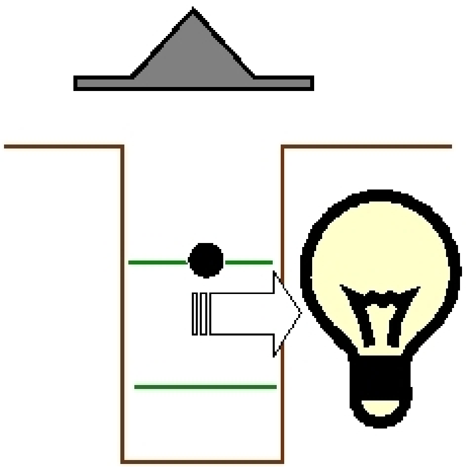
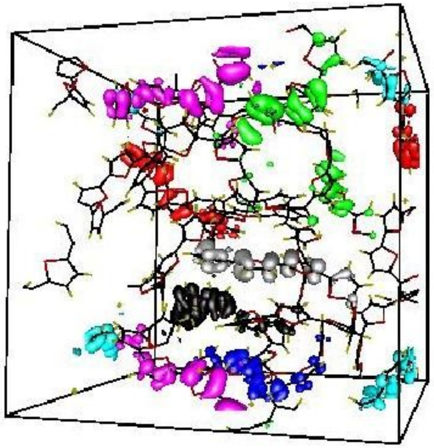
Electronic structure and transport in semiconducting materials





Nenad Vukmirović
Scientific Computing Laboratory
Institute of Physics Belgrade

Institute of Physics Belgrade, 18 November 2010

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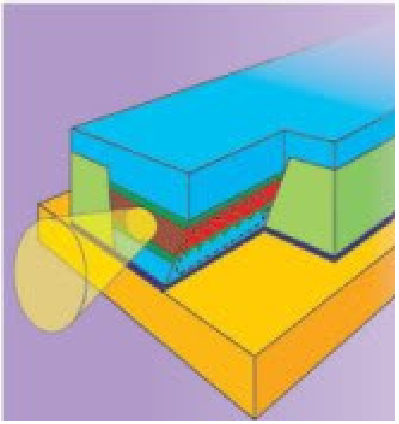
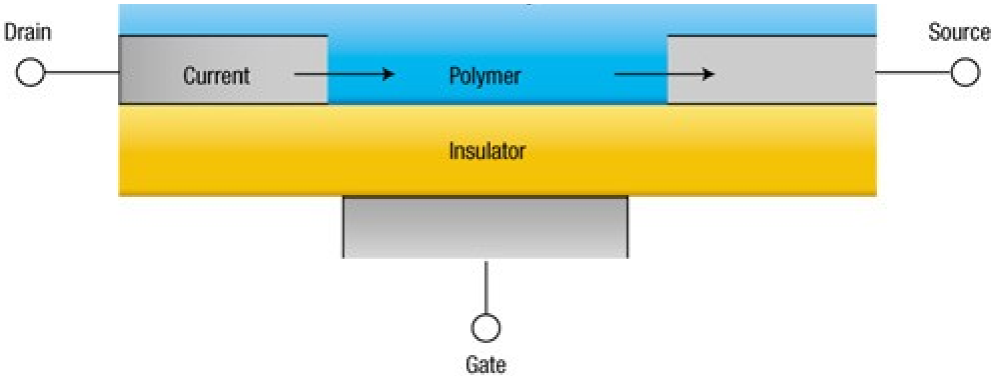
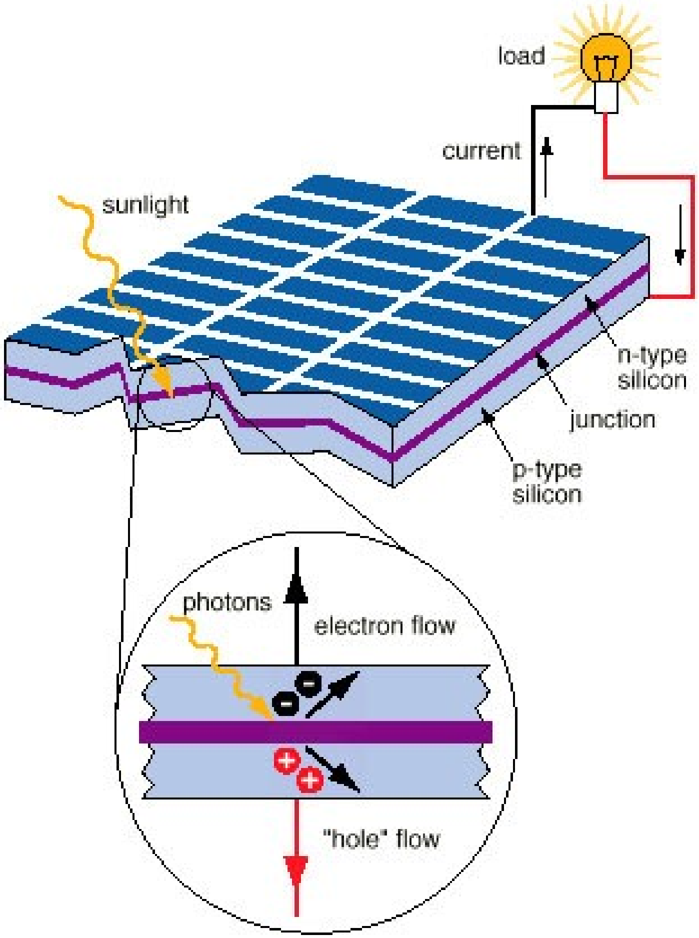
Examples of electrical and optical devices



T. Aellen et al, APL 83, 1929 (2003)



J. Janata et al, Nature Mat. 2, 19 (2003)



http://www.esdalcollege.nl/eos/vakken/na/zonnecel.htm

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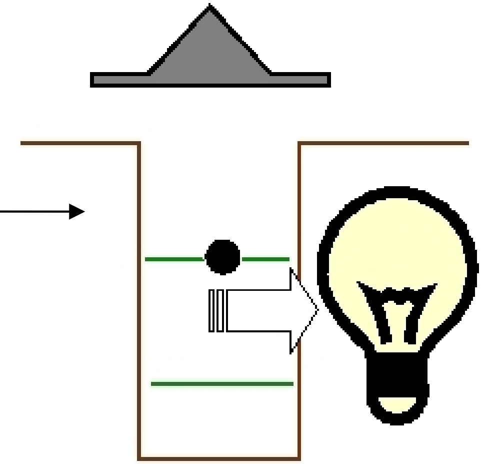
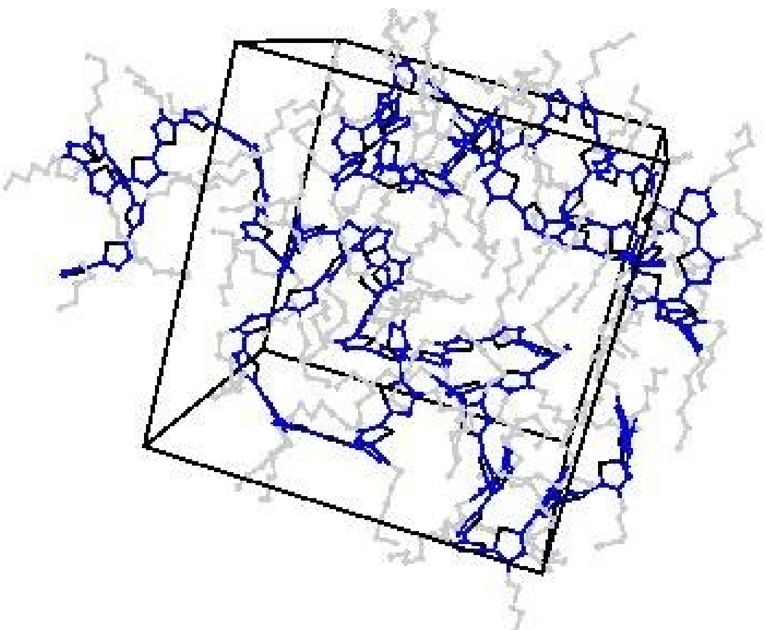
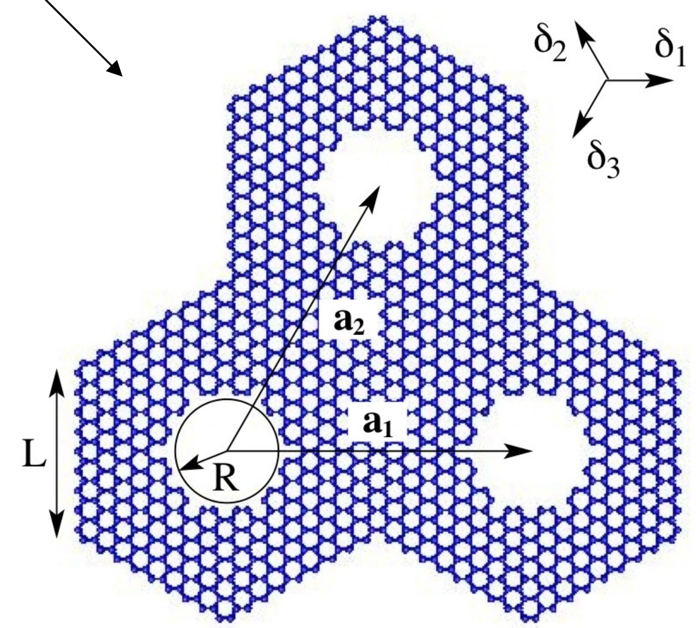
Overview of the talk



Methods for electronic structure and electronic transport





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Methods for electronic structure and electronic transport

Density functional theory

- Many electron problem can be reduced to a set of single particle problems (Kohn-Sham equations)

$$[-\frac{\hbar^2}{2m_0}\nabla^2 + V_{ion} + V_H + V_{xc}(\varrho)]\psi_i = \varepsilon_i \psi_i$$

where V_H is the Hartree potential:

$$V_H(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0}\int d\mathbf{r}' \frac{\varrho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

ρ the electronic charge density:

$$\varrho = -e\sum_{occ}|\psi_i|^2$$

and $V_{xc}(\rho)$ the exchange correlation potential that has to be approximated (for example local density approximation)

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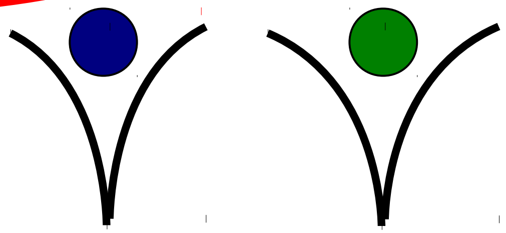
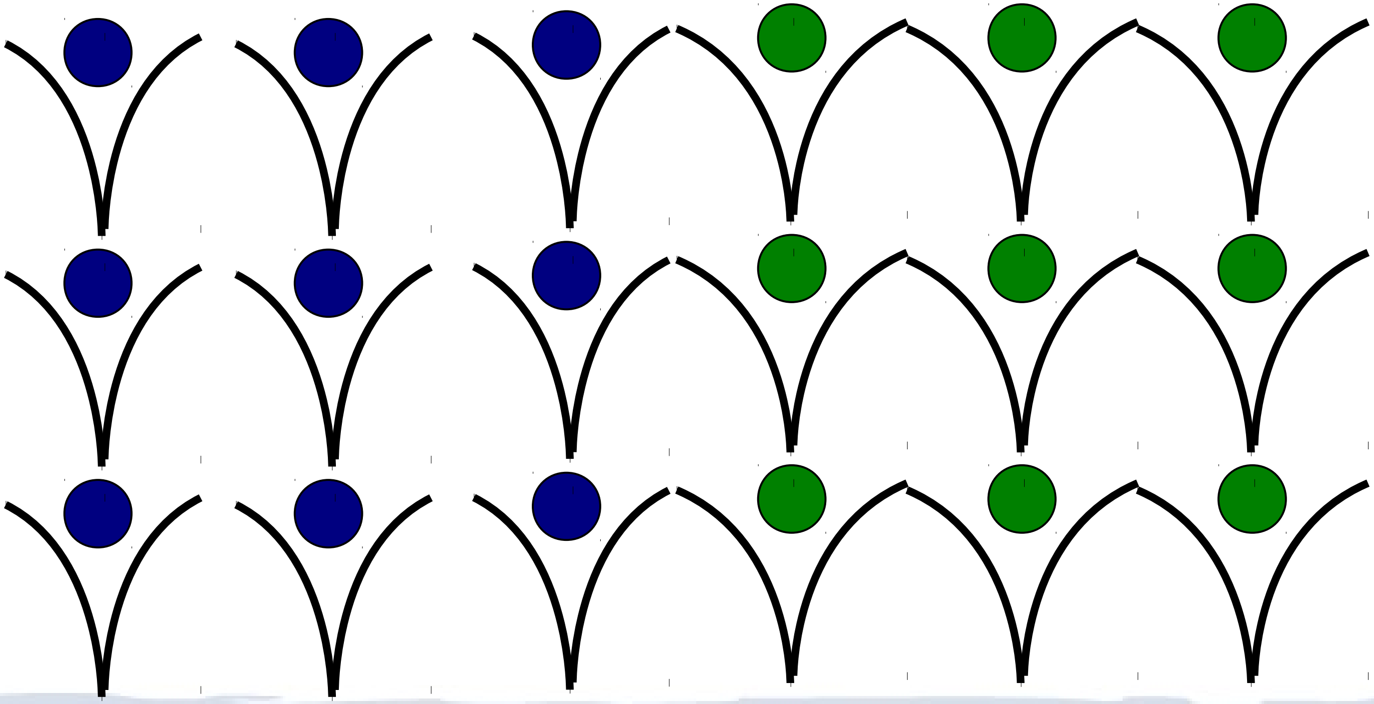
Empirical pseudopotential method

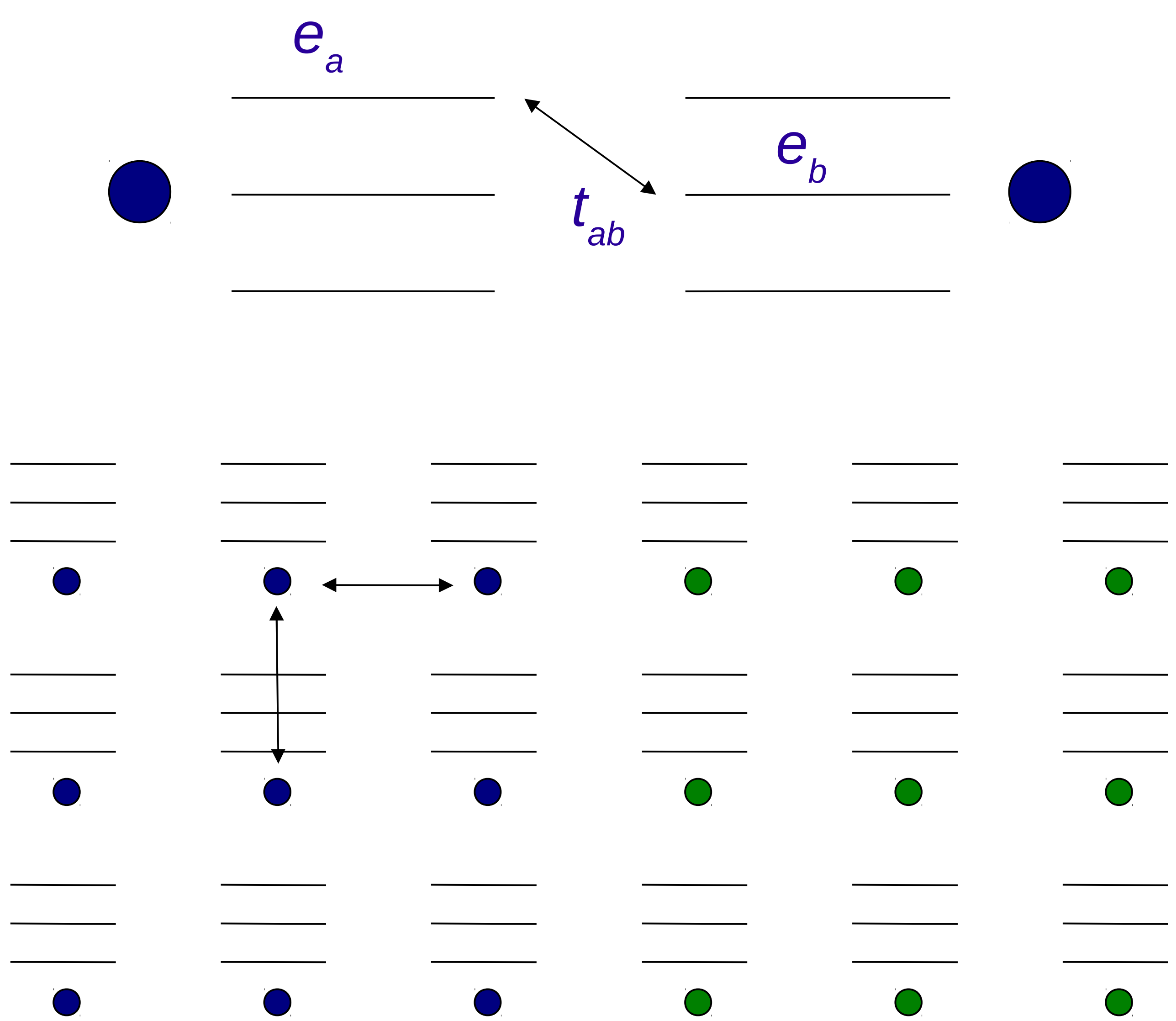
$$[-\frac{\hbar^2}{2m_0}\nabla^2 + V_{ion} + V_H + V_{xc}(\varrho)]\psi_i = \varepsilon_i \psi_i$$

V_{EPP}





Tight-binding method



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Envelope function methods

$$\left(-\frac{\hbar^2}{2m_0}\nabla^2+V\right)\psi=E\psi$$

$$\psi(\mathbf{r})=\sum_n \phi_n(\mathbf{r})u_n(\mathbf{r})$$

Envelope function – slowly varying

Bloch function

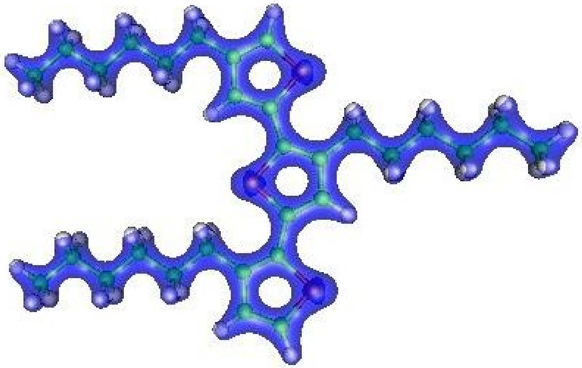
$$\left(-\frac{\hbar^2}{2m_{eff}}\nabla^2+V_{eff}\right)\phi=E\phi$$

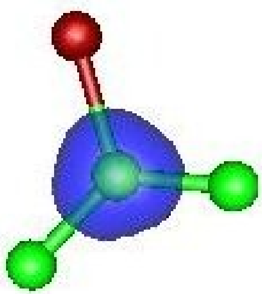
1-band (effective mass) method

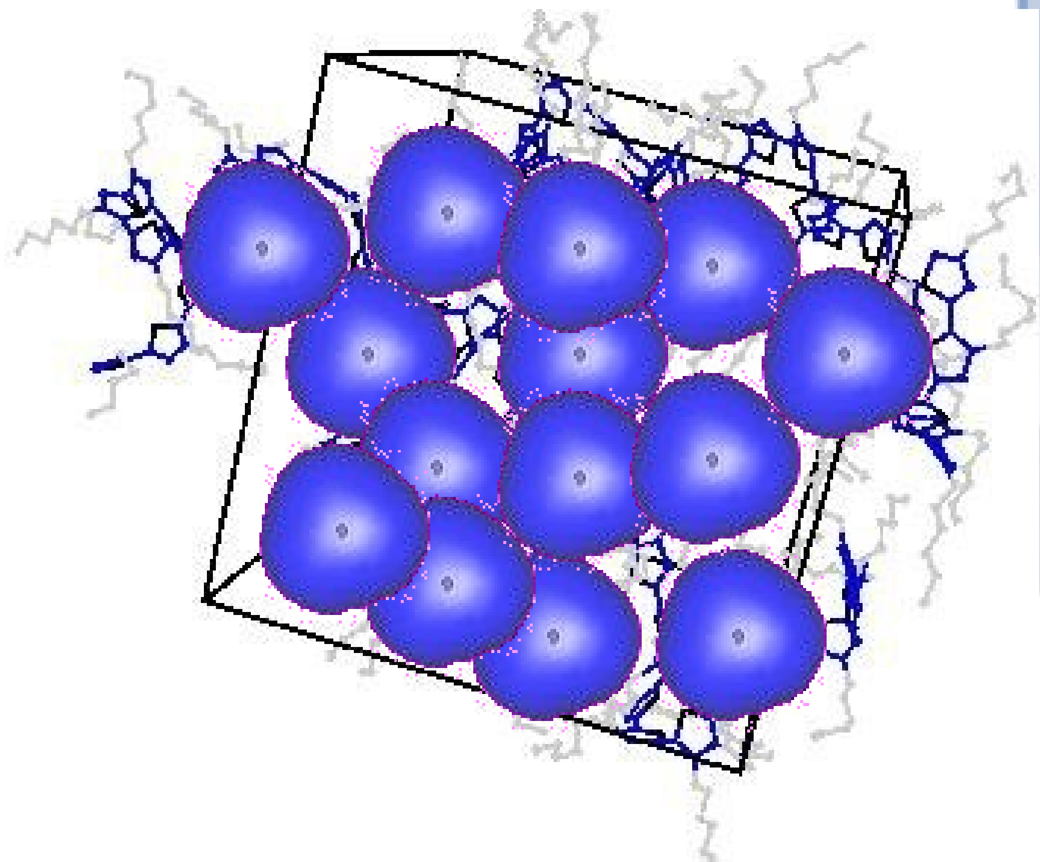
8-band kp for zincblende semiconductors

$$\begin{pmatrix} E_c+\frac{\hbar^2k^2}{2m_0} & Pk_x & Pk_y & Pk_z \\ Pk_x & E_v+\frac{\hbar^2k^2}{2m_0} & 0 & 0 \\ Pk_y & 0 & E_v+\frac{\hbar^2k^2}{2m_0} & 0 \\ Pk_z & 0 & 0 & E_v+\frac{\hbar^2k^2}{2m_0} \end{pmatrix}\begin{pmatrix}\phi_1(\mathbf{r})\\ \phi_2(\mathbf{r})\\ \phi_3(\mathbf{r})\\ \phi_4(\mathbf{r})\end{pmatrix}=E\begin{pmatrix}\phi_1(\mathbf{r})\\ \phi_2(\mathbf{r})\\ \phi_3(\mathbf{r})\\ \phi_4(\mathbf{r})\end{pmatrix}$$

Charge patching method







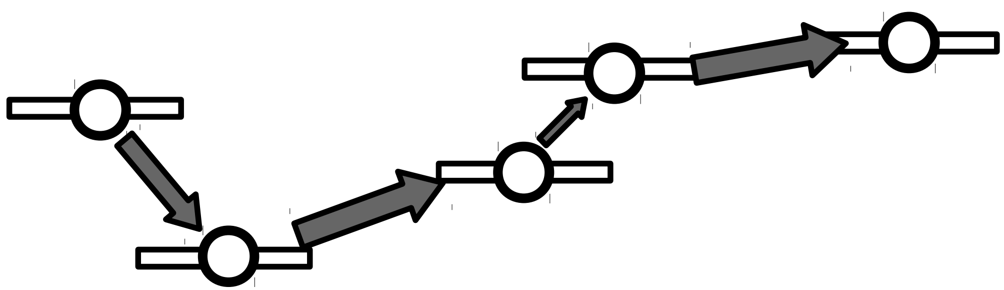
$$m_A(\boldsymbol{r}-\boldsymbol{R}_A)=\frac{w_A(\boldsymbol{r}-\boldsymbol{R}_A)}{\sum_B w_B(\boldsymbol{r}-\boldsymbol{R}_B)}\rho(\boldsymbol{r})$$

$$\rho_{patch}(\boldsymbol{r})=\sum_A m_A(\boldsymbol{r}-\boldsymbol{R}_A)$$

N. Vukmirović and L.-W. Wang, J. Chem. Phys. 128, 121102 (2008)

Methods for electronic transport

- $H = H_0 + H_{int}$
  - where H_0 is the single particle Hamitlonian
  - where H_{int} is the rest (external fields, phonons, impurities,...)
- Semiclassical (Boltzmann) approach $\langle a_\alpha^+(t_1) a_\alpha(t_1) \rangle$



- Density matrix approach
  - central quantities are coherences $\langle a_\alpha^+(t_1) a_\beta(t_1) \rangle$
- Nonequilibrium Green's functions approach
  - central quantities are Green's functions $\langle a_\alpha^+(t_1) a_\beta(t_2) \rangle$

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Treatments of e-ph interaction

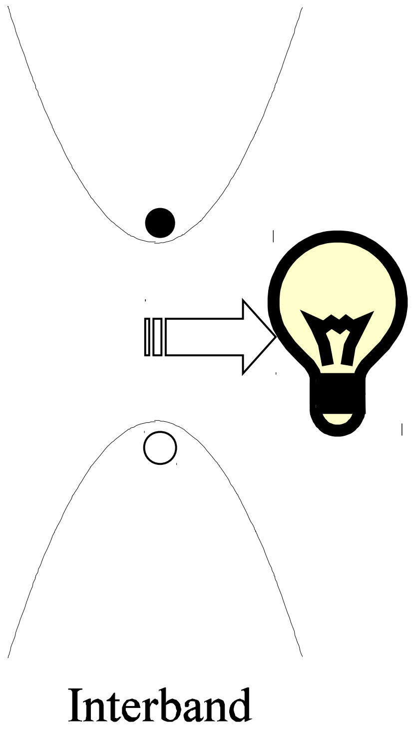
- Atomistic methods
  - e-ph coupling constants can be obtained from the change in single particle Hamiltonian due to displacements of atoms
    - can be extremely computationally expensive

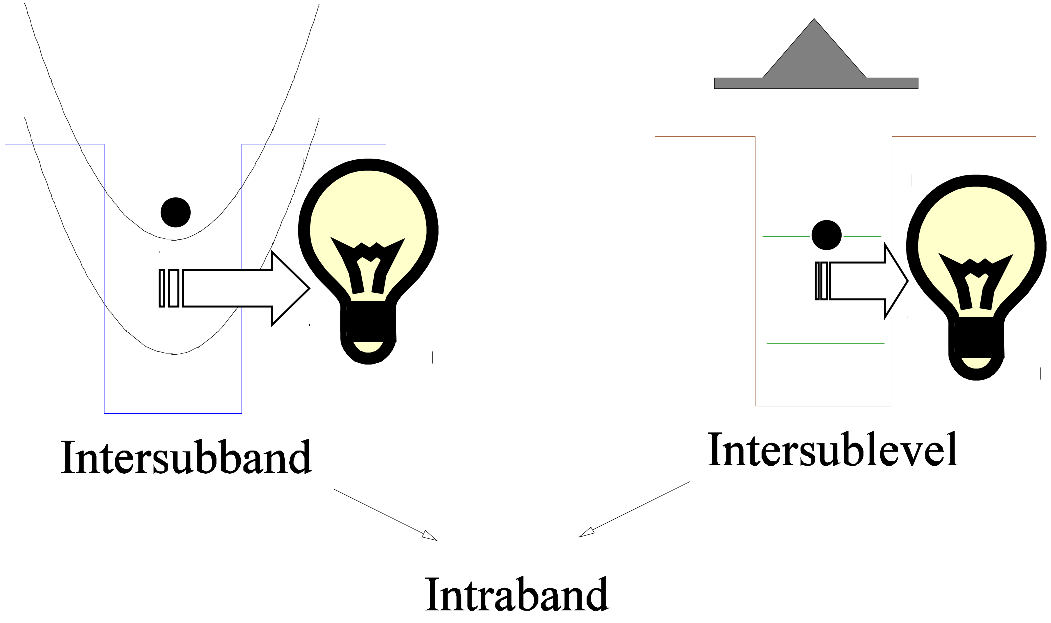
- Models for e-ph interaction in inorganic semiconductor nanostructures:
  - approximation that the e-ph interaction Hamiltonian is the same as in bulk
  - consideration of phonon confinement effects – continuum model for phonons

Intraband quantum dot optoelectronic devices

Interband and intraband transitions

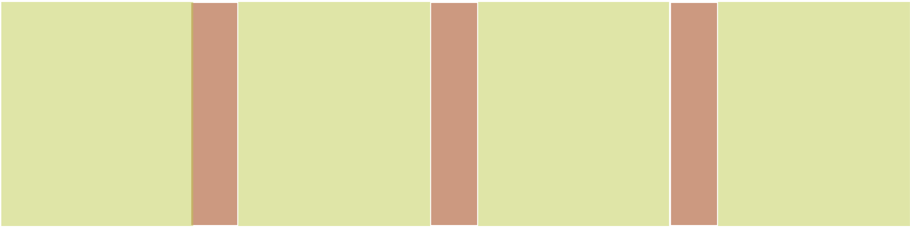
- Interband transitions
  - between conduction and valence band
  - visible, UV, NIR
- Intraband transitions
  - within the conduction (or valence) band
  - NIR, MIR, FIR (THz)



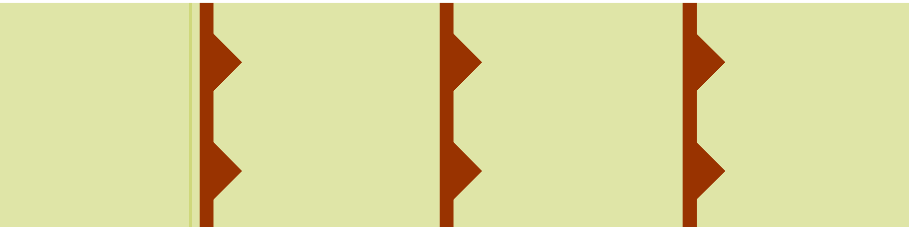


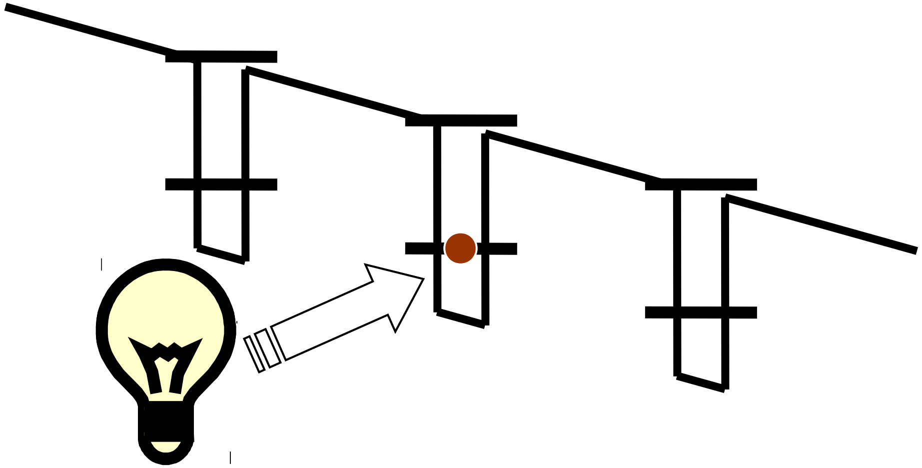
Quantum well and quantum dot intraband optoelectronic devices (1)

- Quantum well infrared photodetectors (QWIPs)
  - realized in mid 1980s



- Quantum dot infrared photodetectors (QDIPs)
  - realized in mid 1990s

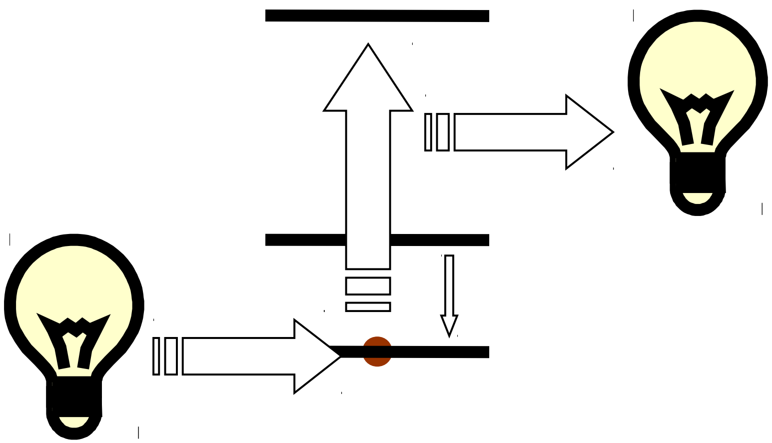


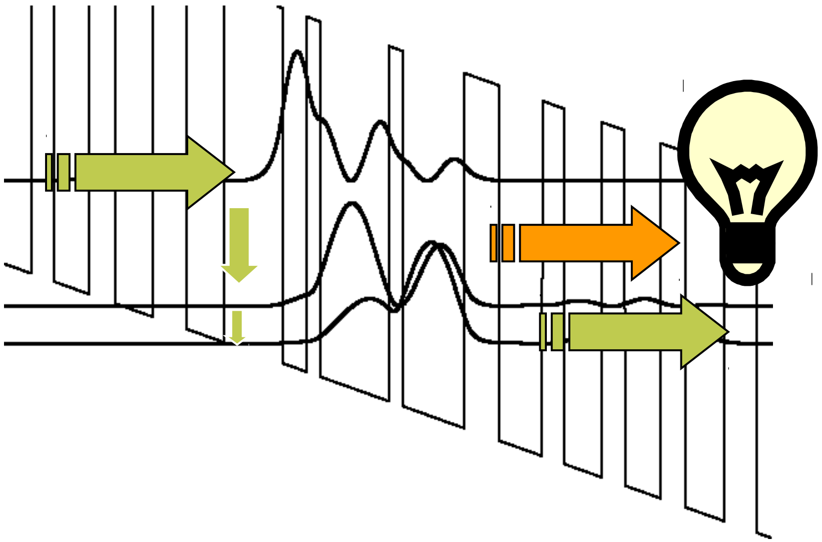


Quantum well and quantum dot intraband optoelectronic devices (2)

- Optically pumped lasers based on quantum wells
  - realized in 1997

- Quantum cascade lasers based on quantum wells
  - realized in 1994





- Optically pumped lasers based on quantum dots
  - not realized yet

- Quantum cascade lasers based on quantum dots
  - not realized yet

Why quantum dot intraband devices ?

- Self-assembled quantum dots – high dot density, D~15-30nm, h~3-7nm, energy levels spacing ~30-60 meV.

- A fully discrete spectrum
  - reduced phase space for relaxation processes.

- Consequences for device characteristics
  - lower dark current in QDIPs:
    - room temperature operation of QDIPs demonstrated.
      - Bhattacharya et al., APL 86 191106 (2005); Lim et al., APL 90 131112 (2007)
  - lower threshold in lasers expected:
    - demonstrated in QCLs in magnetic field.

- However: difficult to engineer QDs, i.e. produce the dots of desired size, shape and composition.

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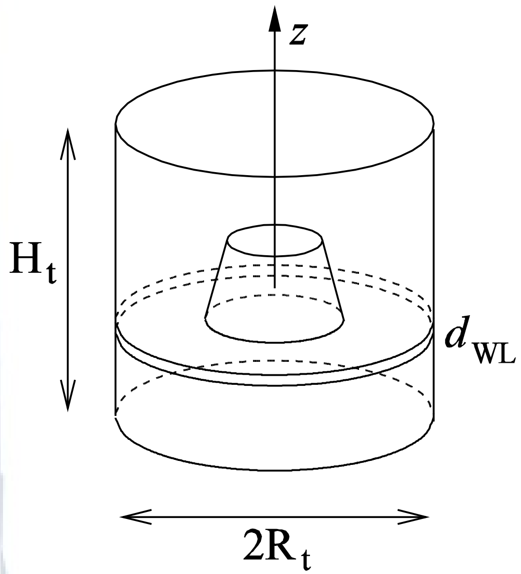
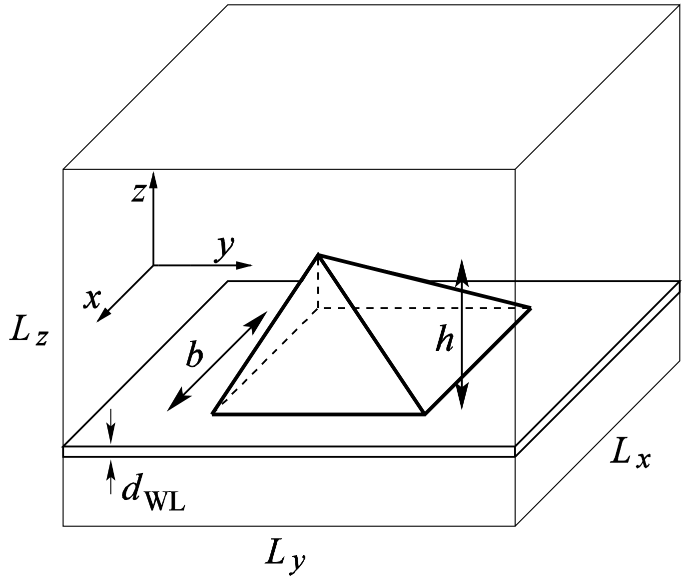
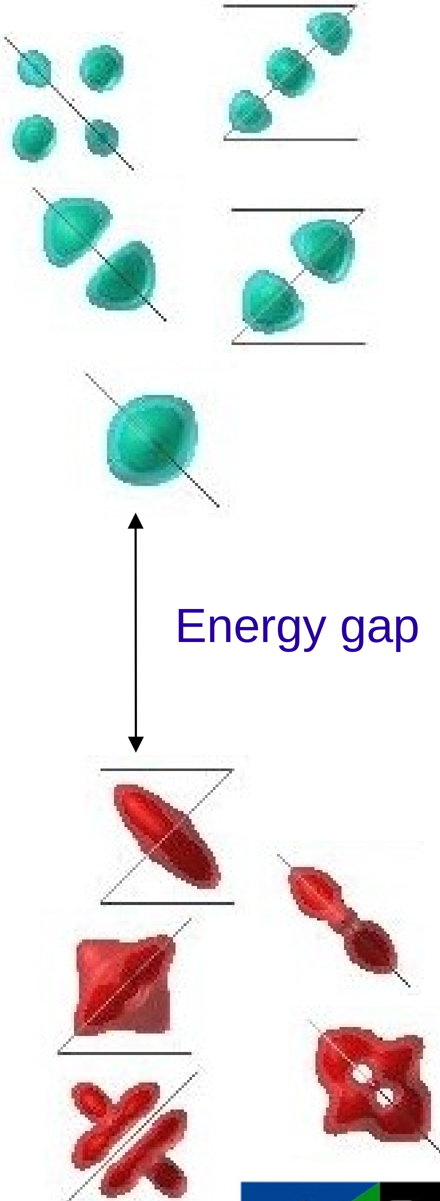
Electronic structure of QDs

- 8-band kp method

- Symmetry used to reduce the computational effort.



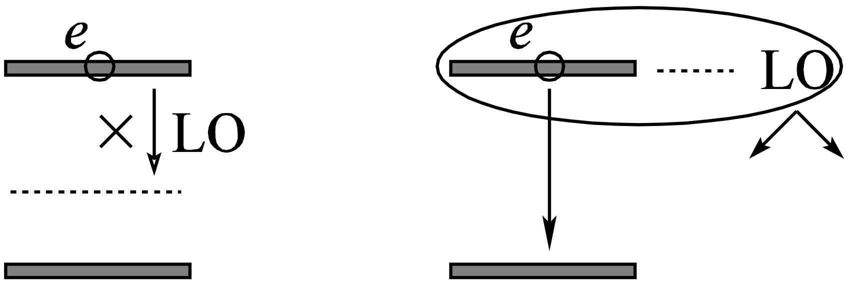




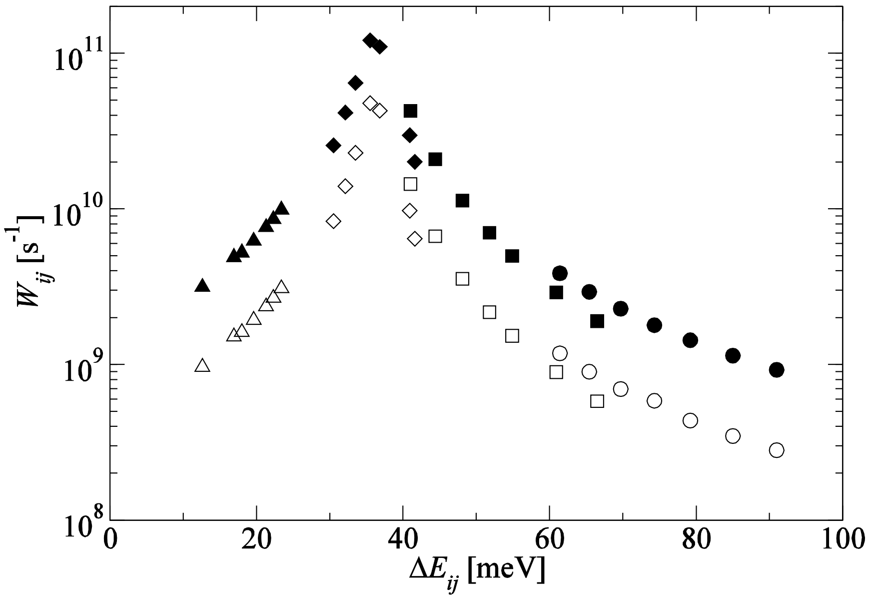
N. Vukmirović et al, PRB 72, 075356 (2005).

Carrier transition rates in QDs

- Interaction with LO phonons
  - Fermi's golden rule not applicable.
  - transition rate determined by anharmonic decay of an LO phonon.



- Interaction with LA phonons
  - weaker, treated within Fermi's golden rule.
  - important only for small ΔE.
- Interaction with EM radiation
  - Dipole approximation + Fermi's golden rule



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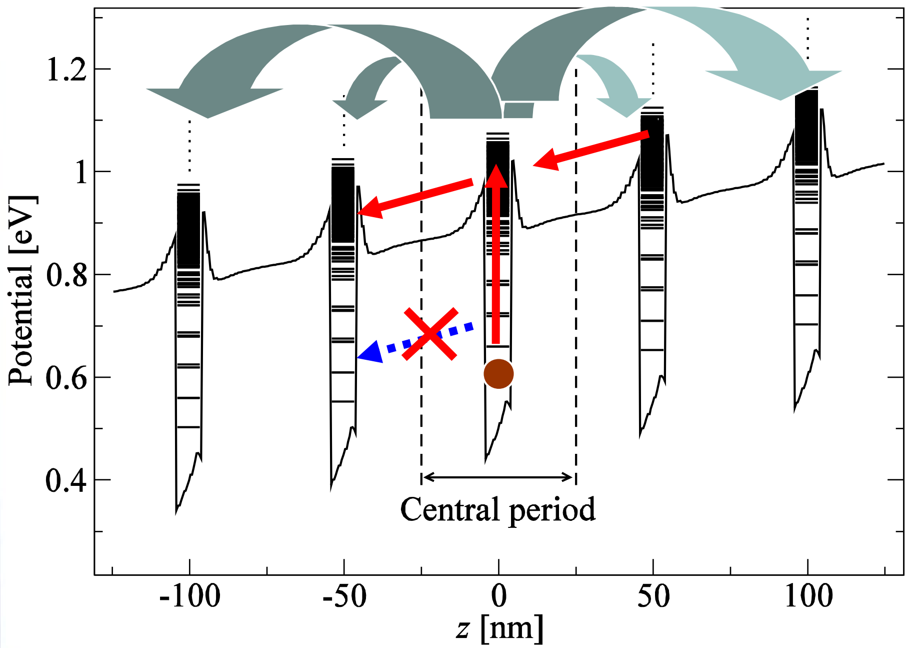
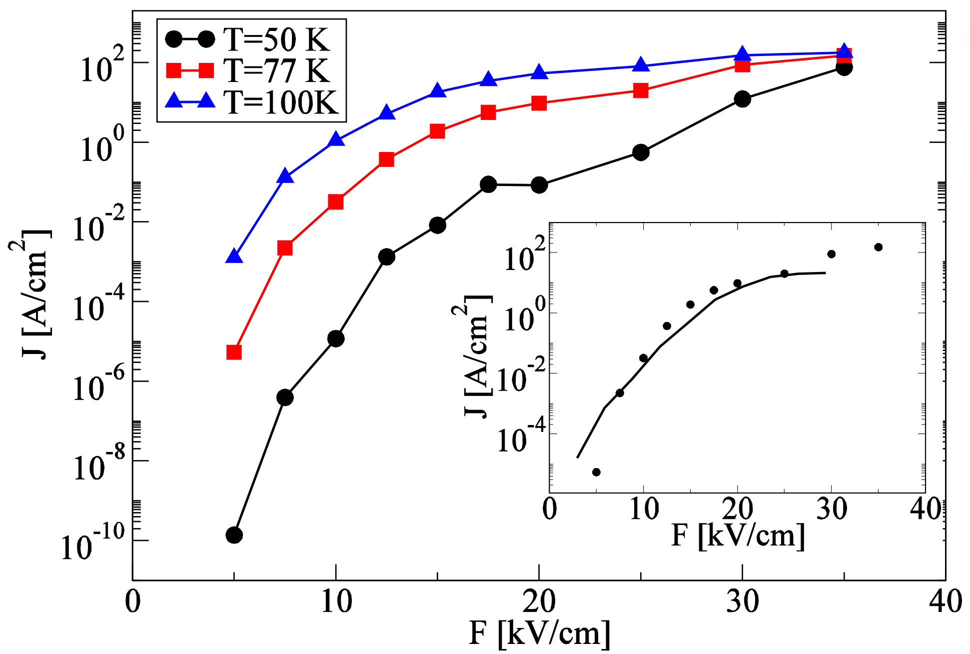
Transport in QDIPs – dark current

- Current calculated by considering all intra- and inter-period transition rates.



- Transport channels causing the increase in dark current were identified.



- Inset: comparison with exp. results of Chen et al, JAP 89, 4558 (2001).

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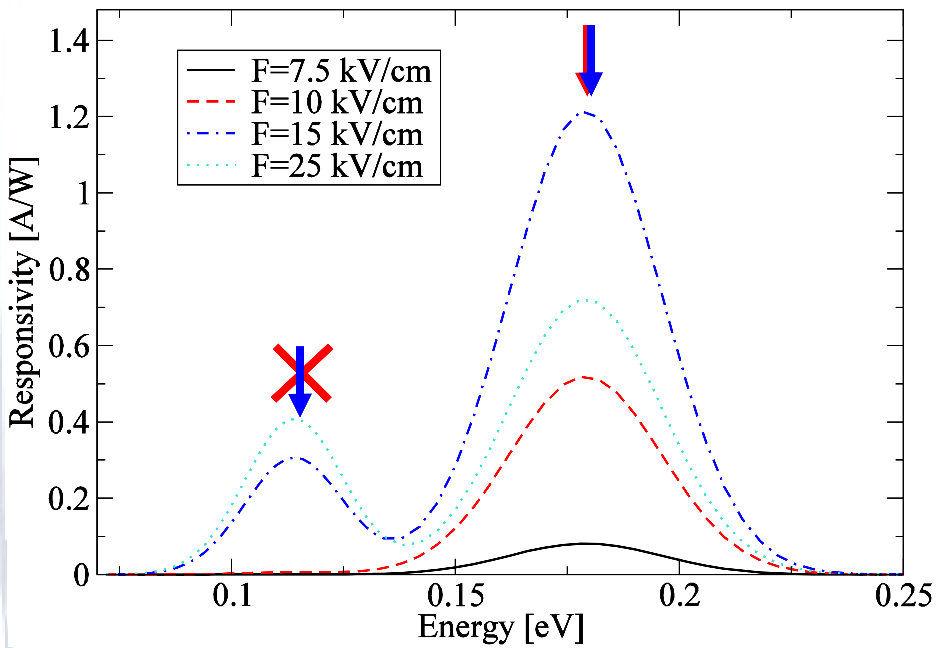
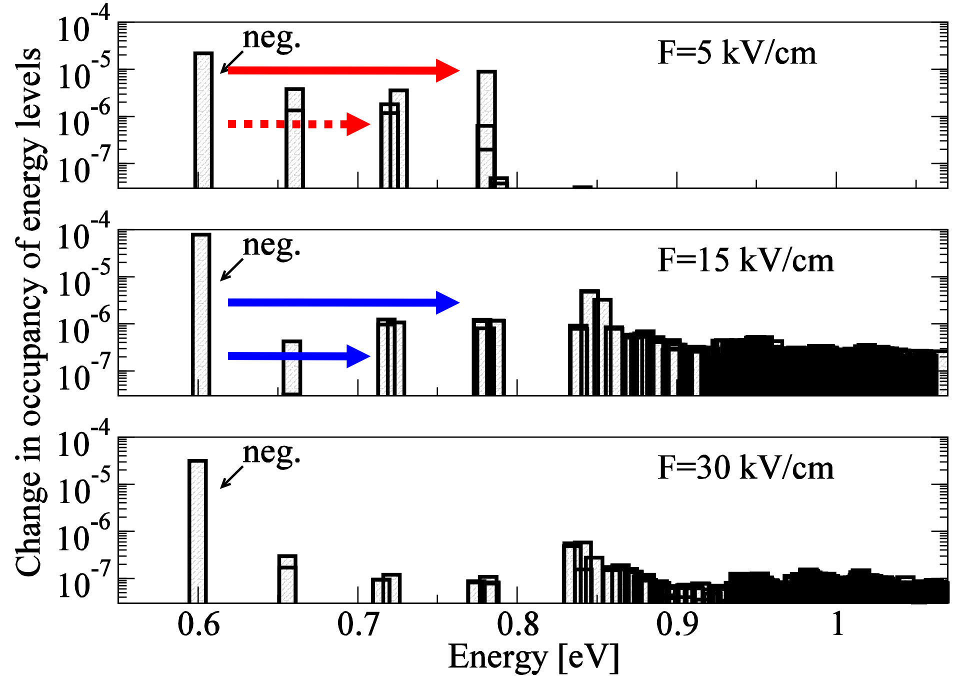
Transport in QDIPs – responsivity

- Appearance of peak at smaller energies and the drop of responsivity at higher voltages predicted in agreement with experiment.
- Calculated values of responsivity are overall consistent with experimental results.



Responsivity at 77K.



Change of populations at 77K and $\Phi=10^{24}cm^{-2}s^{-1}$.

N. Vukmirović et al, JAP 100, 074502 (2006).

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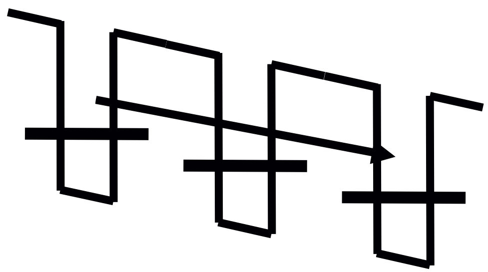
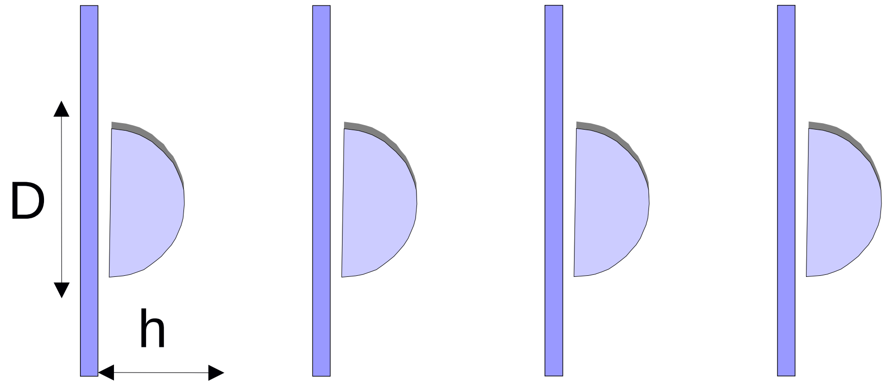
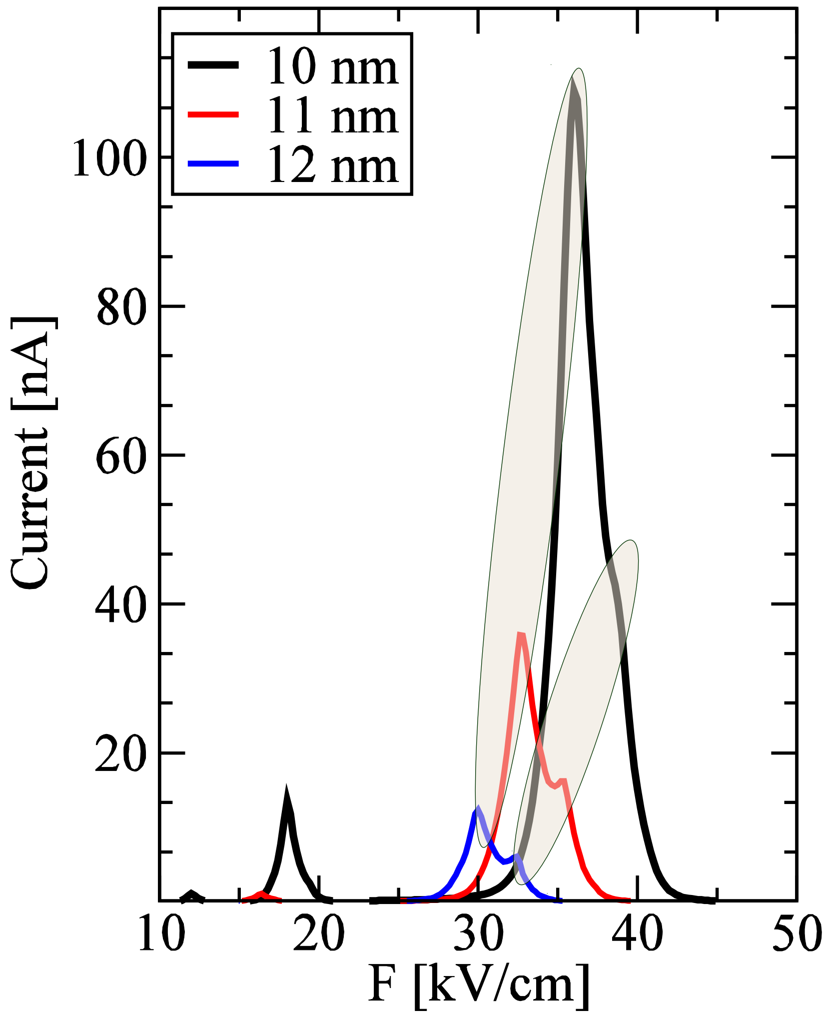
Transport in QD cascades

- NEGF simulation with interaction with LO and LA phonons.
- InAs/GaAs lens-shaped QDs, D=20nm, h=5nm, T=77K.
- Transport takes place through QD ground states.







N. Vukmirović et al, PRB 72, 075356 (2007).

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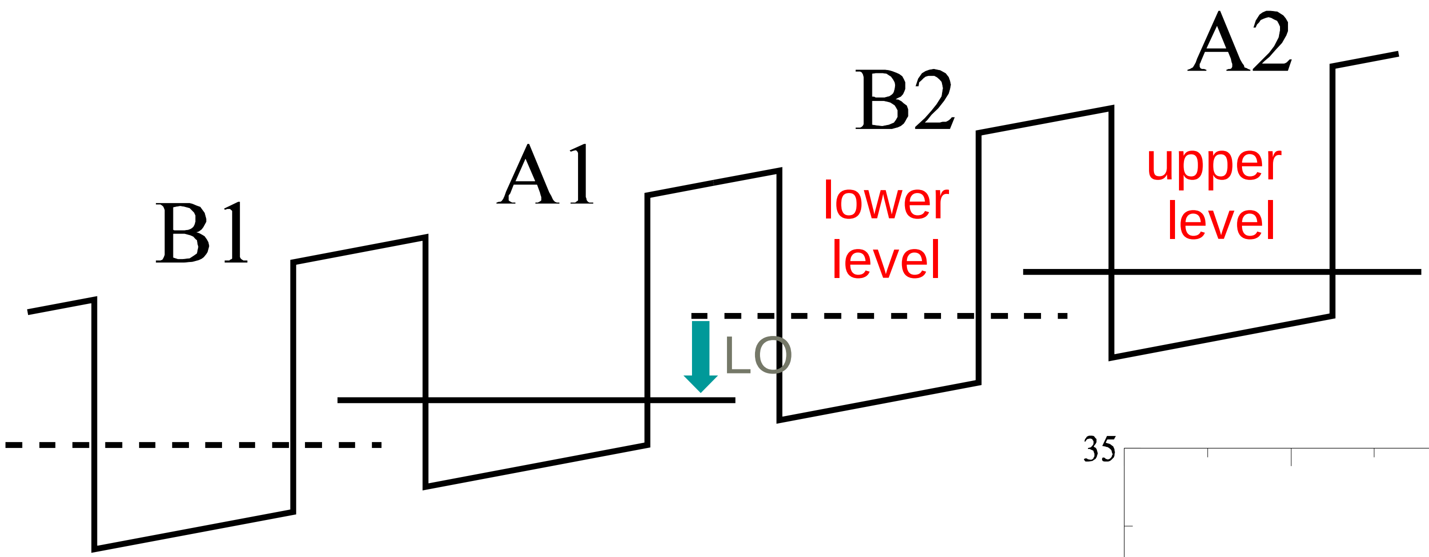
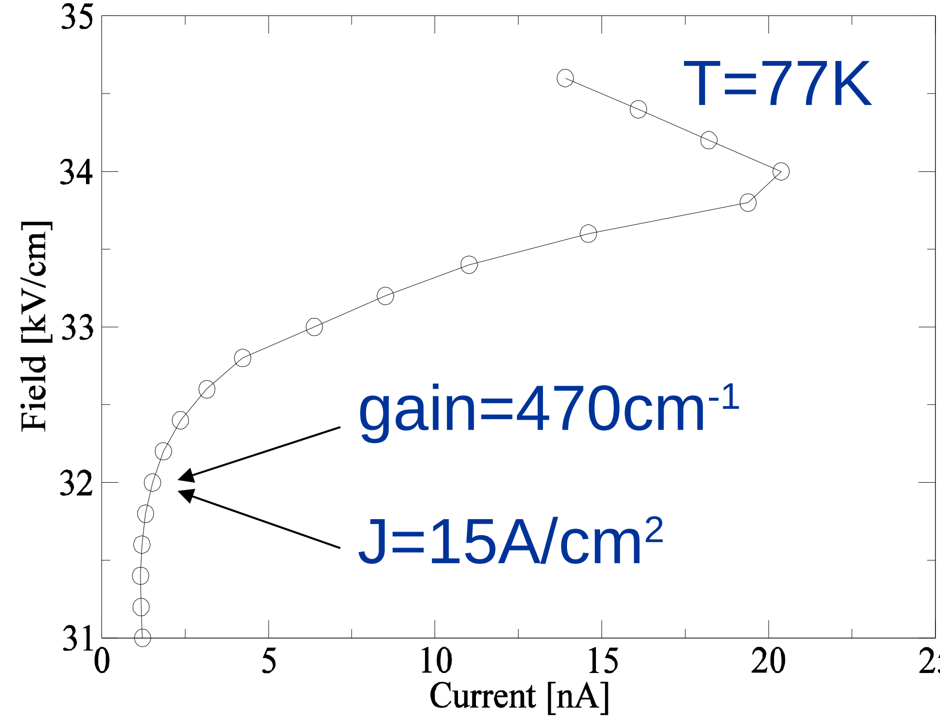
Design and simulation of a THz QD QCL



- A design consisting of two QDs per period (A and B, h_A=5nm, h_B=4.5nm, D=20nm, barrier 3nm)
- At F=32kV/cm and 77K population inversion is 56%, frequency 4.6 THz.



N. Vukmirović et al, IEEE PTL 20, 129 (2008).

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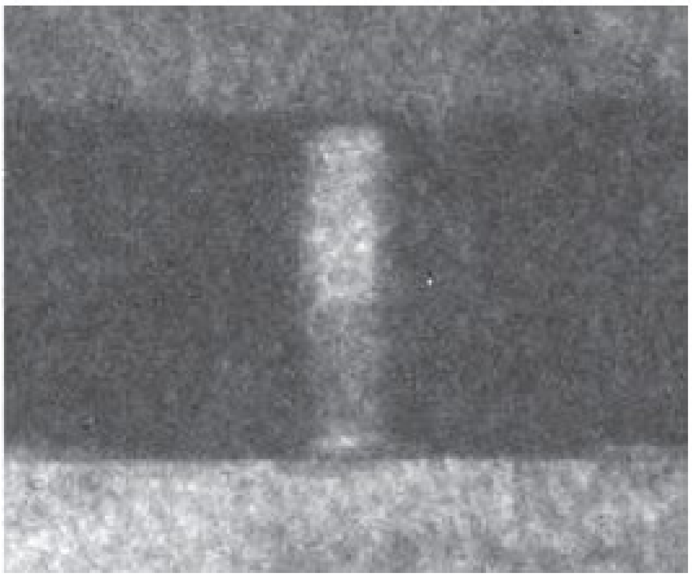
Outlook - emerging structures

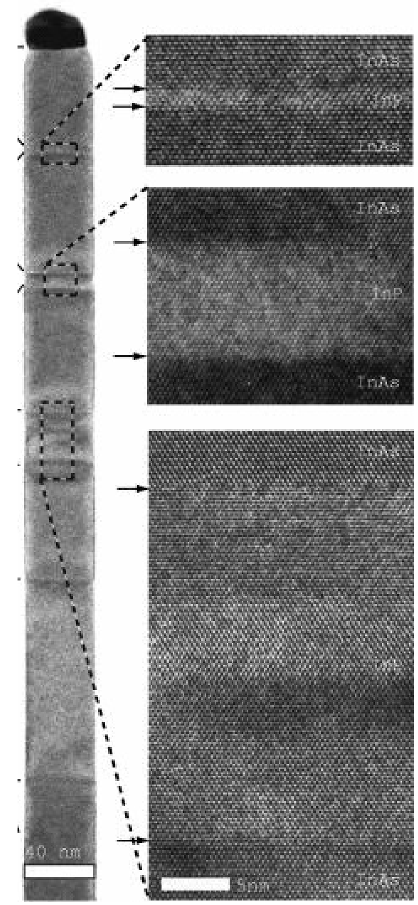
- Columnar quantum rods



L. H. Li et al, IEEE JSTQE 40, 239 (2008).

- Theoretical challenges
  - whole structure with contacts
  - nonuniformities

- Quantum dots in nanowires



M. T. Bjork et al, APL 80, 1058 (2002).

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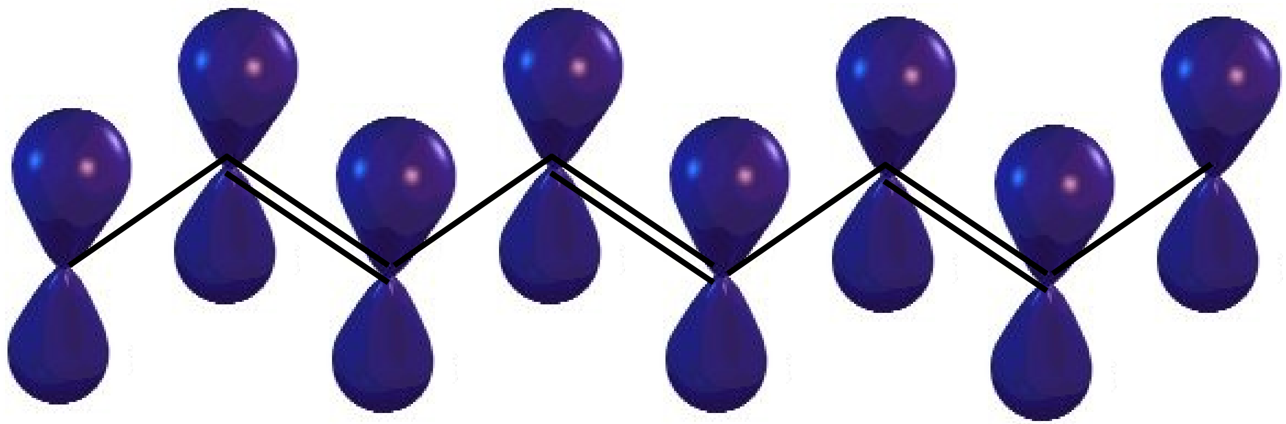
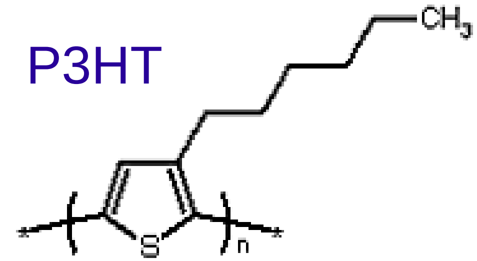
Amorphous conjugated polymers

Conjugated polymers

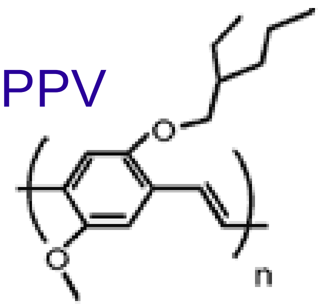
- Single polymer chains:



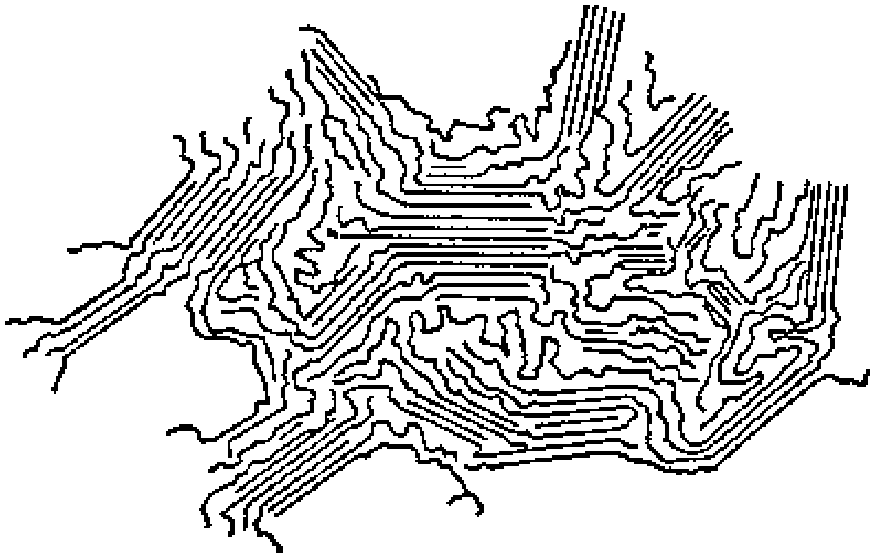
P3HT

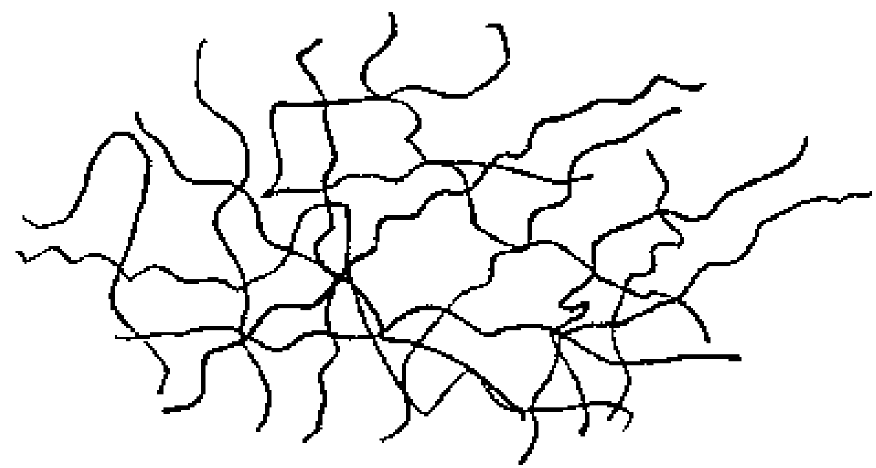


MEH-PPV



- Polymers forming a real material:





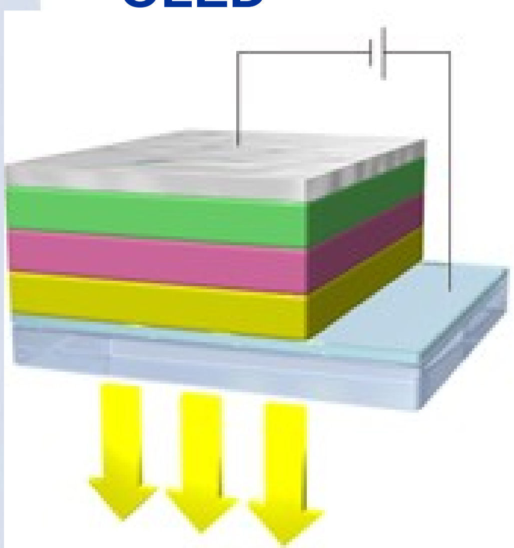
Applications

- Advantages
  - light and flexible
  - easy and cheap processing
  - tailored synthesis

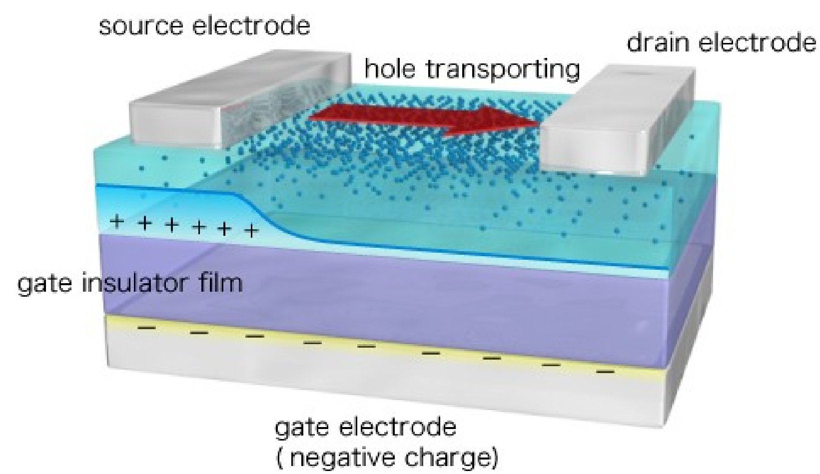
- Drawbacks
  - low mobility
  - sensitive to UV
  - degradation with time

- Applications

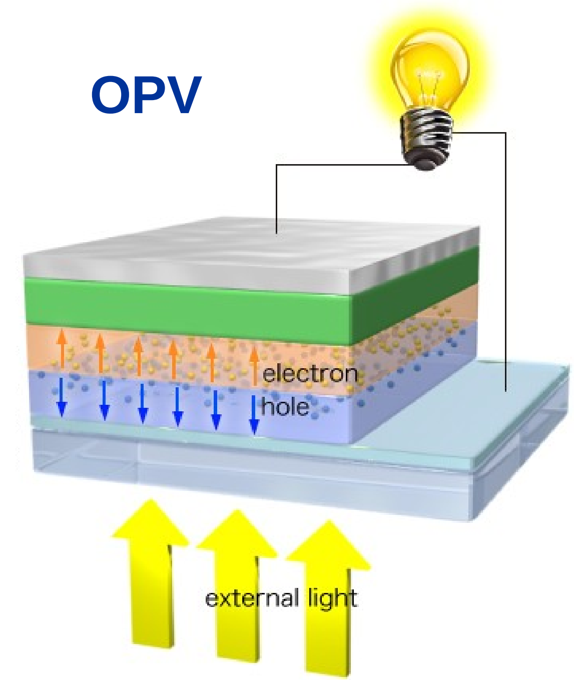
OLED



OFET



OPV



http://www.cstf.kyushu-u.ac.jp/~adachilab/research_b_e.html

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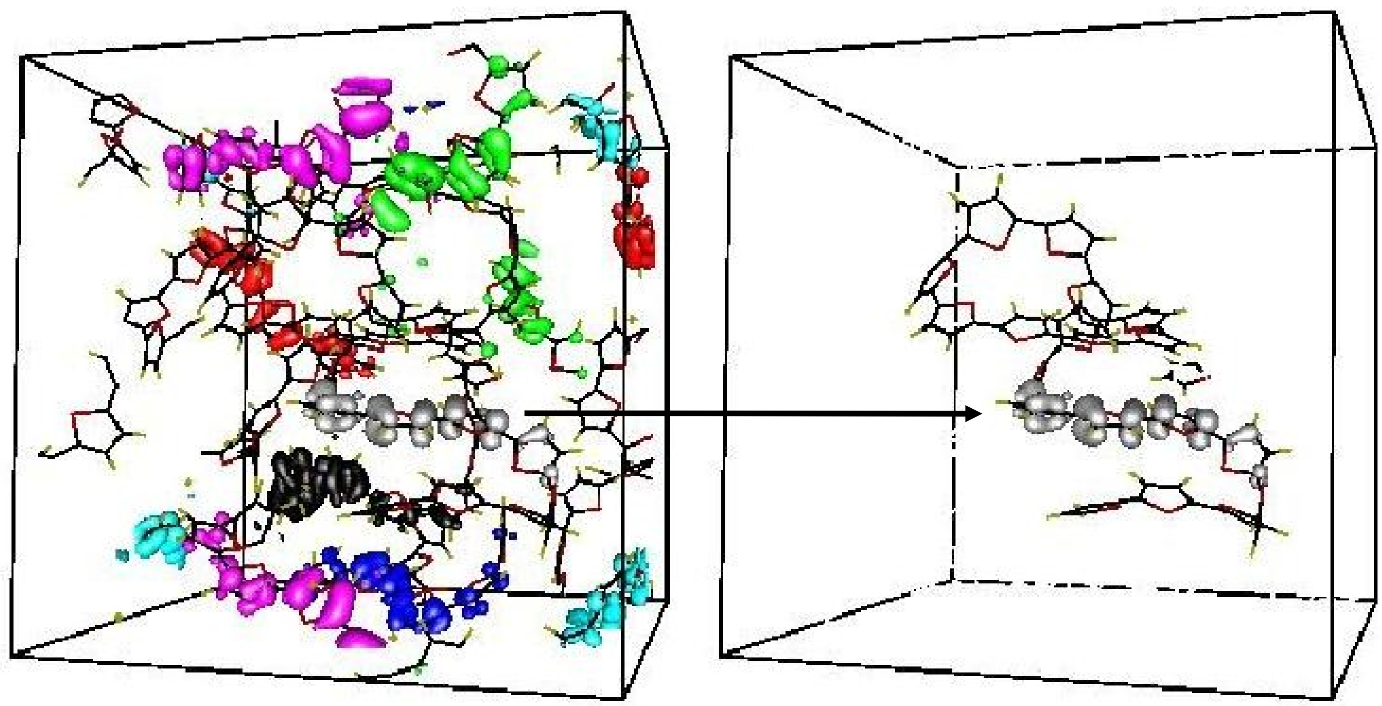
Electronic structure

- Atomic structure – classical MD, simulated annealing
- Charge patching method for electronic structure
- Hole states in P3HT:
    - typically localised to 3-6 rings.

P3HT – 5 chains with 20 rings (2510 atoms)

blue: 18.910eV
green: 18.888eV
cyan: 18.755eV
red: 18.690eV
pink: 18.682eV
black: 18.675eV
white: 18.654eV



N. Vukmirović and L.-W. Wang, J. Phys. Chem. B 113, 409 (2009)

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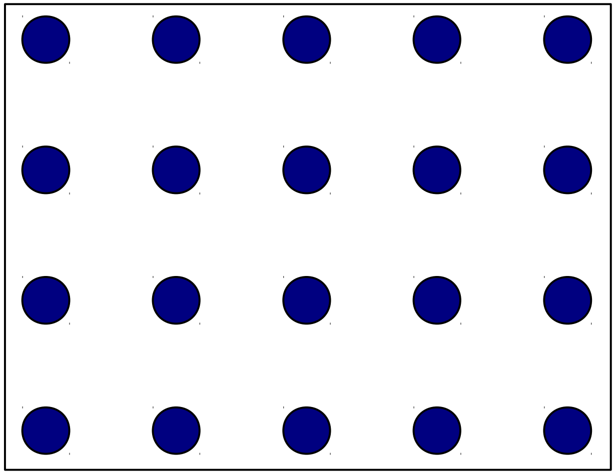
Previous approaches for transport

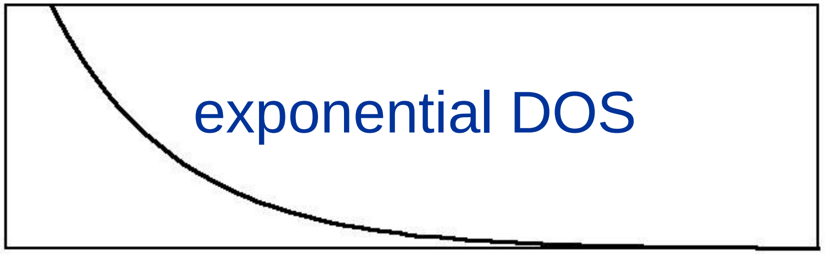
- Gaussian or exponential DOS
- Cubic lattice of sites
- Miller-Abrahams transition rates

$$W_{ij} \sim \exp(-\alpha R_{ij}) \qquad E_i > E_j$$

$$W_{ij} \sim \exp(-\alpha R_{ij}) \exp(-\Delta E_{ji}/kT) \qquad E_i \leqslant E_j$$

- Several fitting parameters

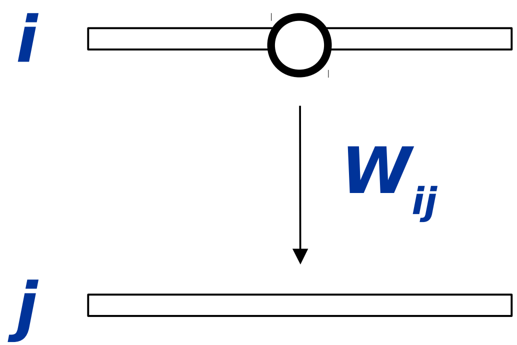




Energy

This approach for transport

- Direct calculation of WFs and energies
- Transition rates calculated by considering interaction with all phonon modes

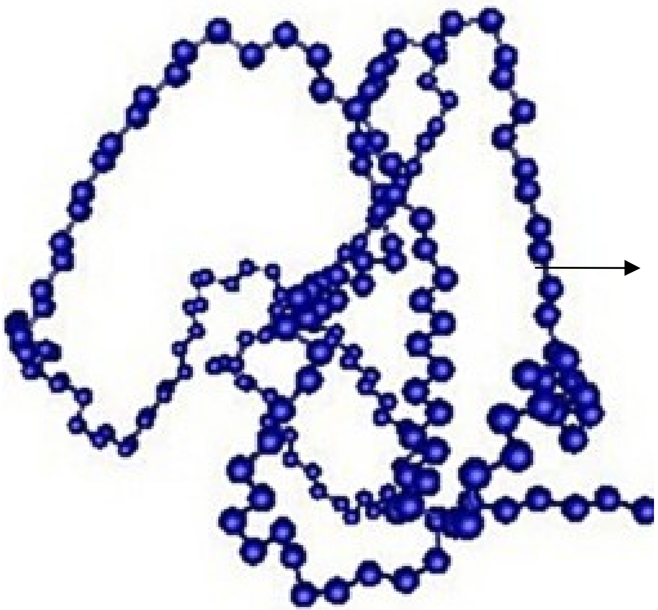


$$W_{ij} = \pi \sum_{\mu} \frac{|M_{ij,\mu}|^2}{\omega_\mu} [N(\hbar\omega_\mu)+1]\delta(E_i - E_j - \hbar\omega_\mu)$$

- Phonon modes from classical force field
- Electron-phonon coupling constants from charge patching

$$M_{ij,\mu} = \langle i | \frac{\partial H}{\partial v_\mu} | j \rangle$$

- No fitting parameters



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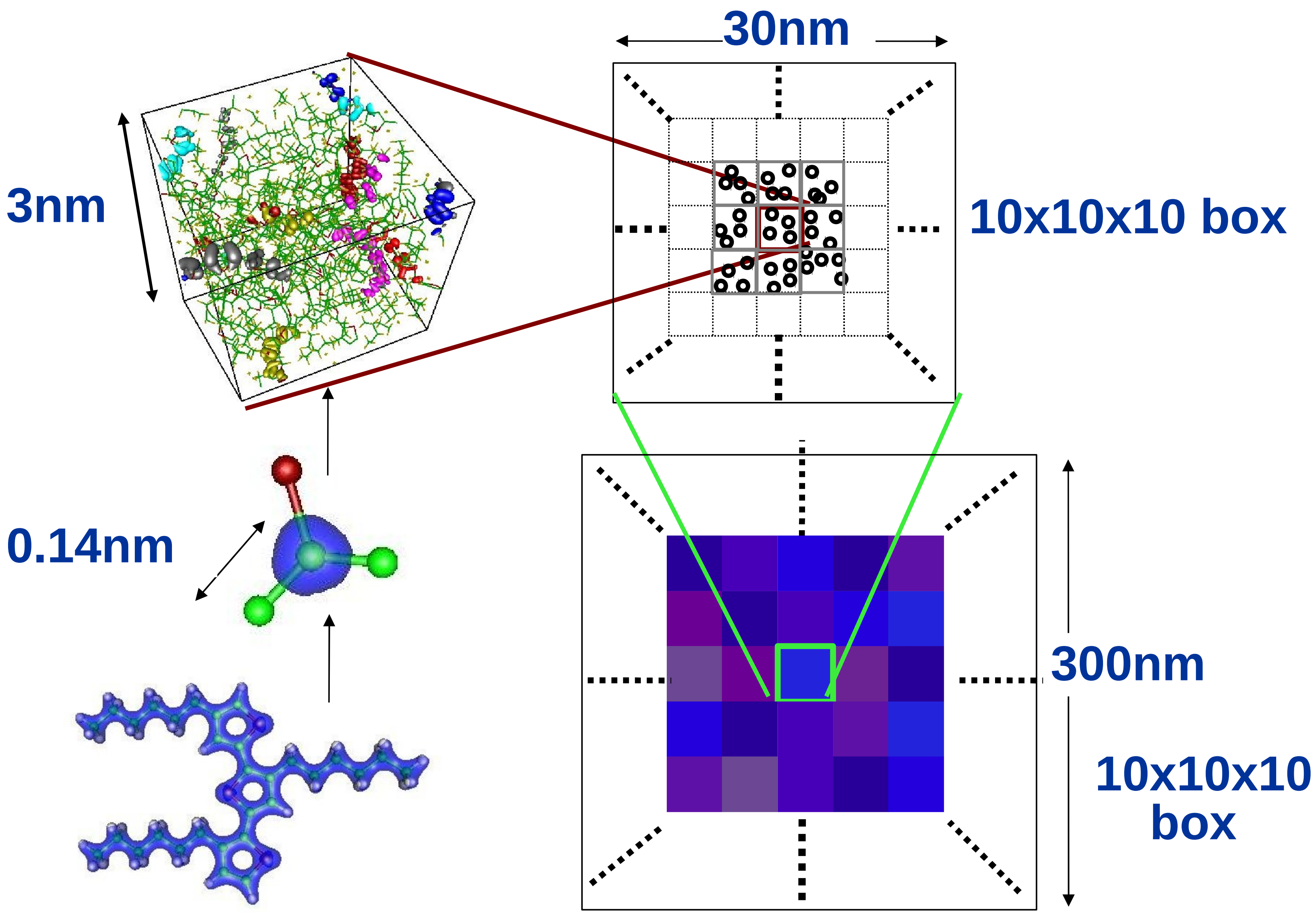
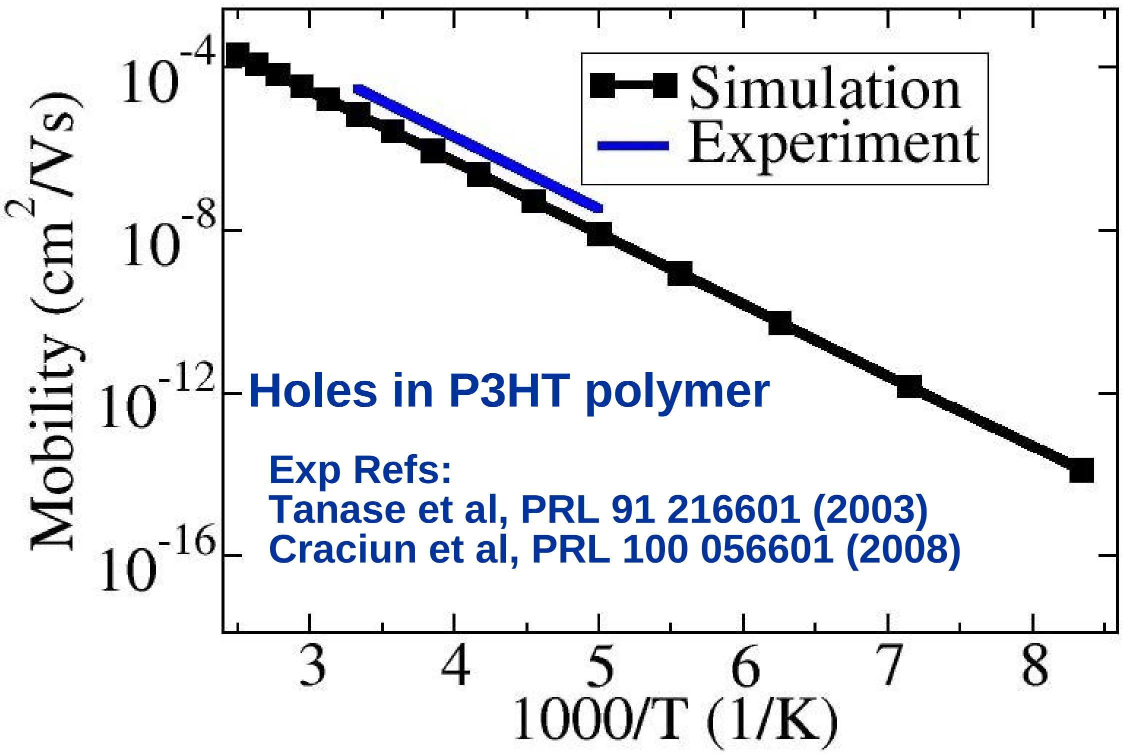
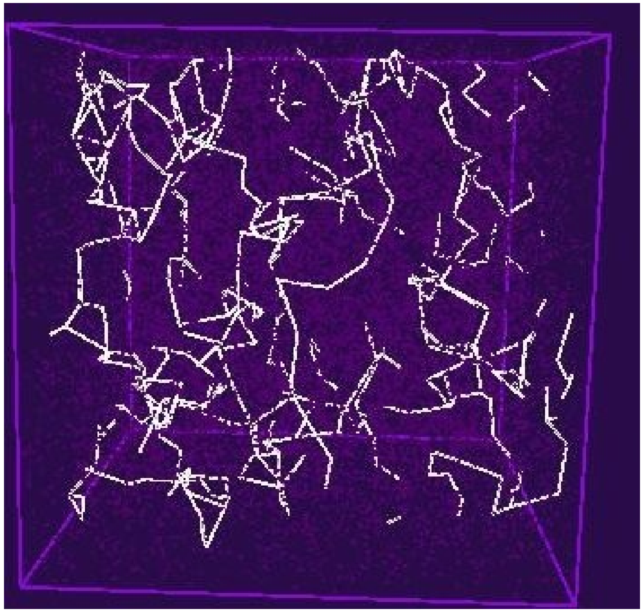
Multiscale method for carrier transport



N. Vukmirović and L.-W. Wang, Nano Lett. 9, 3996 (2009)

Mobility





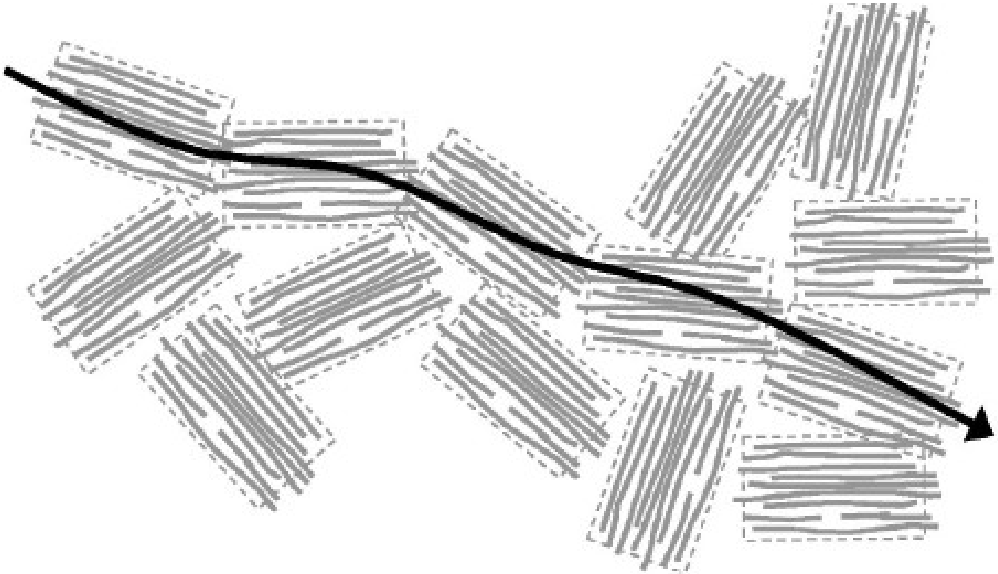
http://www.colourlovers.com/uploads/2008/02/sydney_lightning_bolts.jpg

- Microscopic insight into the current paths in the material.

N. Vukmirović and L.-W. Wang, Nano Lett. 9, 3996 (2009)

Outlook

- Transport in polymers of arbitrary order
  - coherence?
  - polarons?



R. A. Street et al, PRB 71, 165202 (2005).

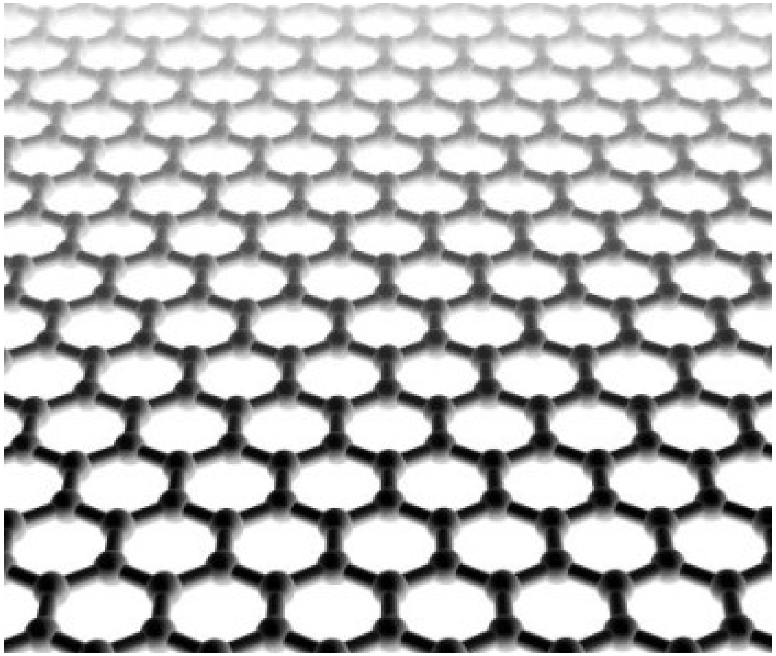
- Organic crystals based on small molecules
  - transport is still not well understood

Pentacene

Graphene antidot lattices

Graphene

- Ultrahigh charge carrier mobility.
- Great mechanical strength.
- Lack of band gap.
- Methods to introduce the band gap
  - graphene nanoribbons
  - covalent functionalization
  - create holes in graphene:
    - graphene antidot lattice



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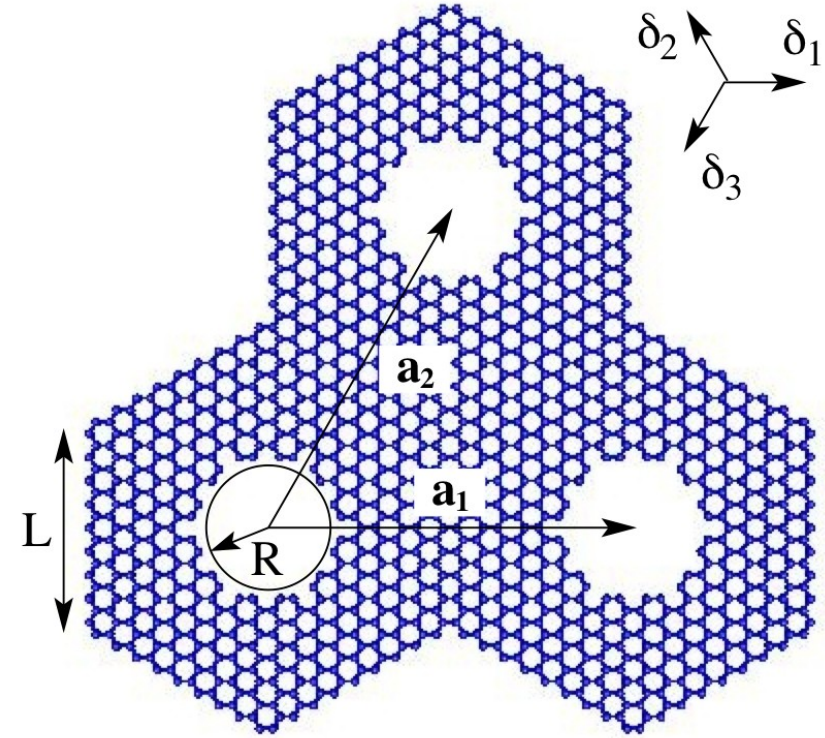
Model for graphene antidot lattices

- TB model for electronic structure
- Empirical potentials for phonons
- E-ph Hamiltonian obtained by assuming linear dependence of TB hopping integrals on the distance



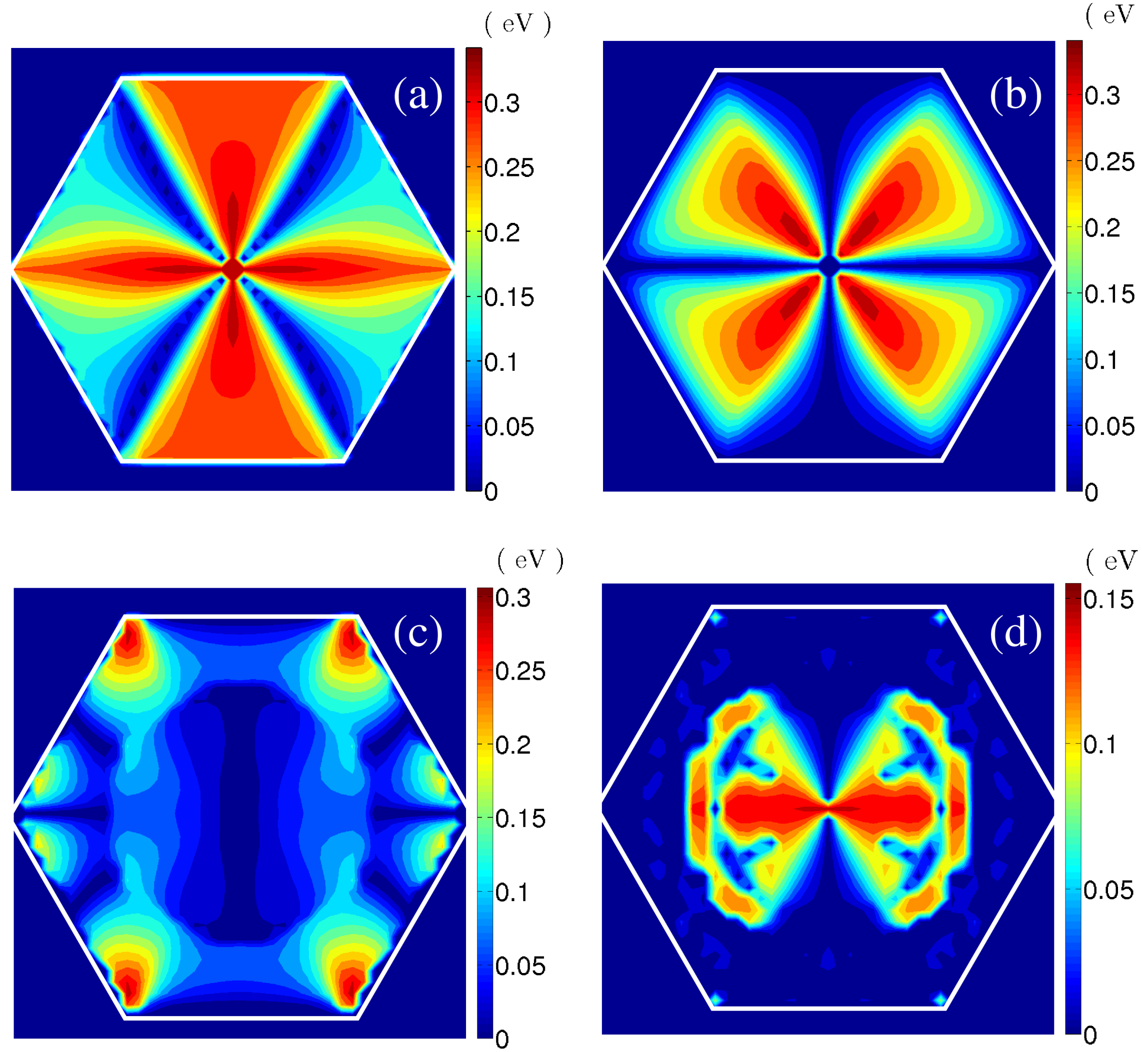
- Quasiparticle spectral weight:

$$Z_c^{-1}(0) = 1 + \frac{1}{N} \sum_{\mathbf{q},\lambda} \frac{|\gamma^{\lambda}_{cc}(\mathbf{k}=\mathbf{0},\mathbf{q})|^2}{\left[\varepsilon_c(0) - \varepsilon_c(\mathbf{q}) - \omega_\lambda\right]^2}$$

N. Vukmirović, V. M. Stojanović and M. Vanević, Phys. Rev. B 81, 041408 (R) (2010).

Polaronic nature of carriers

- $Z_c^{-1}(0)$=3.7-5 for lattices with R=5 and R=7
  - Polaronic nature of carriers
- Physical origin of this result
  - Narrow bare electronic bands
  - Maxima of $\gamma(k=0,q)$ at small q for several phonon modes



$\gamma(k=0,q)$ for several phonon modes

V. M. Stojanović, N. Vukmirović and C. Bruder, Phys. Rev. B 82, 165410 (2010).

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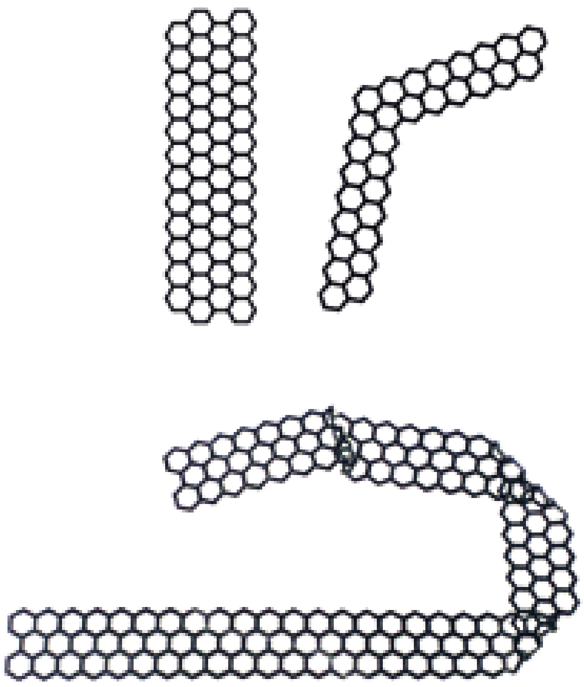
Outlook

- Understand the nature of charge carriers in other graphene-based nanostructures.
- Develop a method for the calculation of transport properties of polaronic carriers.
- What will be the impact of graphene based structures?



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Colleagues and collaborators

- Intraband quantum dot optoelectronic devices
  - D. Indjin, Z. Ikonic, V. D. Jovanovic, I. Savic, P. Harrison, University of Leeds, UK.
  - S. Tomic, Daresbury Laboratory, Warrington, UK
  - P. Aivaliotis, E. A. Zibik, L. R. Wilson, University of Sheffield, UK.
  - L. Fu, G. Jolley, H. H. Tan, C. Jagadish, Australian National University.

- Electronic structure and transport in conjugated polymers
  - L. W. Wang, Lawrence Berkeley National Laboratory (LBNL)
  - F. Martin, M. Salmeron, LBNL
  - Gao Liu, Wanli Yang, LBNL
  - J. Roldan, M. Fernandez-Gomez, University of Jaen, Spain

- Graphene antidot lattices
  - V. M. Stojanovic, C. Bruder, University of Basel
  - M. Vanevic, Delft.

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