Charge and energy transport in films of touching nanocrystals

Kostya Reich, Han Fu, Boris Shklovskii

University of Minnesota
Touching nanocrystals

Houtepen group, ACS Nano (2014)

Touching nanocrystals

How many electrons make a semiconductor nanocrystal film metallic?

How excitons hop between semiconductor nanocrystals?
How many electrons make bulk semiconductor metallic?

Mott criterion

\[ n_M a_B^3 \approx 0.02 \]
Metal insulator transition

In bulk Si

\[ n^{-1/3} \]

In touching Si "metallic" nanocrystals

\[ n \simeq 3 \times 10^{18} \text{ cm}^{-3} \]

\[ n_M a_B^3 \simeq 0.02 \]

\[ n_c \rho^3 \simeq 0.3 \]

\[ n_c \simeq 5 \times 10^{20} \text{ cm}^{-3} \]
Metallic connection

\[ G = \frac{1}{R} > \frac{e^2}{\hbar} \]

\[ \frac{\hbar}{RC} > \frac{e^2}{C} \]
Sharvin conductance

$G = \frac{e^2}{\hbar} \left( \frac{\rho}{\lambda} \right)^2$

$\lambda \approx n^{-1/3}$

Sharvin (1965)
Approaching metal-insulator transition from the metallic side

\[ G_c = \frac{e^2}{\hbar} \]

\[ G = \frac{e^2}{\hbar} \left( \frac{\rho}{\lambda} \right)^2 \]

\[ \rho \simeq \lambda \simeq n_c^{-1/3} \]

\[ n_c \simeq \frac{1}{\rho^3} \]
Approaching metal-insulator transition from insulator side

\[ n_M \ll n \ll n_c \]

\[ \rho \ll \lambda \]
Energy spectrum

$(2l+1)$-degenerate levels

\[ n, l \]

\[ \Delta = \frac{\hbar^2}{md^2} \]

\[ N = nd^3 \]

\[ \varepsilon_F = \frac{\hbar^2}{md^2} N^{2/3} = N^{2/3} \Delta \]

\[ \varepsilon_F = \frac{\hbar^2}{m \lambda^2} \]
Neutral nanocrystals with different numbers of donors:

\[ N + \sqrt{N} \]

\[ N - \sqrt{N} \]

\[ \delta \varepsilon_F = N^{1/6} \Delta \]
Charging of nanocrystals

$Q \sim \sqrt{N}$

+ Diameter variations
Wave functions of electrons inside a nanocrystal

\[ t \approx \frac{\hbar}{\tau} \approx \hbar \int j dS \approx \frac{\hbar^2}{m} \int \frac{d\psi}{dx} \psi dS \]
Evaluation of $t$

\[
\frac{d\Psi}{dx} \approx \frac{1}{\lambda^{3/2} d}
\]

\[
\Psi \approx \frac{\rho}{\lambda^{3/2} d}
\]

\[
t = \frac{\hbar^2}{m} \int \frac{d\Psi}{dx} \Psi dS = \frac{\hbar^2}{md^2} \left( \frac{\rho}{\lambda} \right)^3
\]
Calculating localization length

$$\Psi \sim \exp \left( -\frac{x}{\xi} \right)$$

$$\left( \frac{t}{\Delta} \right)^{x/d} \propto \exp \left( -\frac{x}{\xi} \right)$$

$$\xi \sim \frac{d}{\ln(\Delta/t)}$$

Transition happens at $$\Delta = t$$

$$\rho \sim \lambda \sim n_c^{-1/3}$$
Metal-insulator transition from insulator side

\[ G \sim \exp \left[ - \left( \frac{T_{ES}}{T} \right)^{1/2} \right] \]

\[ T_{ES} \sim \frac{e^2}{\xi(n)} \]

\[ \xi = \frac{d}{\ln \left( \frac{1}{n\rho^3} \right)} \]
Exciton hopping between nanocrystals

\[ E_c = \frac{e^2}{\kappa d} \quad E_c \gg T \]

\[ d \pm \alpha d \]

\[ t \ll \alpha \Delta \ll E_c \ll \Delta \]
p-n junction solar cell

\[ L_D \sim \sqrt{\frac{\tau_l}{\tau_h}} d \]

\( \tau_l \)-life time

\( \tau_h \)-hopping time
Experimental study: photoluminescence

\[ \frac{1}{\tau_h} \sim |M|^2 \]

Bayer et al., PRB (2015)
Forster transfer

\[ M_F = \frac{e^2 a_0^2}{\kappa d^3} \]

PbSe

orbitals Pb

orbitals Se

\[ a_0 \approx a \]
Forster troubles in direct semiconductors like PbSe

\[ \delta = \int \Psi_S^*(r_1, r_2) \frac{e^2}{|r_1 - r_2|} \Psi_S(r_1, r_2) d^3r_1 d^3r_2 \]

\[ \Psi_T(r_1 = r_2) = 0 \]

\[ a_0 \ll a \]
Forster troubles in Si and other indirect semiconductors: Forbidden dipole transition

$\alpha_0 \ll \alpha$
Forster alternative: Tandem tunneling

$MT = \frac{t^2}{E_c}$
Room temperature comparison

\[ M_T = \frac{t^2}{E_c} \]

\[ M_F = \frac{e^2 a_0^2}{\kappa d^3} \]

\[ \frac{\tau_T^{-1}}{\tau_F^{-1}} = \left( \frac{M_T}{M_F} \right)^2 = \left[ \frac{\Delta}{E_c a_0} \left( \frac{\rho}{d} \right)^3 \right]^4 \]
Dexter transfer

\[ M_D = \int \Psi^L(r_1) \Psi^R(r_2) V(r_1, r_2) \Psi^R(r_1) \Psi^L(r_2) d^3r_1 d^3r_2. \]

\[ V(r_1, r_2) = 0 \]

\[ V(r_1, r_2) = E_c \]
Comparison

\[ M_T = \frac{t^2}{E_c} \quad M_D = E_c \left( \frac{t}{\Delta} \right)^2 \]

\[ \frac{\tau_T^{-1}}{\tau_D^{-1}} = \left( M_T M_D \right)^2 = \left( \frac{\Delta}{E_c} \right)^4 \gg 1 \]