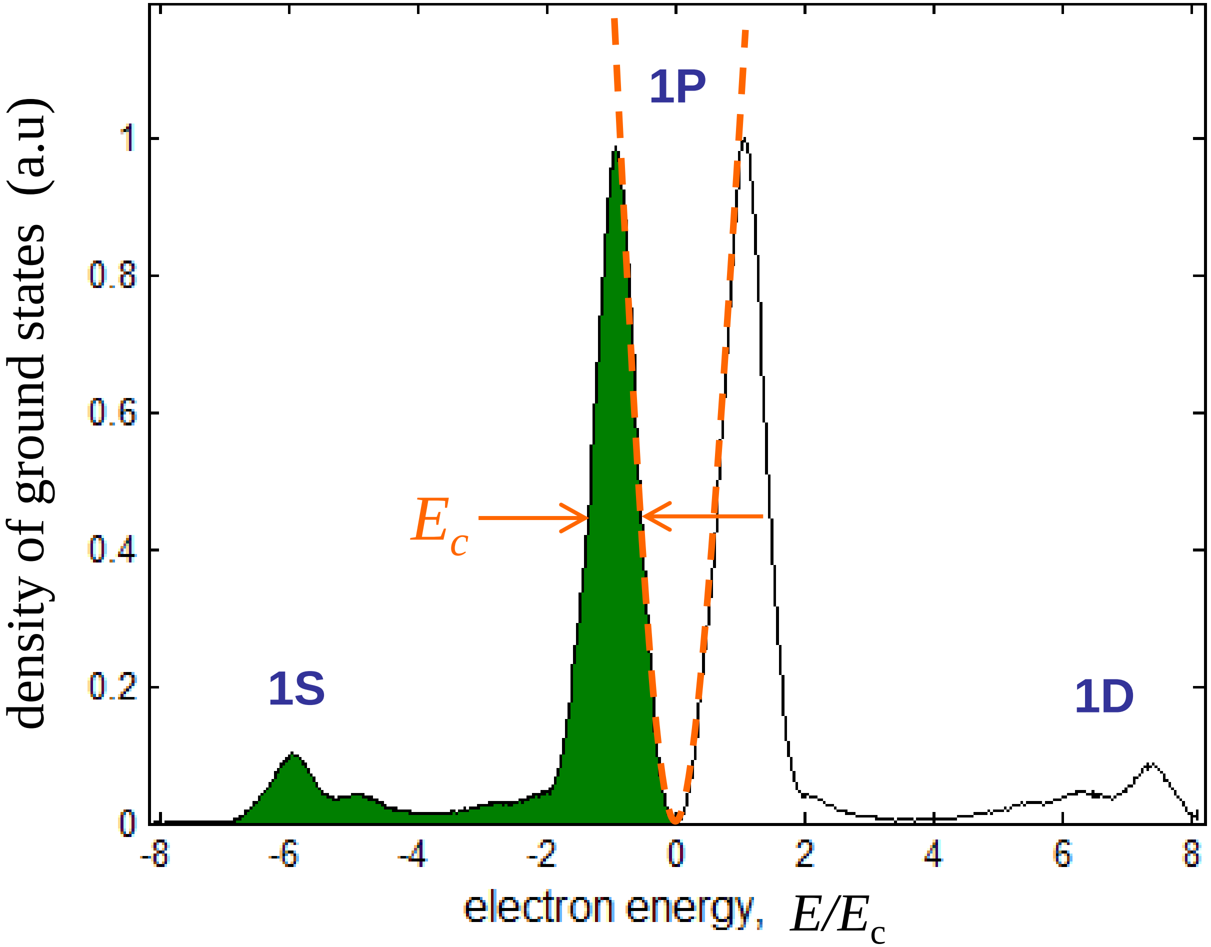


$$R_{ij} = R_0 \exp\left[\frac{2r_{ij}}{\xi} + \frac{\Delta E_{ij}}{k_B T}\right]$$

$$\Delta E_{ij} = \begin{cases} |E_j - E_i| - e^2 / 4\pi\varepsilon r_{\mathrm{ij}}, & E_j E_i < 0 \\ \max\left[|E_j|, |E_j|\right], & E_j E_i > 0 \end{cases}$$

ρ is equated with the minimum percolating resistance.

Density of ground states: $\nu = 5$, $\Delta = 5E_c$



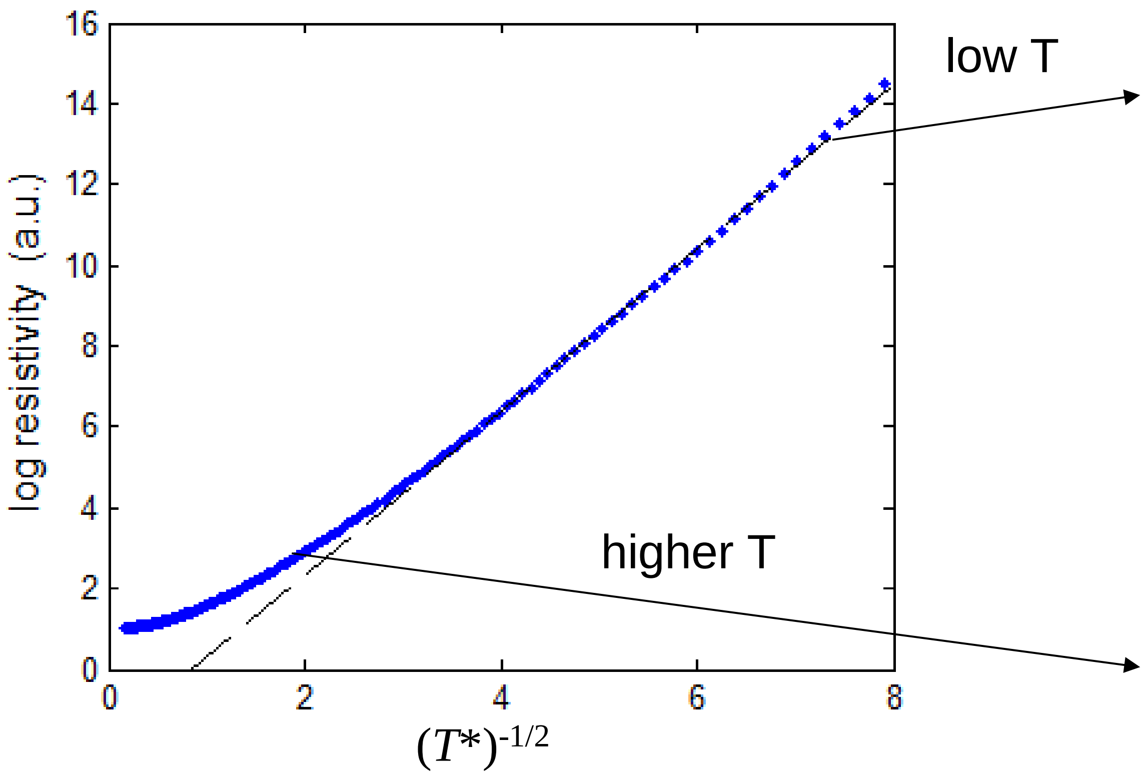
Electrons abandon upper shells, fill lower shells.

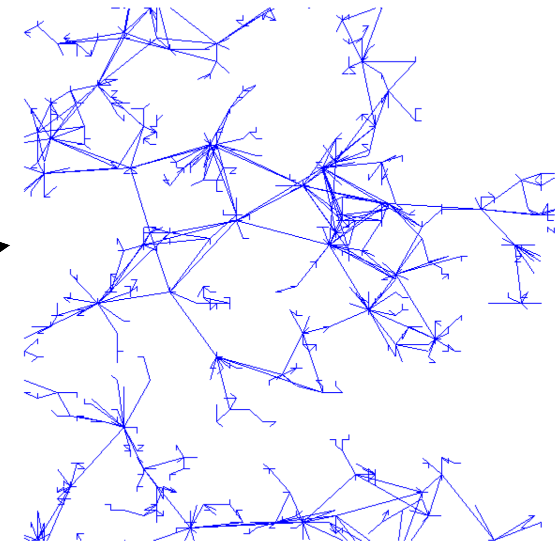
Charge correlations create Coulomb gap.

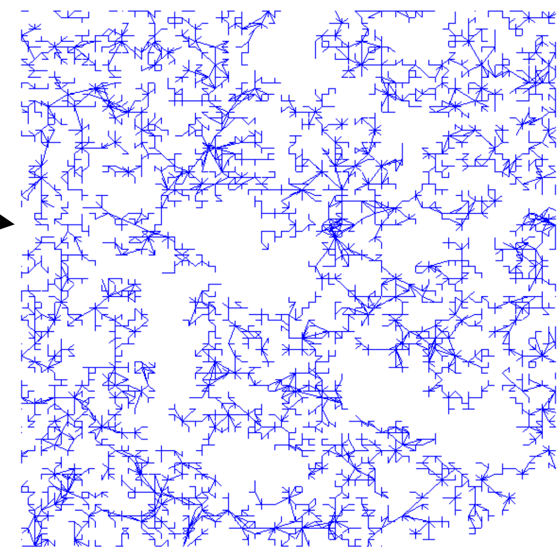
Typical amplitude of the Coulomb potential is E_c.

Efros-Shklovskii conductivity

$$\rho \propto \exp\left[\left(\frac{T_{ES}}{T}\right)^{1/2}\right]$$





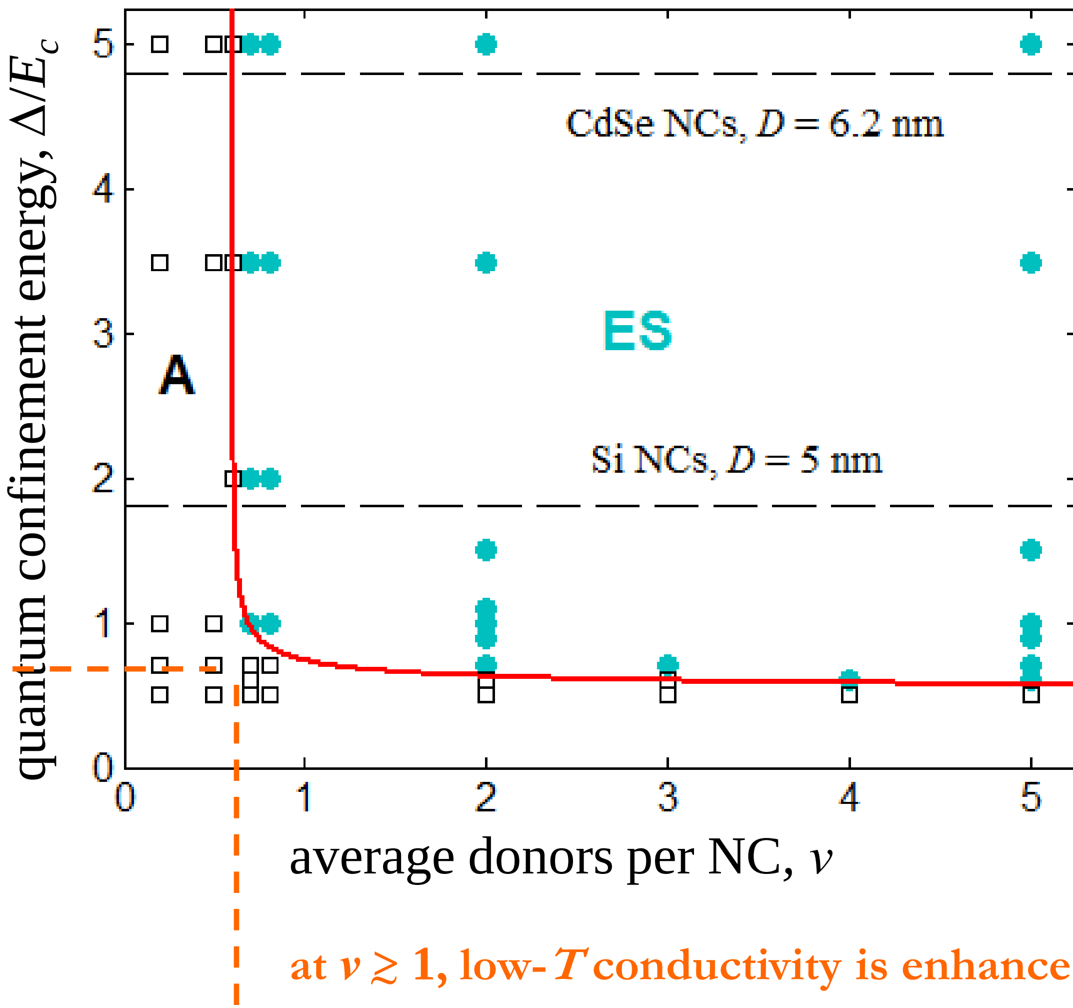


$$T^* = \frac{2Dk_BT}{E_c\xi}$$

Phase diagram of conduction mechanism

At low temperature: $k_B T < E_c \xi / D$

Decreasing temperature *or* increasing ξ leads to VRH conduction



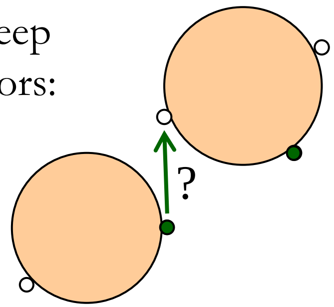
small NC size also promotes VRH

at $\nu \gtrsim 1$, low-T conductivity is enhanced by VRH

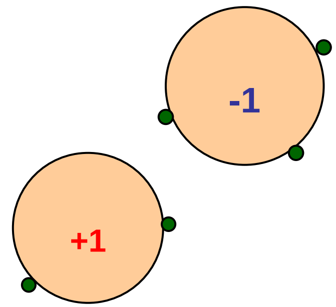
Factors outside of our model

- Surface traps can act like random donors

traps are like deep acceptors/donors:



filled traps can leave the system charged:



ES VRH can arise even at very low (intentional) doping

- Dispersion in NC size/spacing can affect NNH strongly, VRH weakly

$$R_{ij}^{(NNH)} \sim \exp\left[\frac{2d_{ij}}{a} + \frac{\Delta E_{ij}}{k_B T}\right]$$

$$R_{ij}^{(VRH)} \sim \exp\left[\frac{2r_{ij}}{\xi_{ij}} + \frac{\Delta E_{ij}}{k_B T}\right]$$

At large r_{ij}, $\xi_{ij} \rightarrow \langle \xi_{ij} \rangle$

- Gating is not the same as "random doping"

With random doping, Coulomb potential always grows to bring states to the Fermi level.

In gated devices, disorder can be smaller → especially at gaps between energy shells

Factors outside of our model

Mott and Efros-Shklovskii Variable Range Hopping in CdSe Quantum Dots Films

Heng Liu, Alexandre Pourret,[†] and Philippe Guyot-Sionnest*

James Franck Institute, The University of Chicago, 929 E. 57th Street Chicago, Illinois 60637. [†]Current address: Laboratoire Photons Et Matiére (UPMC-CNRS) ESPCI, 75005 Paris, France.

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ABSTRACT The model of variable range hopping conductivity predicts a crossover between Mott and Efros-Shklovskii as a function of temperature and density of states. This is observed using monodispersed CdSe colloidal quantum dot 3D solids where the density of states at the Fermi level is varied by electrochemistry. At low density of states, both below the lowest state ($<0.4e^-$/dot) and **in the conductivity gap between the first and second state ($2e^-$/dot), the temperature dependence of the conductivity shows the 1/4 exponent of Mott hopping. At other fillings up to $6e^-$/dot, the conductivity shows the 1/2 exponent of Efros-Shklovskii hopping.** The non-Ohmic conductivity is also found to be explained quantitatively by the variable range hopping model.

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- Gating is not the same as “random doping”

With random doping, Coulomb potential always grows to bring states to the Fermi level

In gated devices, disorder can be smaller
→ especially at gaps between energy shells

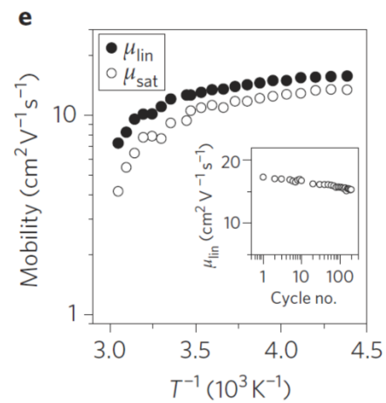
Factors outside of our model

- **Metal-Insulator Transition!**

LETTERS
PUBLISHED ONLINE: 24 APRIL 2011 | DOI: 10.1038/NNANO.2011.46
nature nanotechnology

Band-like transport, high electron mobility and high photoconductivity in all-inorganic nanocrystal arrays

Jong-Soo Lee[1], Maksym V. Kovalenko[1], Jing Huang[1], Dae Sung Chung[1] and Dmitri V. Talapin[1,2*]



NANO LETTERS
Letter
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Bandlike Transport in Strongly Coupled and Doped Quantum Dot Solids: A Route to High-Performance Thin-Film Electronics

Ji-Hyuk Choi,[‡,∥] Aaron T. Fafarman,[†] Soong Ju Oh,[‡] Dong-Kyun Ko,[‡] David K. Kim,[‡] Benjamin T. Diroll,[§] Shin Muramoto,[⊥] J. Greg Gillen,[⊥] Christopher B. Murray,[†,§] and Cherie R. Kagan*[,†,‡,§]

[†]Department of Electrical and Systems Engineering, [‡]Department of Materials Science and Engineering, and [§]Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States

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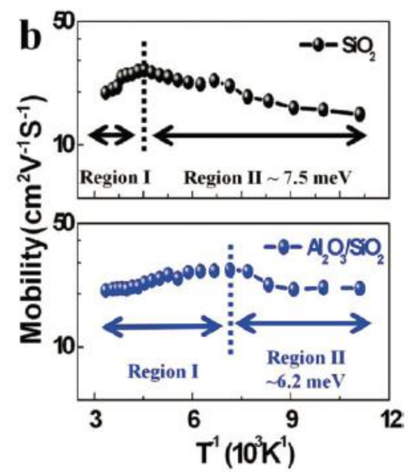


Critical behavior of T_{ES} near transition?

$$T_{ES} \propto (\nu - \nu_c)^2$$

Conclusions

- For semiconductor NCs, fluctuations in donor number leading to charging of NCs.

  Charging leads to ES-VRH, and enhanced low-*T* conductivity.

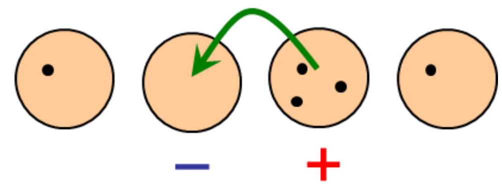
- VRH appears under three conditions:

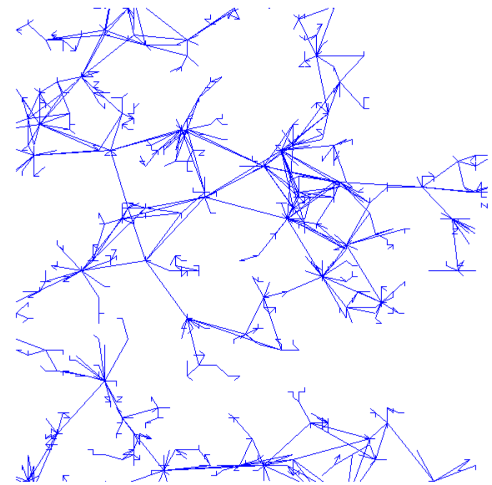
  (i) $\nu > 0.5$

  (ii) $D < 34(\varepsilon_{\mathrm{I}}/\varepsilon_{\mathrm{NC}})\, a_B$

  (iii) $k_B T < E_c \xi / D$

  elsewhere, conduction is by activated, nearest-neighbor hopping.





Phys. Rev. B **85**, 205316 (2012).

Thank you.

Reserve Slides

Hamiltonian and computer model

- Simulate a lattice of NCs with random interstitial charges $(\delta q)_i \in (-e, e)$

- Search for the electron occupation numbers $\{n_i\}$ that minimize the total energy

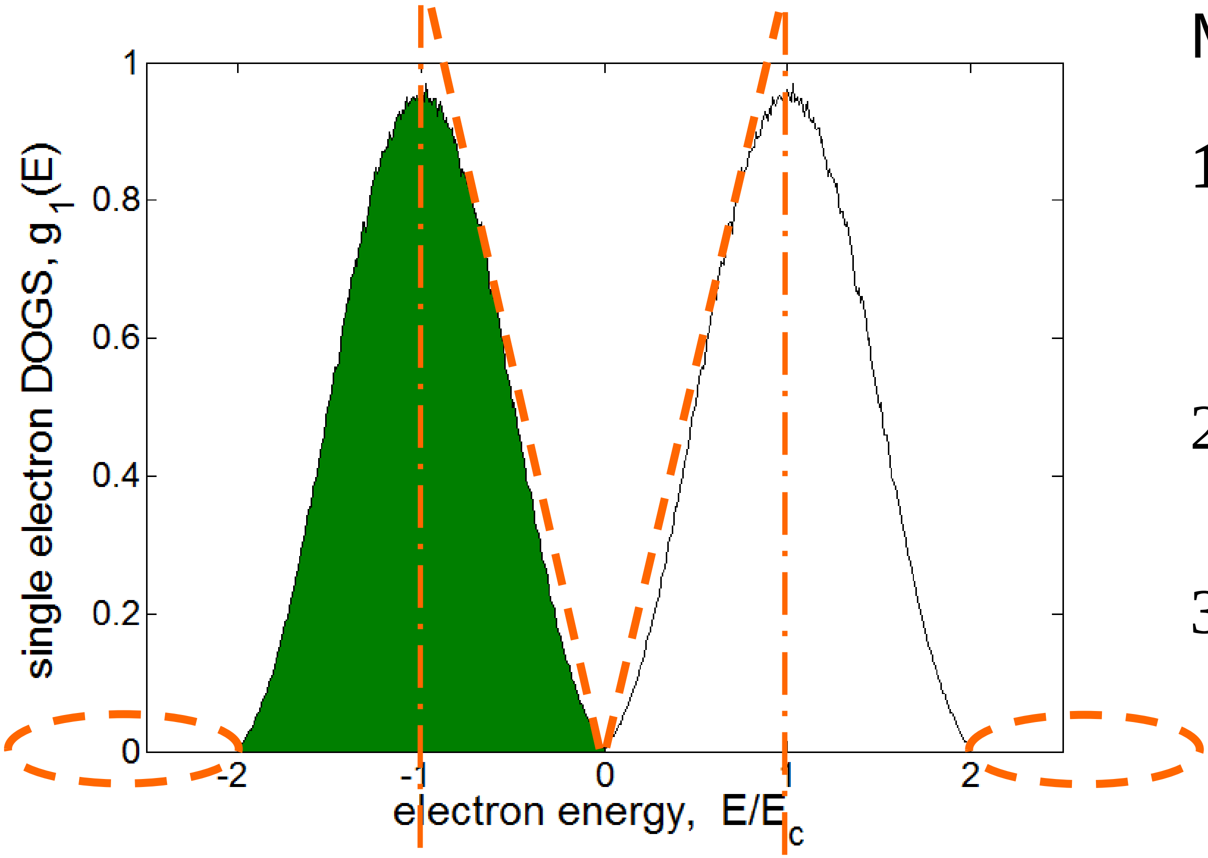
$$\boxed{H = \sum_i \frac{q_i^2}{2C_0} + \sum_{i,j} C_{ij}^{-1} q_i q_j}$$

$$q_i = (\delta q)_i - e n_i$$

- Calculate DOGS by making a histogram of the single-electron ground state energies at each NC: $E_i^{\pm}$

- Calculate resistivity ρ as a function of temperature T by mapping the ground state arrangement to a resistor network

DOGS - results



Main features:

1. $g(E)$ vanishes near $E = 0$

2. $g(|E| > 2) = 0$

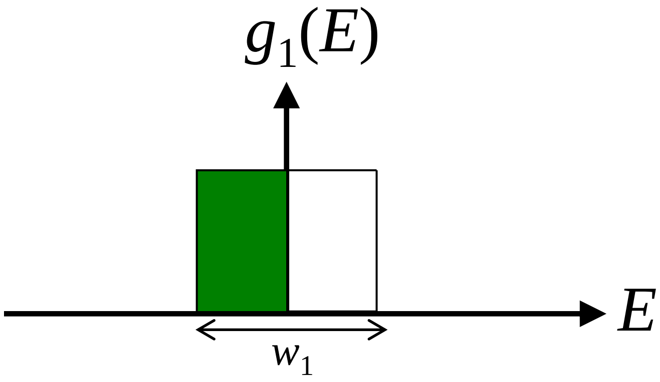
3. Perfect symmetry

Absence of deep energy states

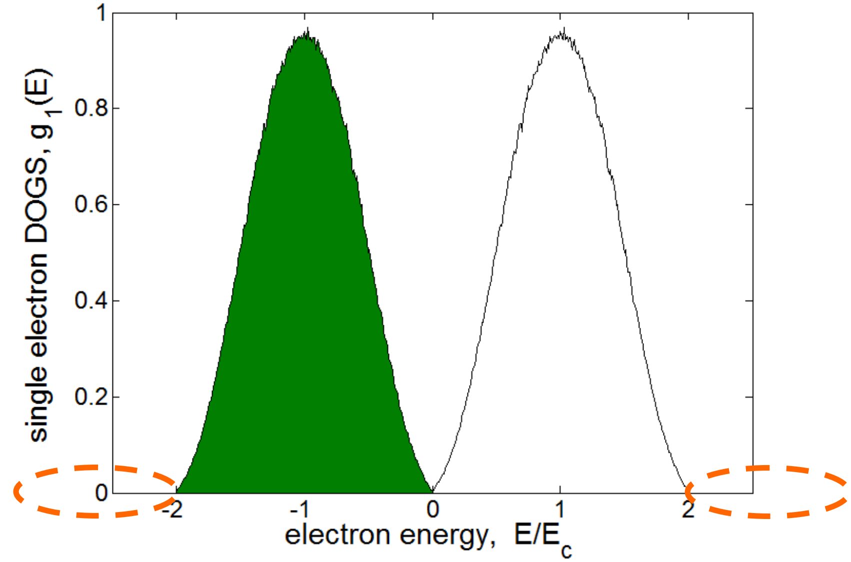
Usual situation:

(lightly-doped semiconductors)

small disorder, w_1:



Here:



Absence of deep energy states

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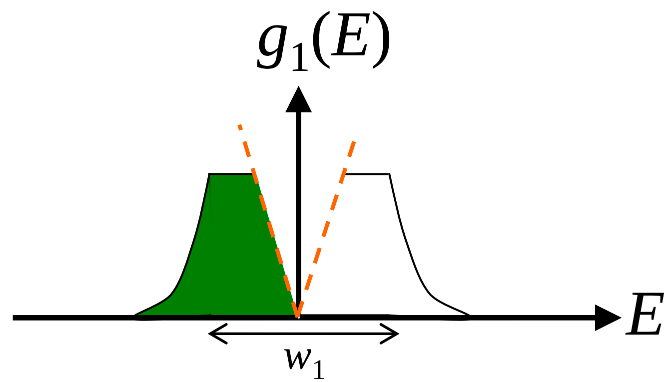
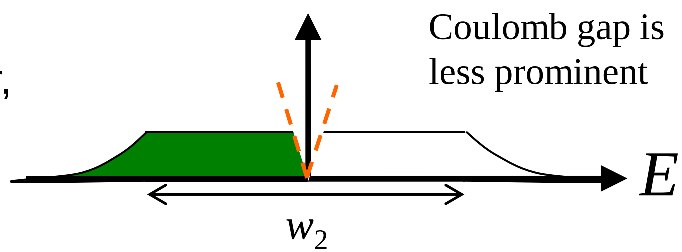
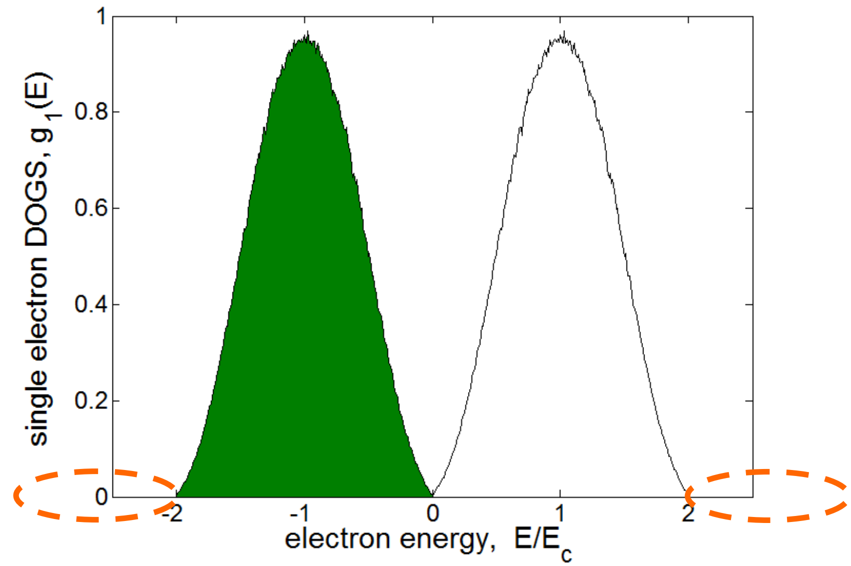


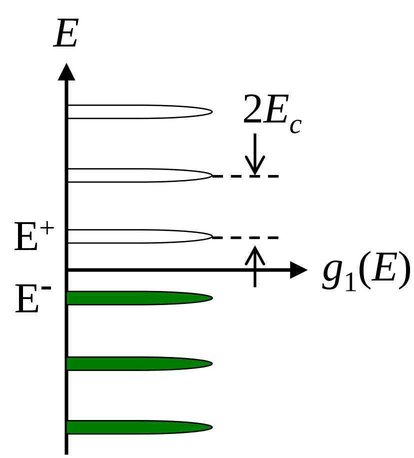
large disorder, w_2 :



Here, deep states are not possible:

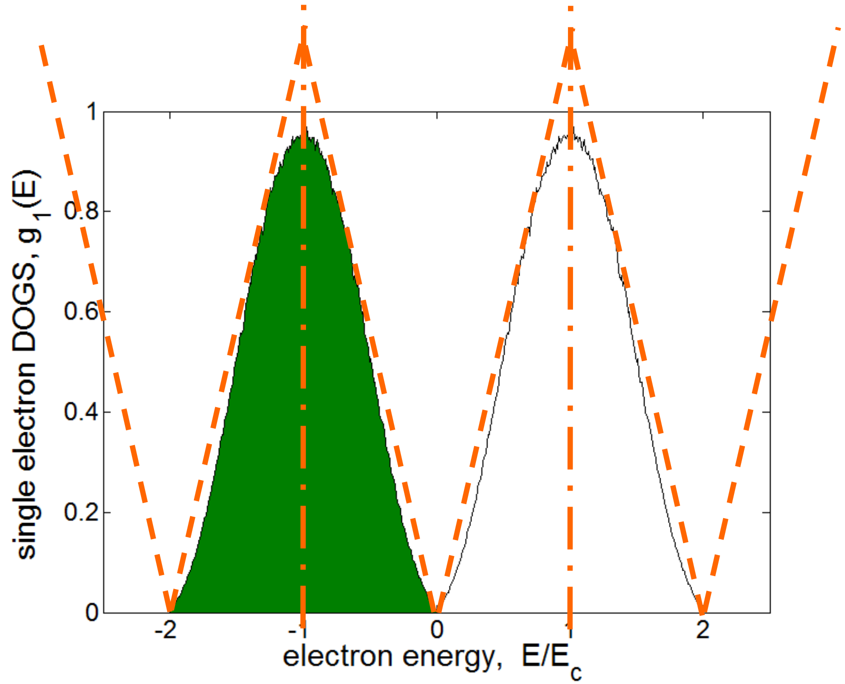
Here:





$$E_i^+ = E_i^- + 2E_c$$

“Triptych” symmetry



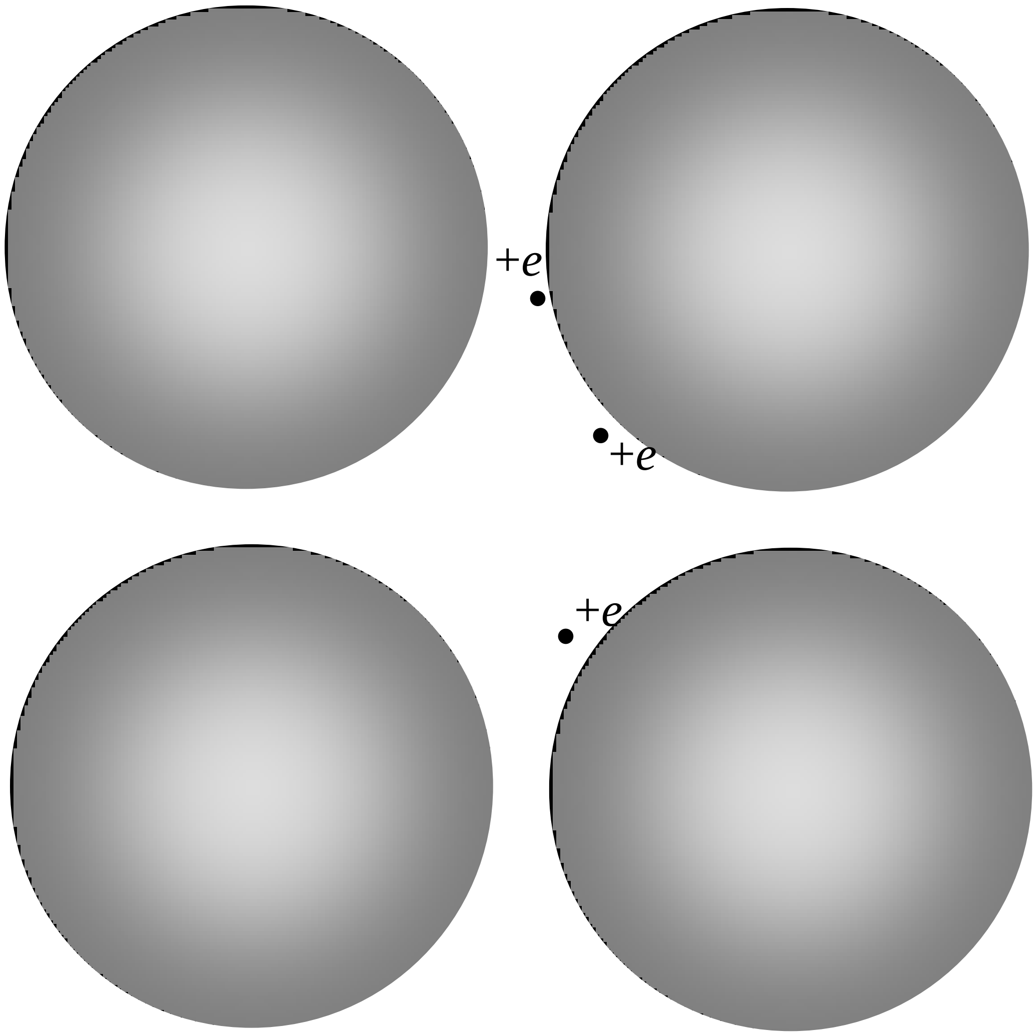
[orthodoxy-icons.com]

$$E_i^+ = E_i^- + 2E_c$$

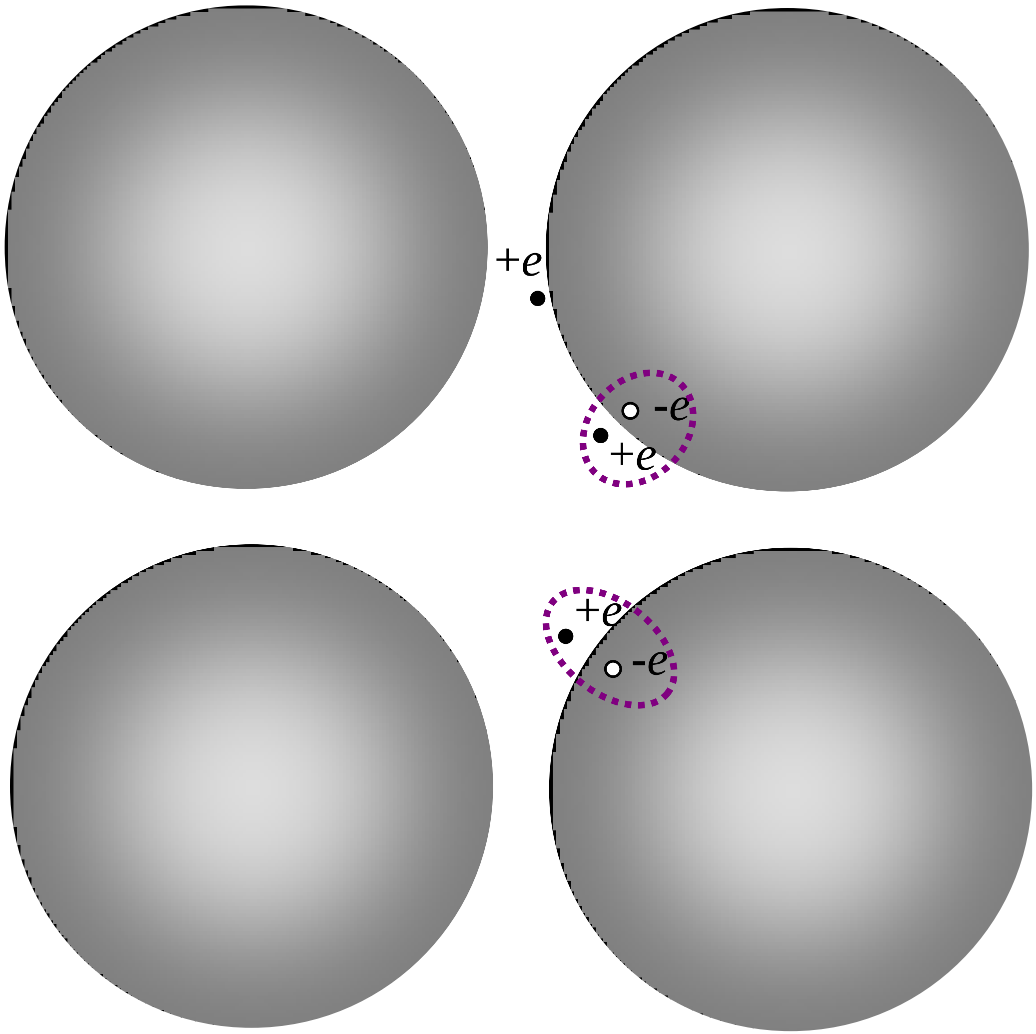
DOGS is completely constrained by symmetry and Coulomb gap.

$g(E)$ is invariant in the limit of large disorder.

Disorder

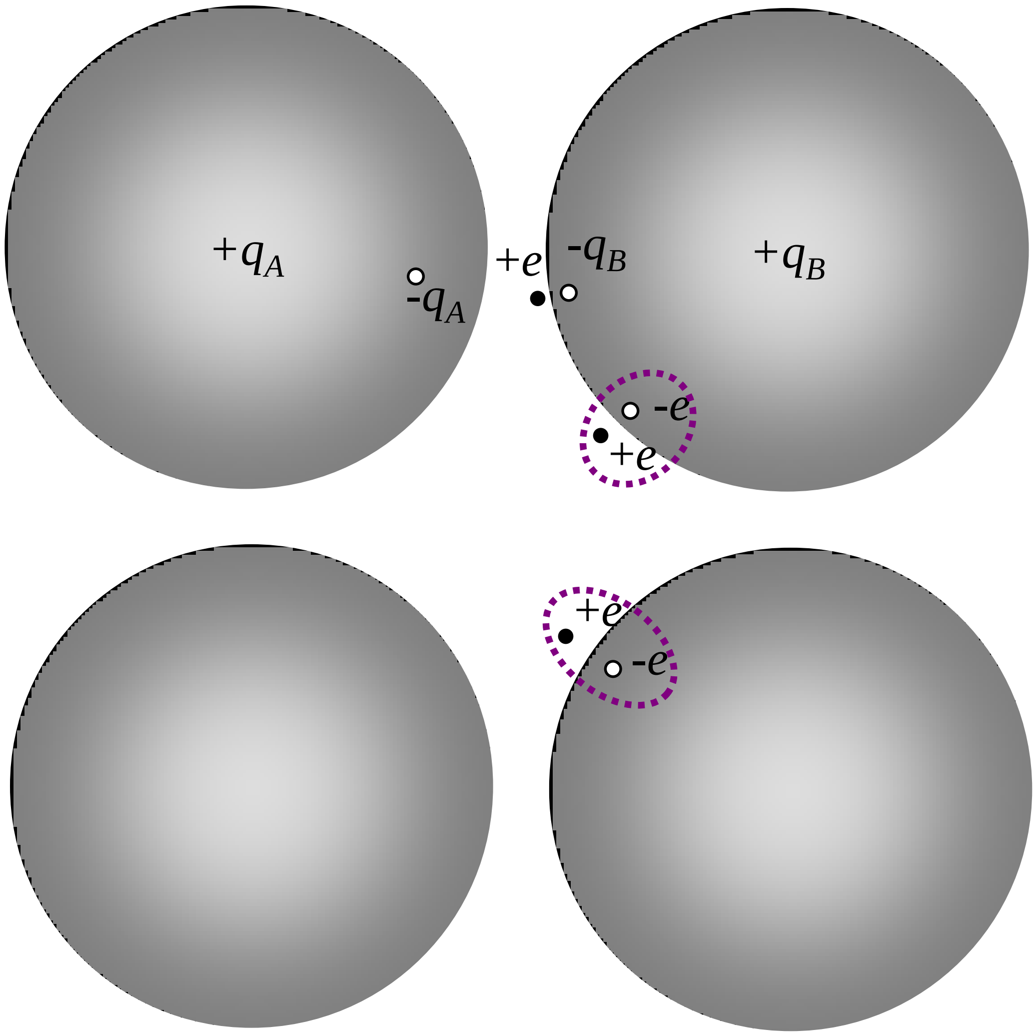


Disorder



Some impurities are effectively screened out by a single NC

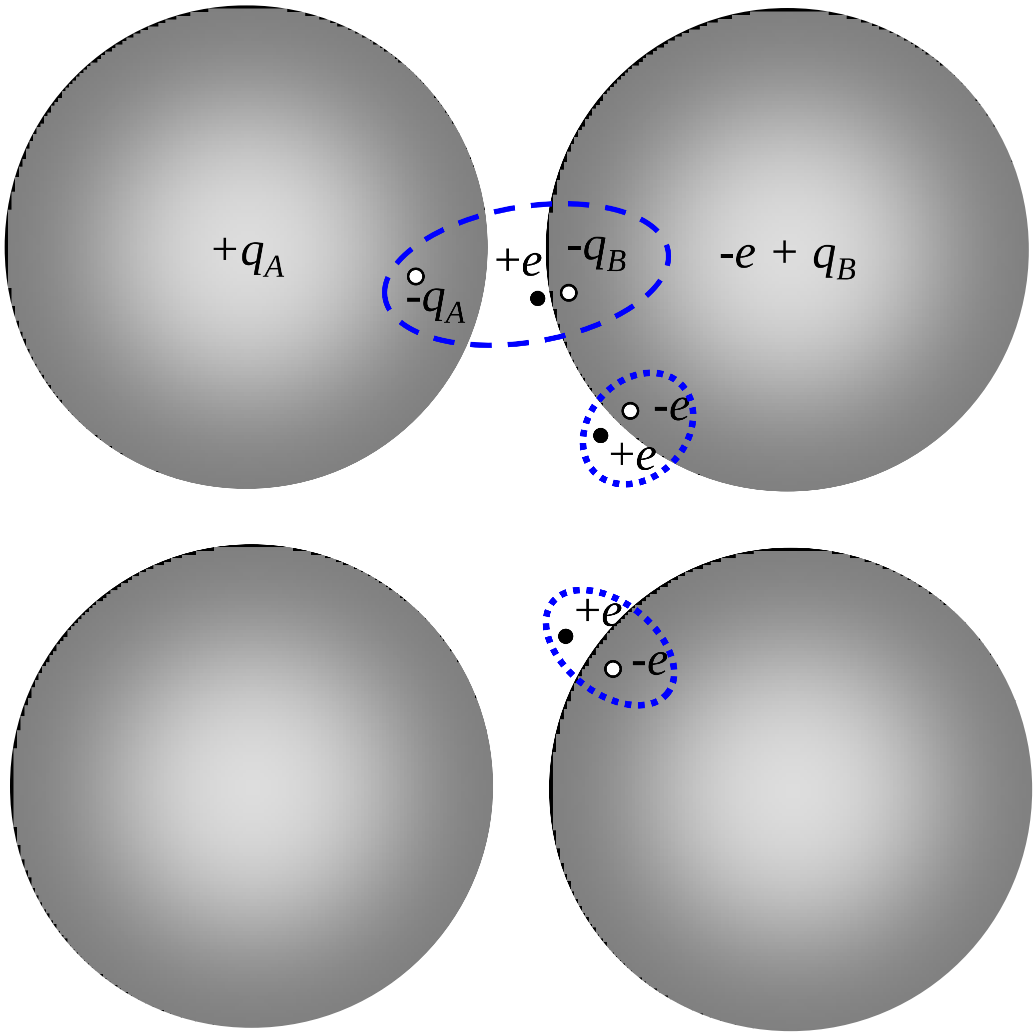
Disorder



Some impurities are effectively screened out by a single NC

Others get "fractionalized"

Disorder

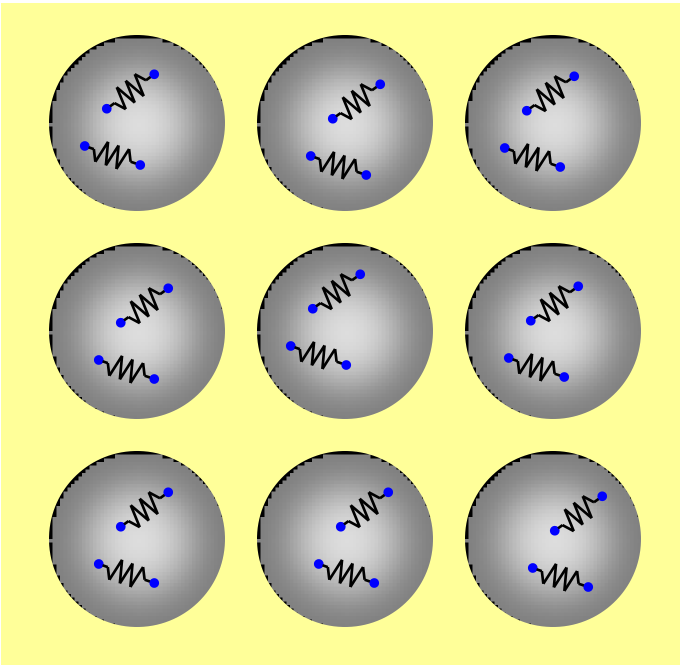


Some impurities are effectively screened out by a single NC

Others get "fractionalized"

Result is a net fractional charge on each NC

Model of an insulating granular superconductor



Uniform superconducting pairing energy, 2Δ

Weak Josephson coupling

$J \sim \Delta \cdot G/(e^2/h) << E_c$

→ heavily insulating, with *decoherent* tunneling

Focus on the case where Δ and E_c are similar in magnitude

$$H = \sum_i \frac{q_i^2}{2C_0} + \sum_{i,j} C_{ij}^{-1} q_i q_j - 2\Delta \sum_i \left\lfloor \frac{N_i}{2} \right\rfloor$$

pairs in grain *i*

pairing energy

Single-electron hopping

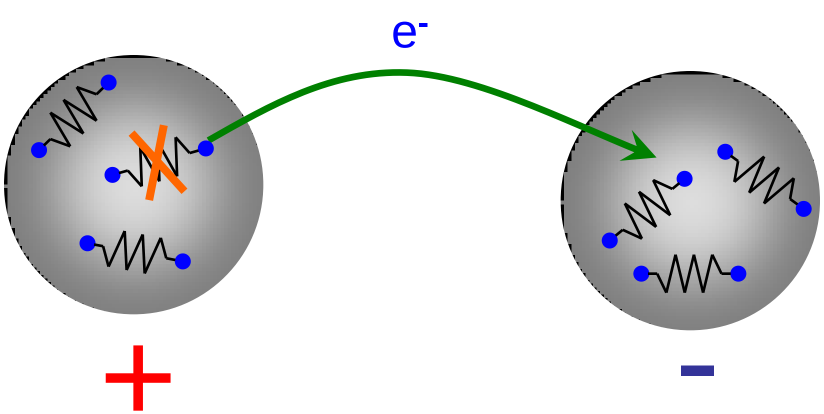
single-electron hopping in the presence of Cooper pairing:

Coulomb self-energy:

$$E_c = e^2/2C_0$$

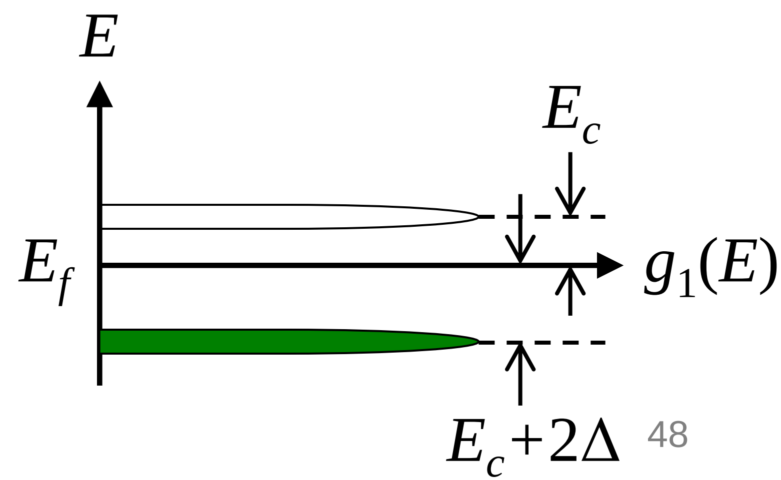
energy required for hop:

$$2E_c + 2\Delta$$



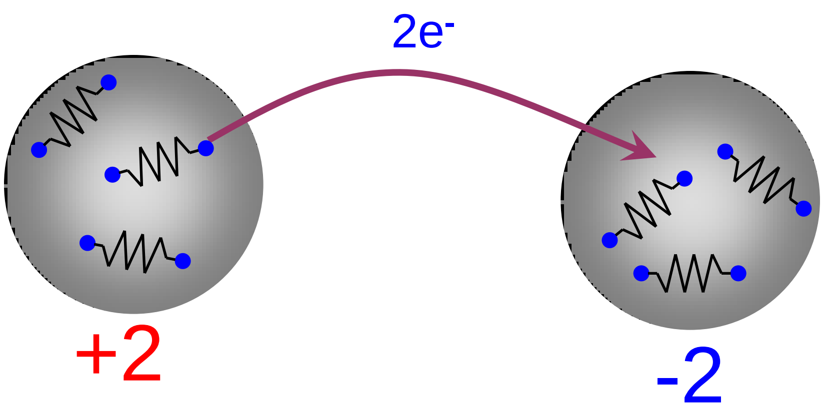
localization length ξ_1

single electron density of ground states:



Electron pair hopping

hopping of Cooper pairs:



localization length ξ_2

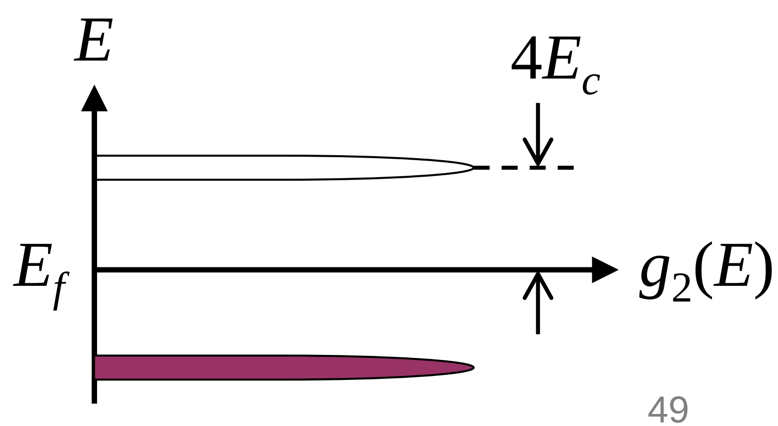
Coulomb self-energy:

$$(2e)^2/2C_0 = 4E_c$$

energy required for hop:

$$2 \times 4E_c$$

pair density of ground states:



DOGS - results

singles

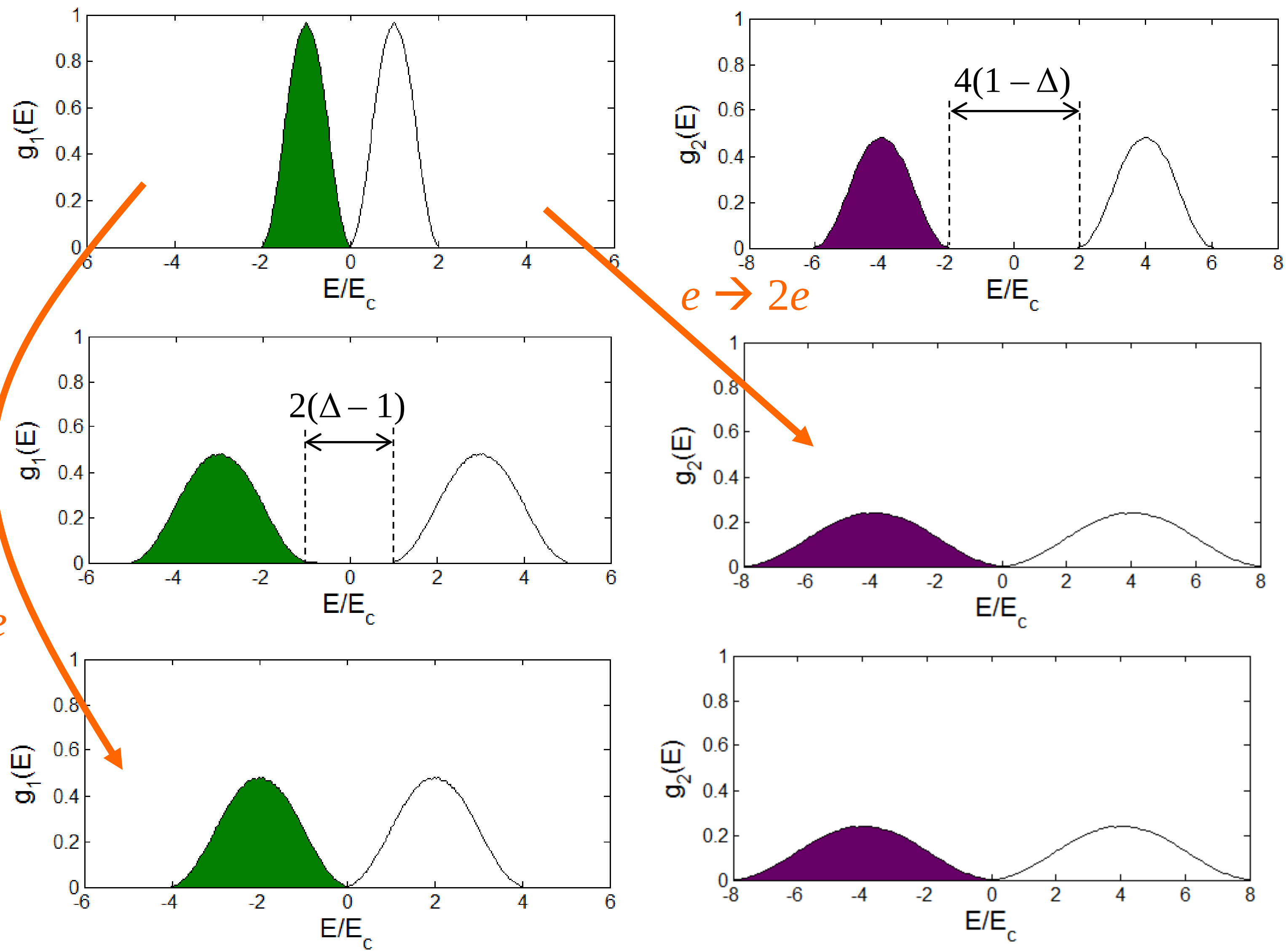
pairs

$\Delta = 0$:

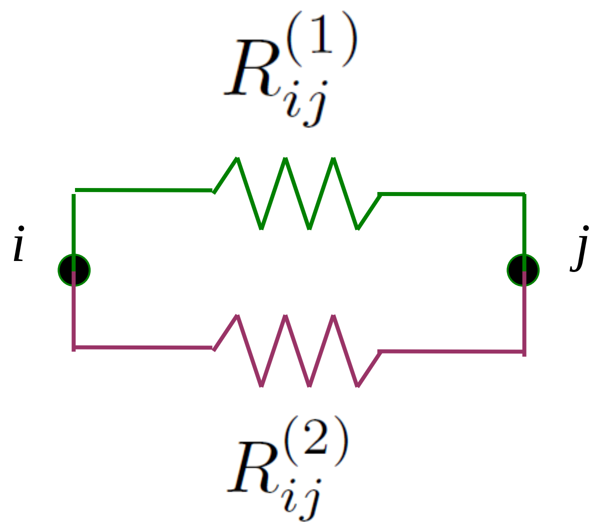
$\Delta = 2E_c$:

$e \to \sqrt{2}e$

$\Delta = E_c$:



Miller-Abrahams network for singles and pairs



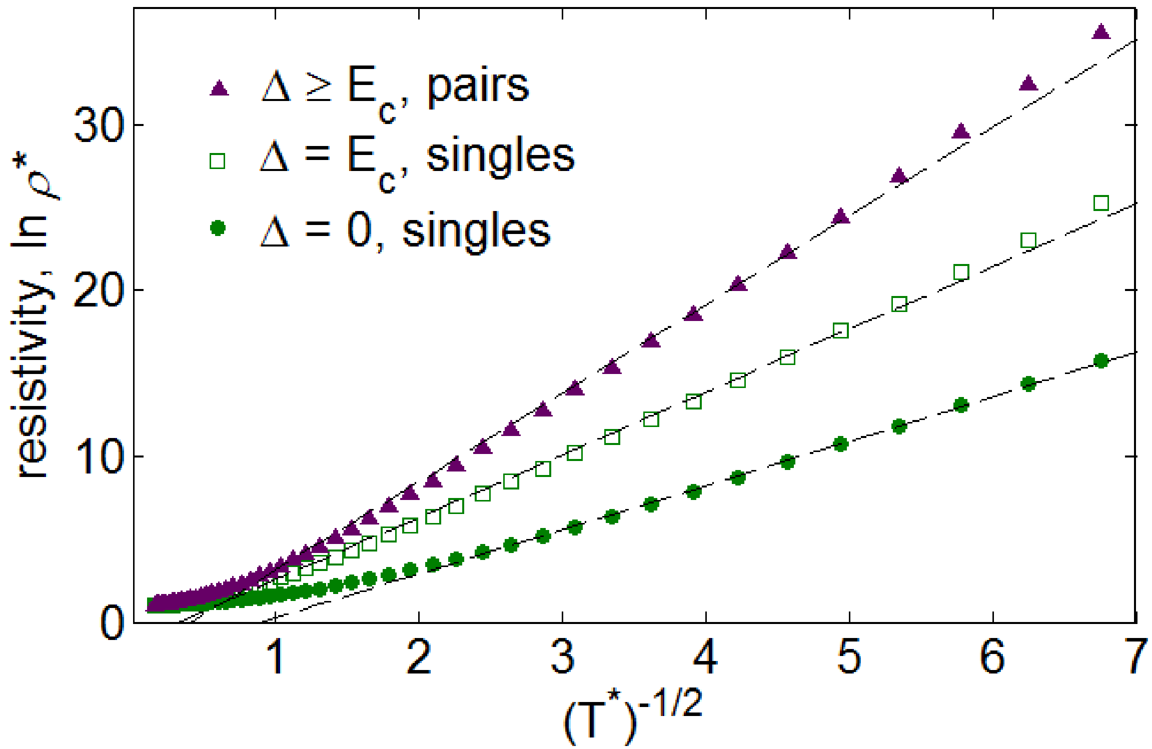
$$R_{ij}^{(1)} = R_0 \exp\left[\frac{2r_{ij}}{\xi_1} + \frac{\Delta E_{ij}^{(1)}}{k_B T}\right]$$

$$R_{ij}^{(2)} = R_0 \exp\left[\frac{2r_{ij}}{\xi_2} + \frac{\Delta E_{ij}^{(2)}}{k_B T}\right]$$

- **ϱ_1 is the percolating resistance of the singles network.**
- **ϱ_2 is the percolating resistance of the pair network.**
- **ϱ is the percolating resistance of the parallel network.**

Effective charges in hopping transport

ES hopping: $\rho \propto \exp\left[\left(\frac{T_{ES}}{T}\right)^{1/2}\right]$



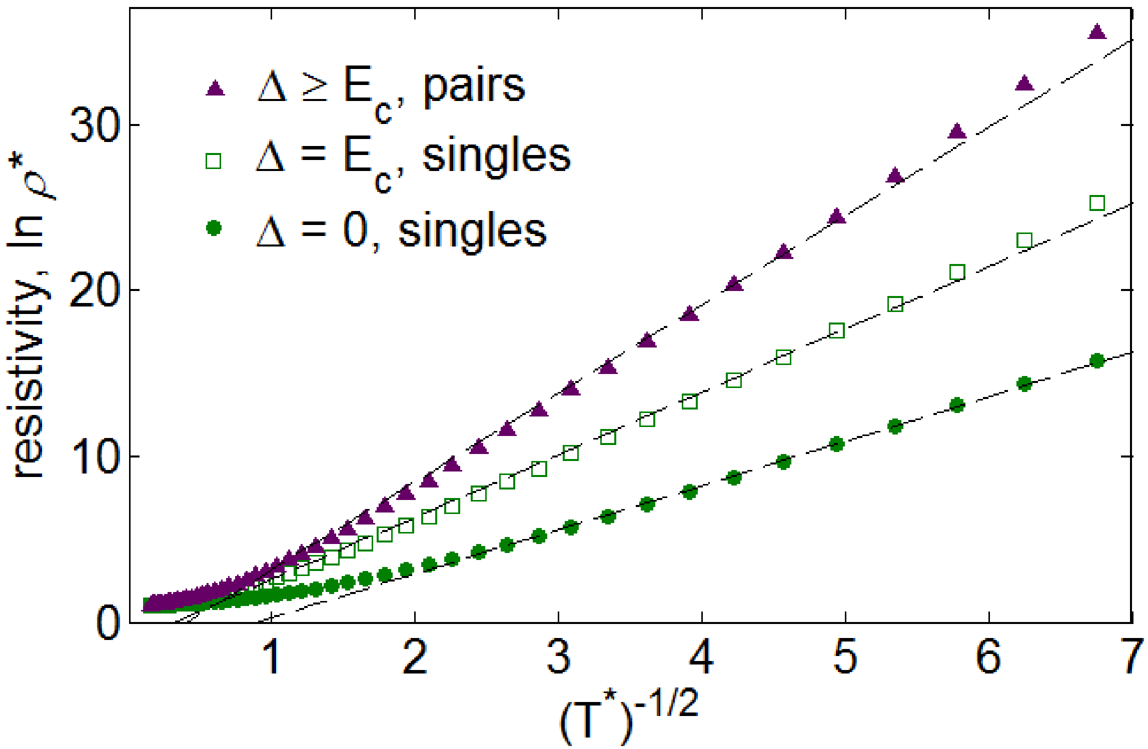
$$\ln \rho^* = \frac{\xi}{2D'} \ln(\rho / \rho_0)$$

$$T^* = \frac{2Dk_B T}{E_c \xi}$$

Effective charges in hopping transport

ES hopping: $\rho \propto \exp\left[\left(\frac{T_{ES}}{T}\right)^{1/2}\right]$

Slope gives $T_{ES} = C\,\frac{e^2}{\kappa\xi}$

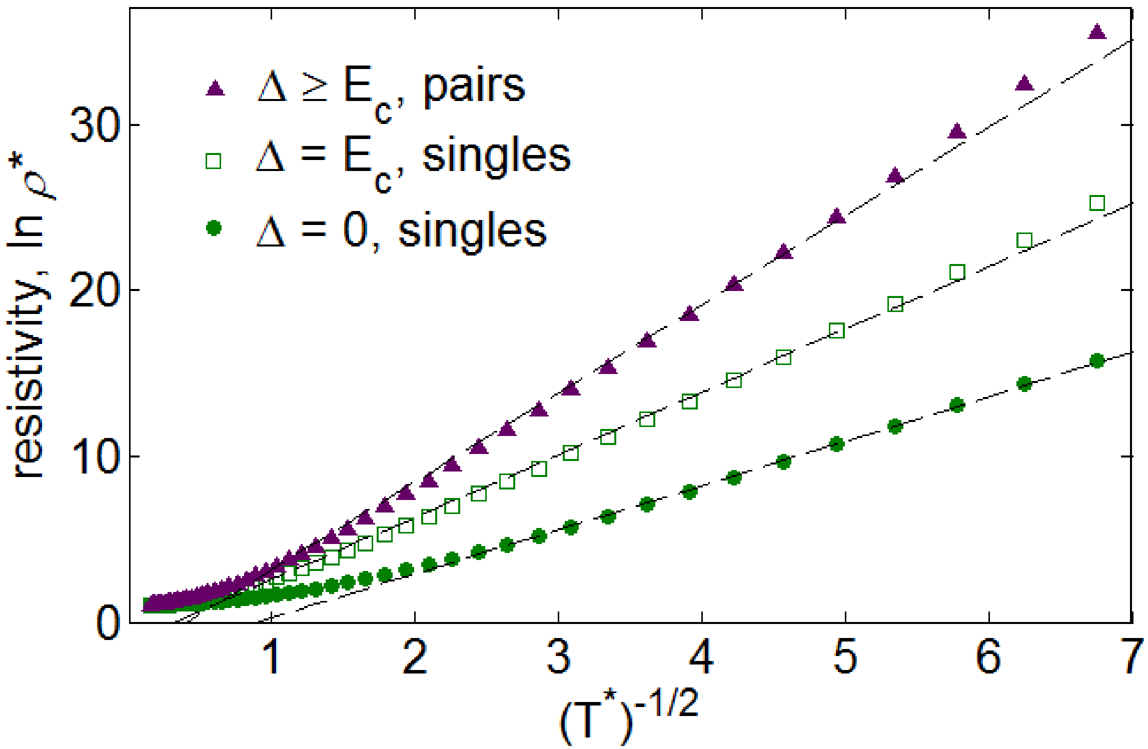


$\ln\rho^* = \frac{\xi}{2D'}\ln(\rho/\rho_0)$

$T^* = \frac{2Dk_BT}{E_c\xi}$

Effective charges in hopping transport

ES hopping: $\rho \propto \exp\left[\left(\frac{T_{ES}}{T}\right)^{1/2}\right]$ Slope gives $T_{ES} = C\frac{e^2}{\kappa\xi}$



$e^* = 2e$

$e^* = \sqrt{2}e$

$e^* = e$

$$\ln\rho^* = \frac{\xi}{2D'}\ln(\rho/\rho_0)$$

$$T^* = \frac{2Dk_BT}{E_c\xi}$$

Magnetoresistance

Superconducting gap is reduced by a transverse field:

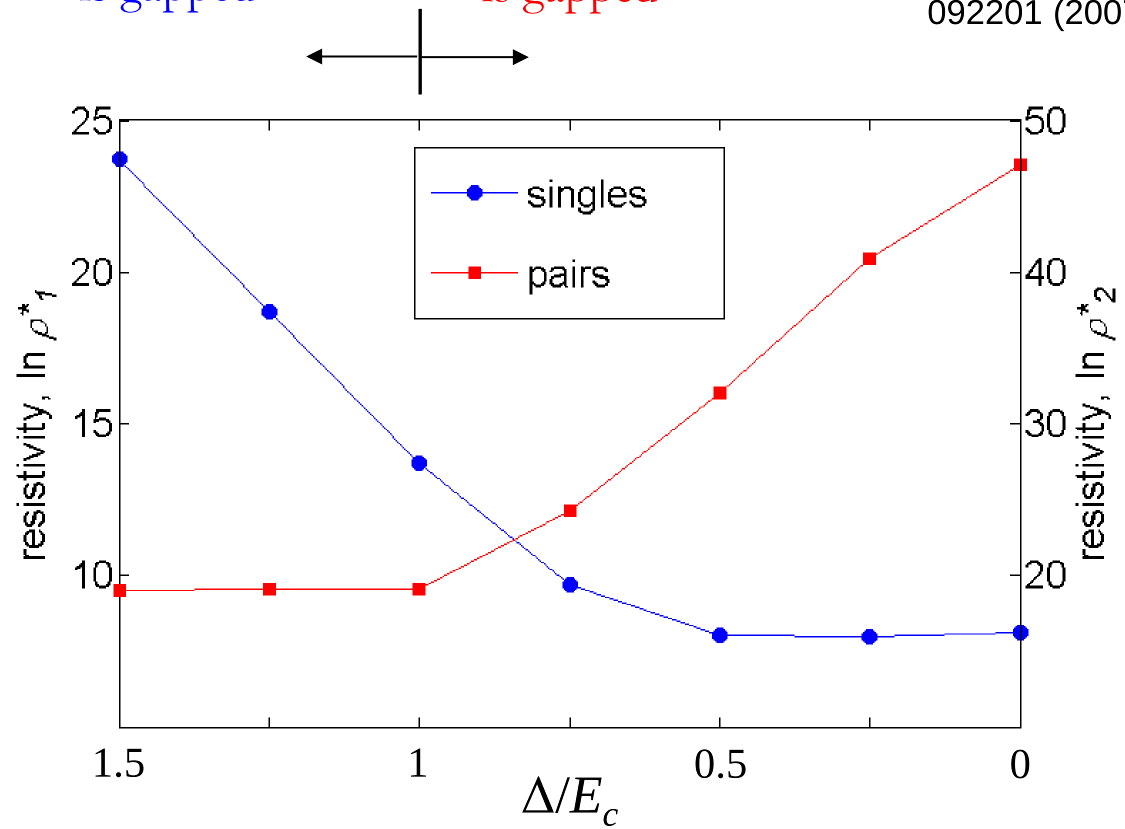
(For example, Zeeman effect:

$\Delta = \Delta_0 \sqrt{1-(B/B_c)^2}$)

single e^- hopping is gapped

pair hopping is gapped

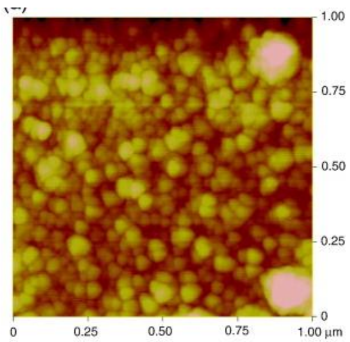
[Lopatin and Vinokur, PRB **75**, 092201 (2007)]



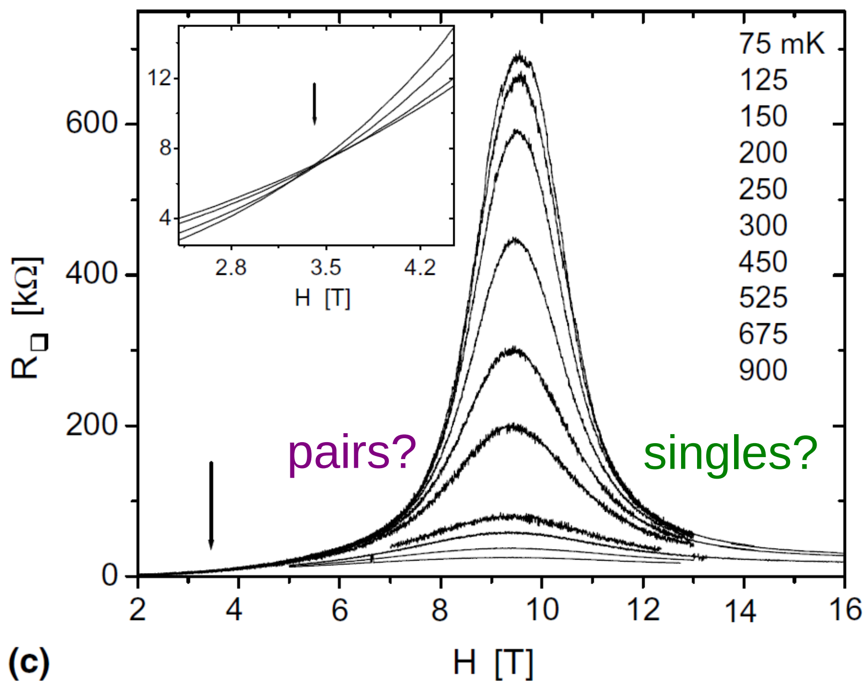
increasing magnetic field: →

MR peak: single versus pair conduction?

granular InOx:

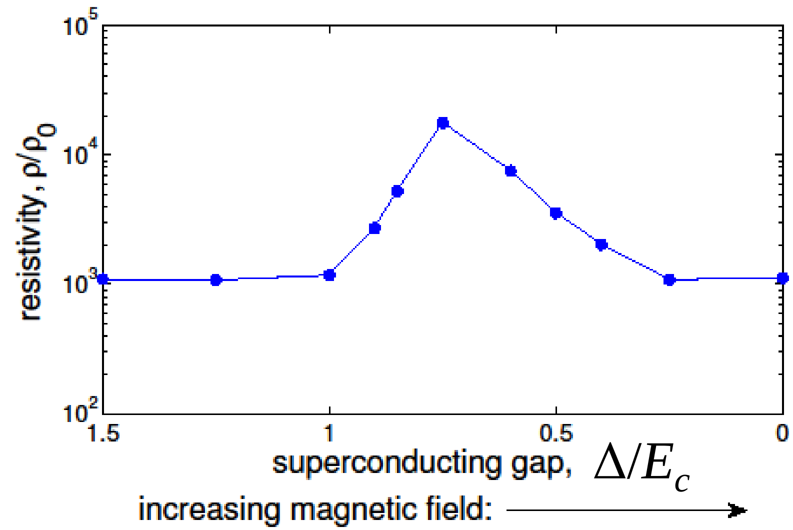


[Thin Solid Films **520**, 1242 (2010)]



[Steiner and Kapitulnik, Physica C **422**, 16 (2005)]

In principle, our model can produce a MR peak :



$\xi_1 = D'$ $\qquad k_BT = 0.1\ E_c$

$\xi_2 = 10D'$

...but is not a satisfactory explanation of experiment