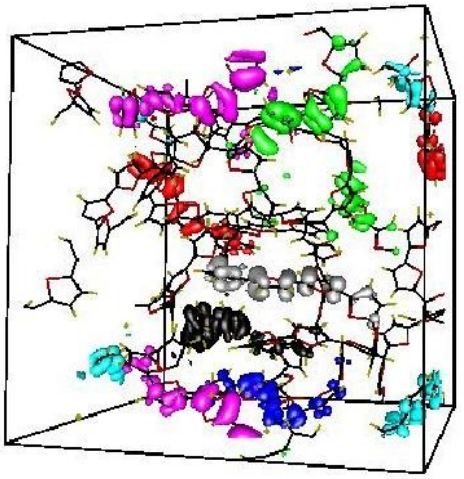
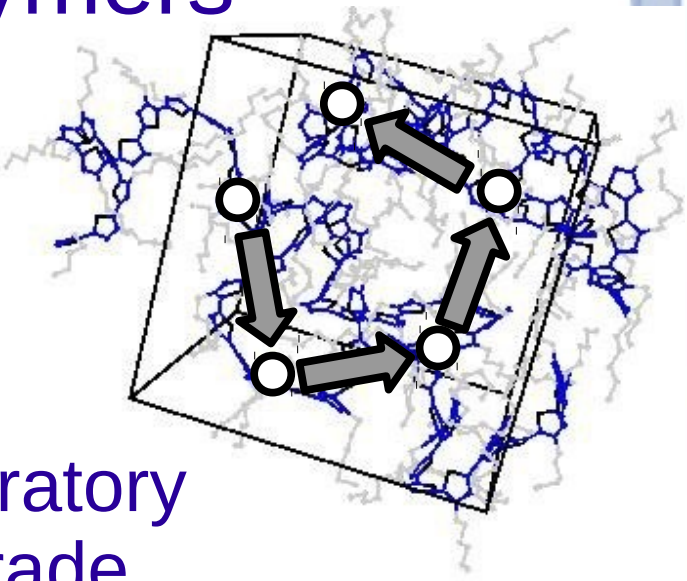
Simulations of charge carrier transport in disordered organic polymers





Nenad Vukmirović
Scientific Computing Laboratory
Institute of Physics Belgrade

Lin-Wang Wang
Lawrence Berkeley National Laboratory

Lund University, 28 January 2011

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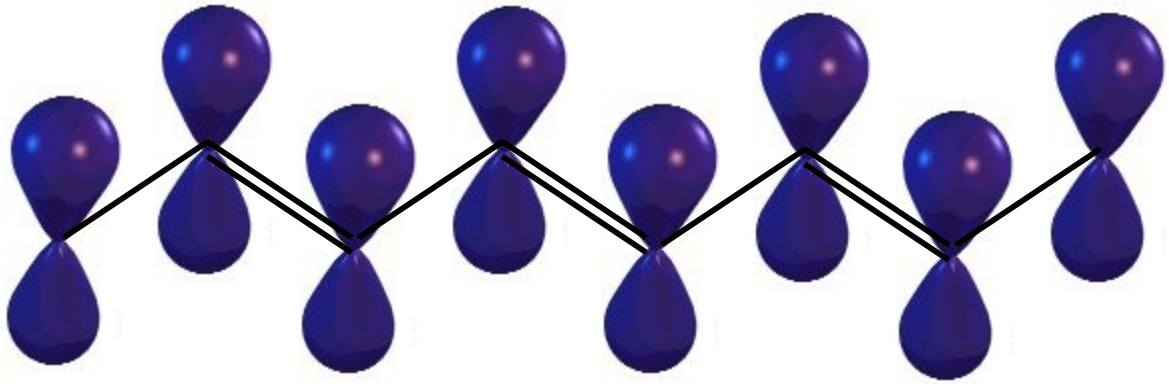
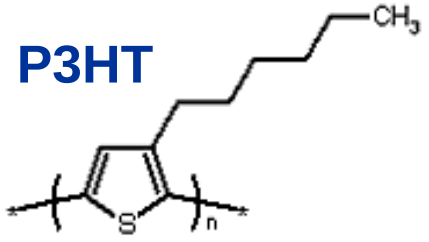
Conjugated polymers

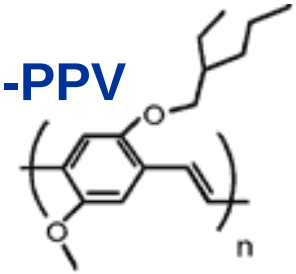
- **Single polymer chains:**



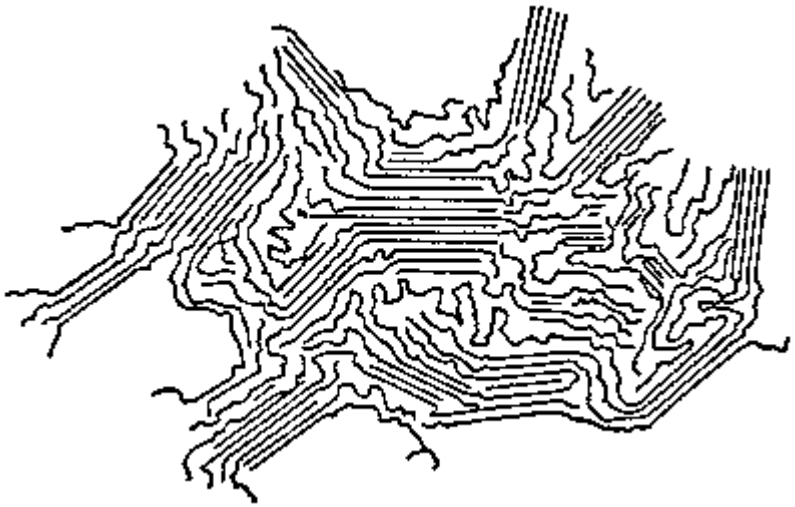
P3HT

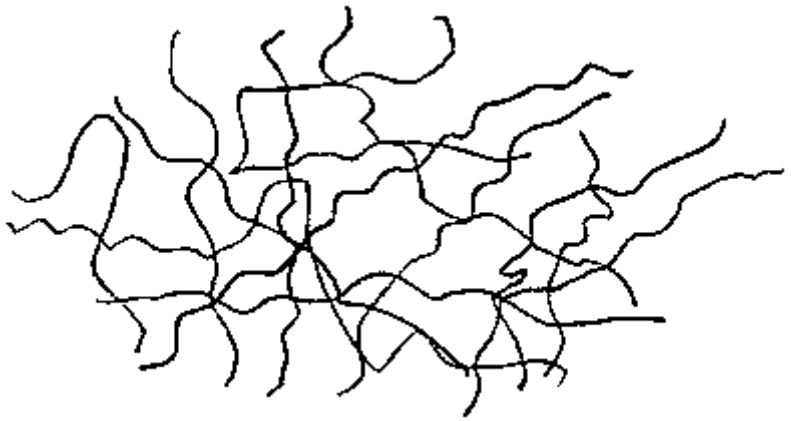


MEH-PPV



- **Polymers forming a real material:**

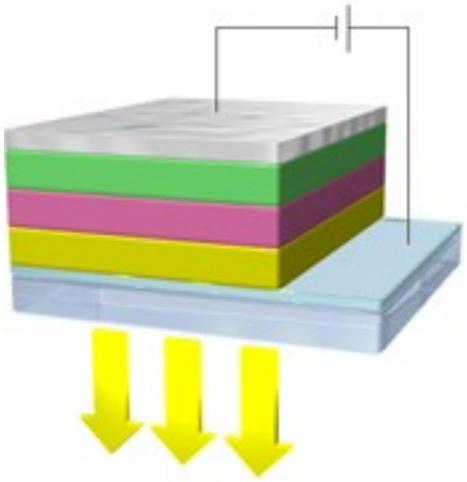




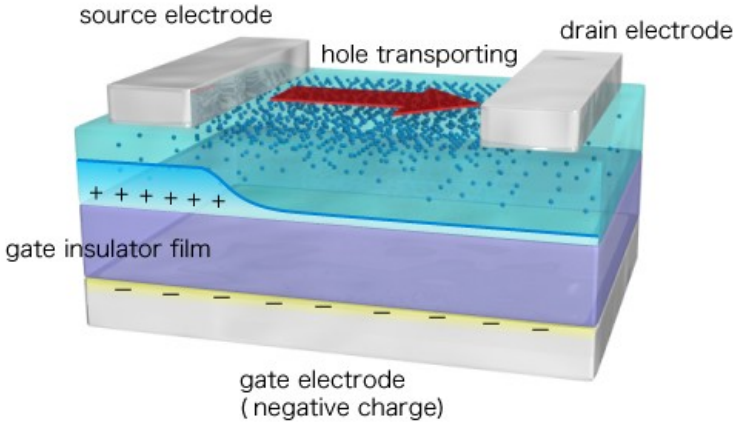
Advantages and applications

- Advantages
  - light and flexible
  - easy and cheap processing
  - tailored synthesis
- Drawbacks
  - low mobility
  - sensitive to UV
  - degradation with time
- Applications

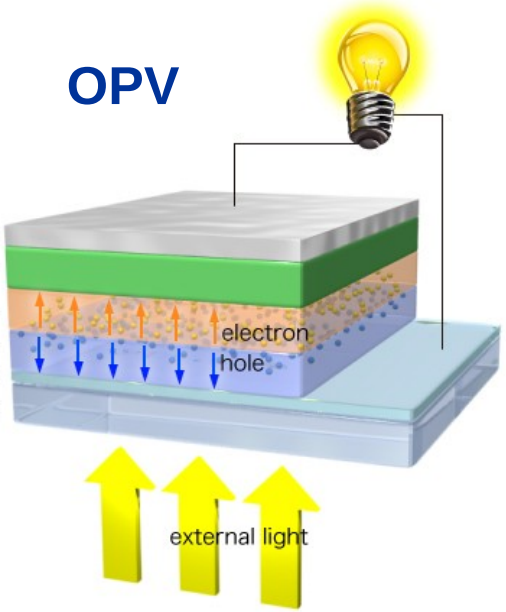
OLED



OFET



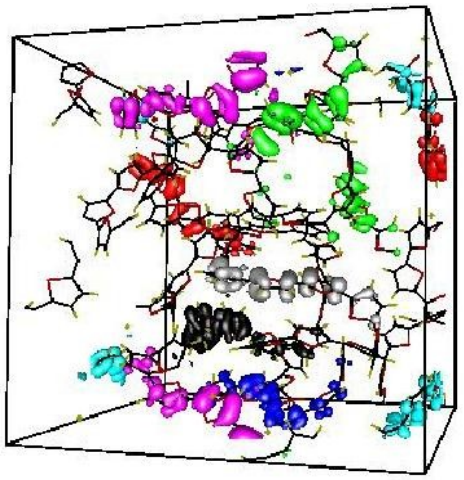
OPV



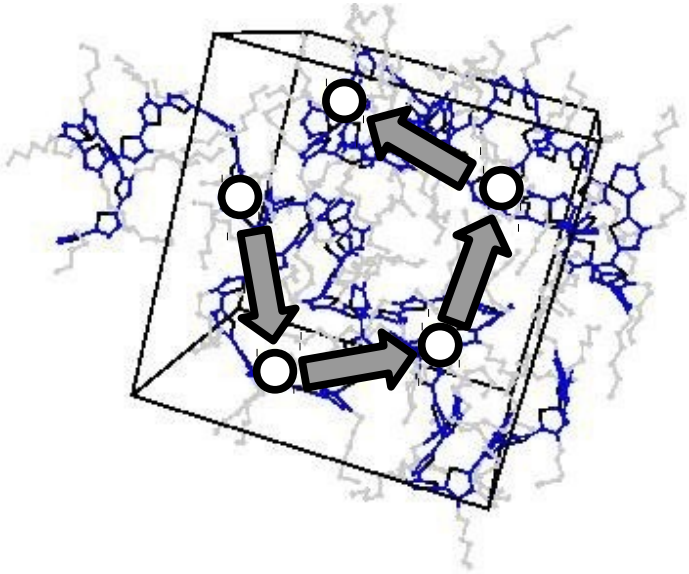
http://www.cstf.kyushu-u.ac.jp/~adachilab/research_b_e.html

Overview of the talk

- Electronic structure
  - Methods
  - Results and lessons learned

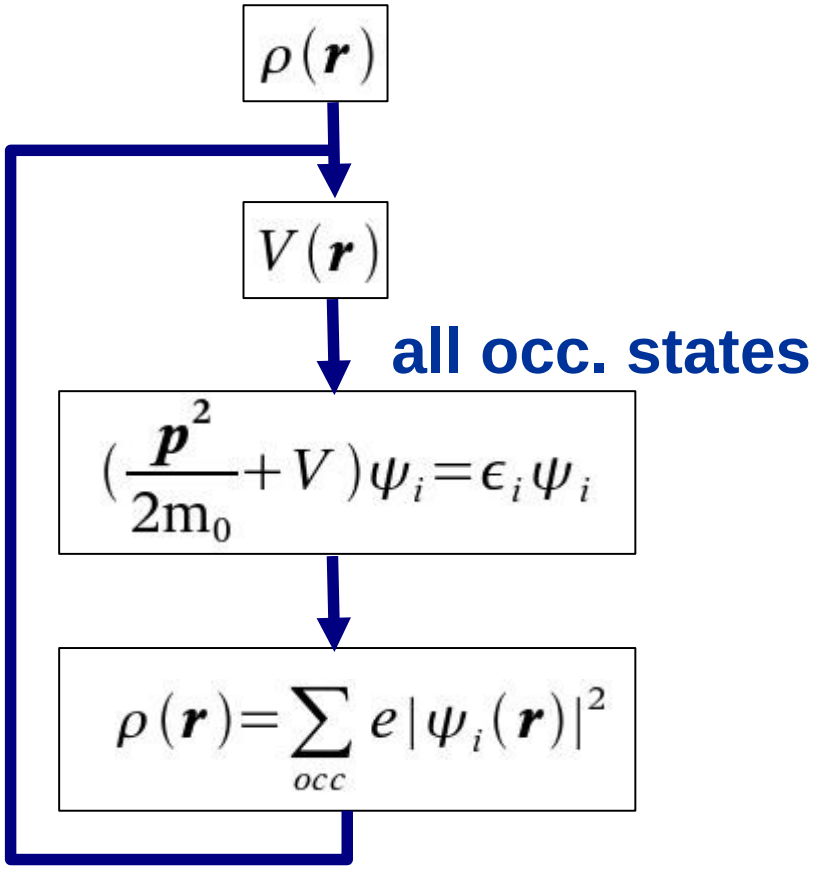


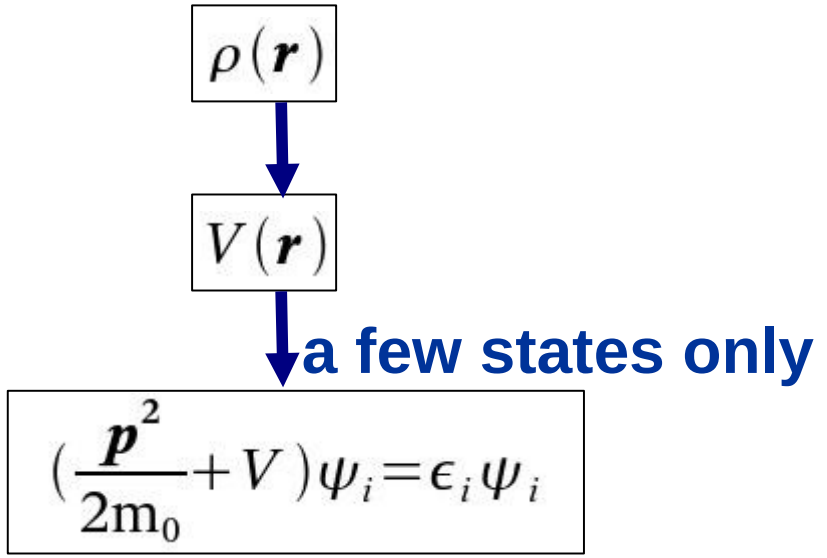
- Electronic transport
  - Methods
  - Results and lessons learned



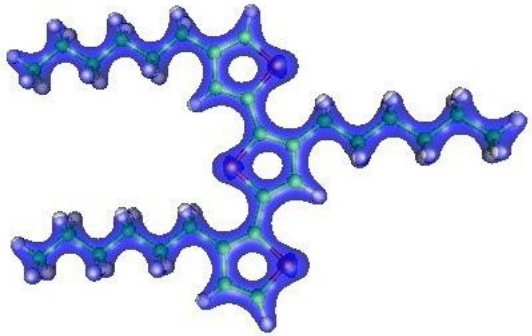
Electronic structure: Methods

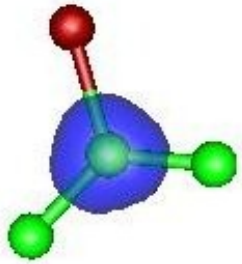
DFT vs. Charge patching

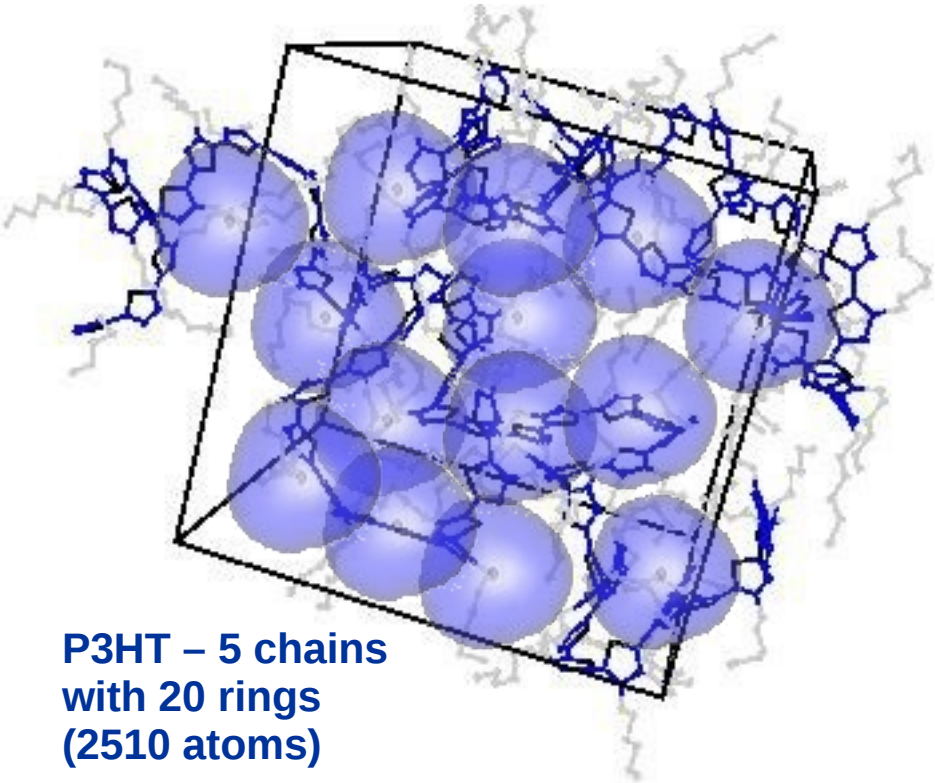




Charge patching method







P3HT – 5 chains
with 20 rings
(2510 atoms)

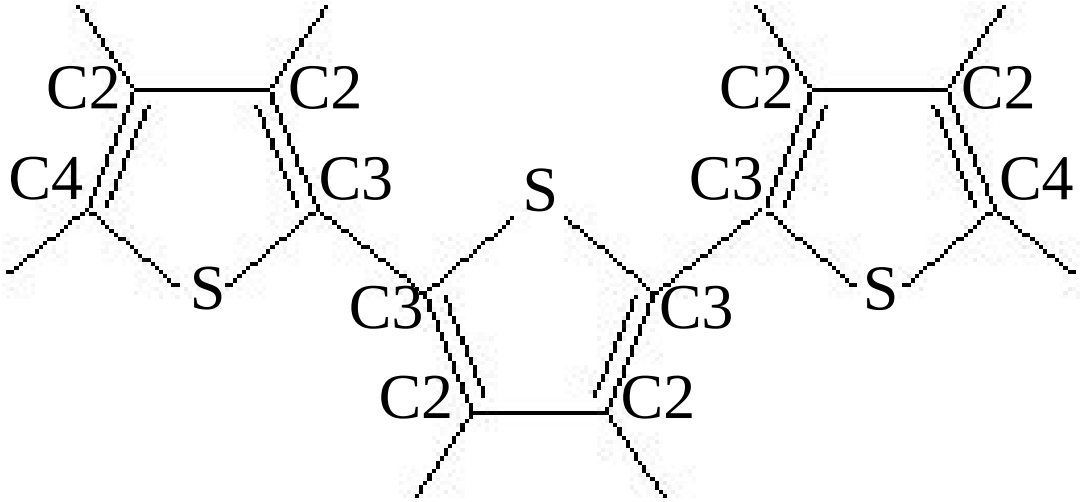
$$m_A(\boldsymbol{r}-\boldsymbol{R}_A)=\frac{w_A(\boldsymbol{r}-\boldsymbol{R}_A)}{\sum_B w_B(\boldsymbol{r}-\boldsymbol{R}_B)}\rho(\boldsymbol{r})$$

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

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

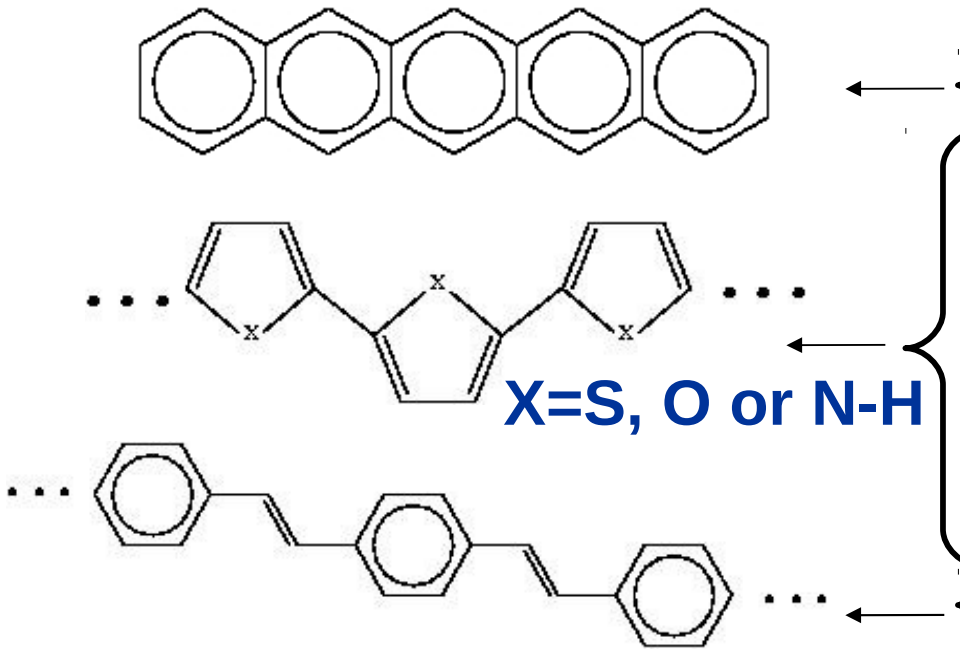
Atom and motif classification

- **Example (polythiophene):**



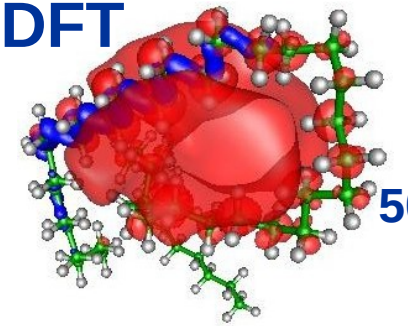
- **Motifs: C3-C3C2S, C2-C3SH, C2-C4C2H, C4-C2SH, S-C3C3, S-C4C3, H-C2-C3C2, H-C2-C4C2, H-C4-C2S**

Test of the CPM for various systems



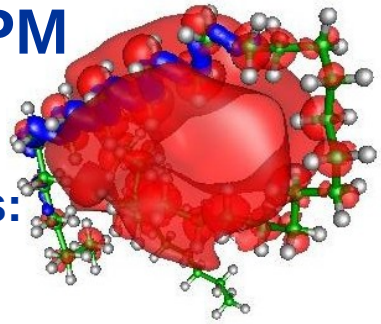
	av. err. (meV)
pentacene	10.0
polythiophene	1.6
6-ring thioph.	15.9
polyfurane	8.5
6-ring furane	27.9
polypyrrole	20.0
6-ring pyrrole	27.5
PPV	19.8

DFT



50% isosurfaces:
HOMO (blue)
LUMO (read)

CPM



Comparison in the case of 50 unit chain – av. error 7.6 meV

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

Scientific Computing Laboratory

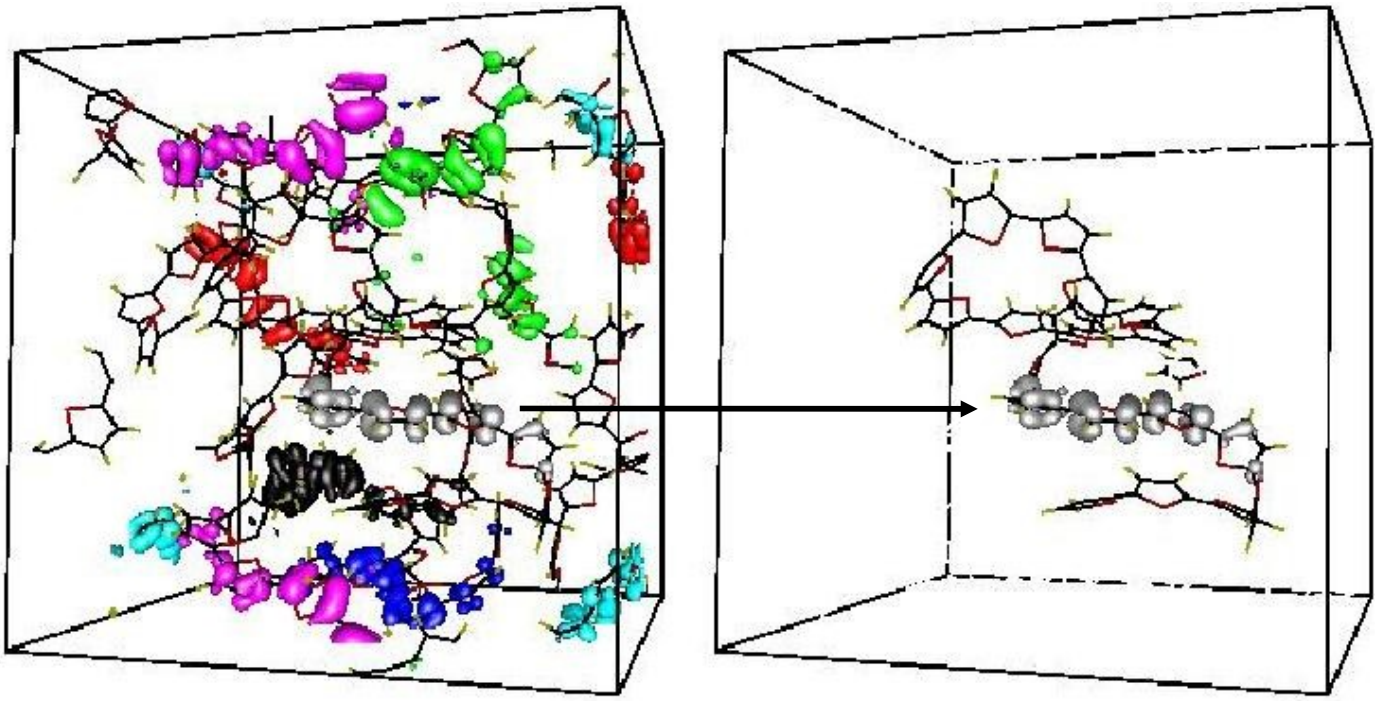
Electronic structure:
Results and lessons learned

Wave functions

- 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)

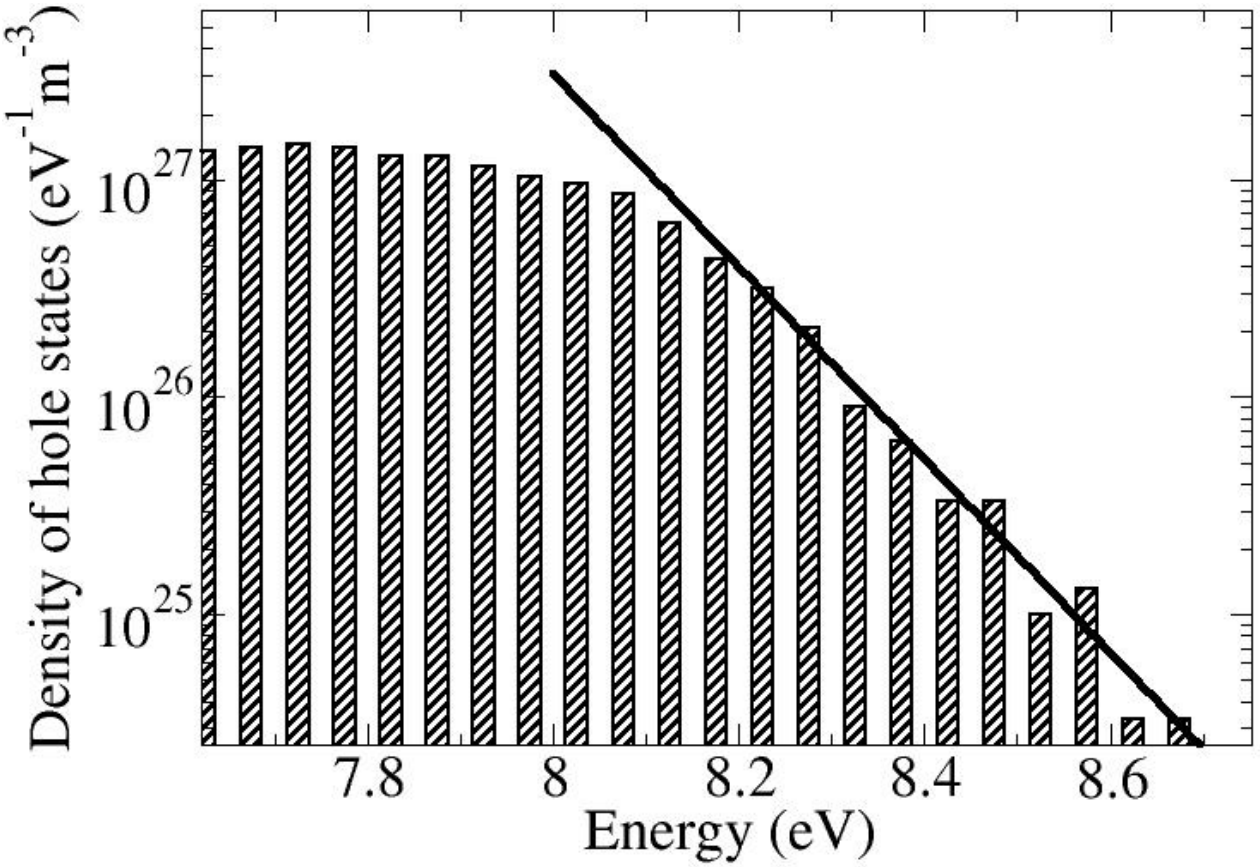
blue: 18.910eV
green: 18.888eV
cyan: 18.755eV
red: 18.690eV
pink: 18.682eV
black: 18.675eV
white: 18.654eV



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

Density of electronic states

- Statistics obtained from 50 calculations on 12024 atom P3HT system.
- Exponential density of states in the tail.



N. Vukmirović and L.-W. Wang, J. Phys. Chem. B (in press).

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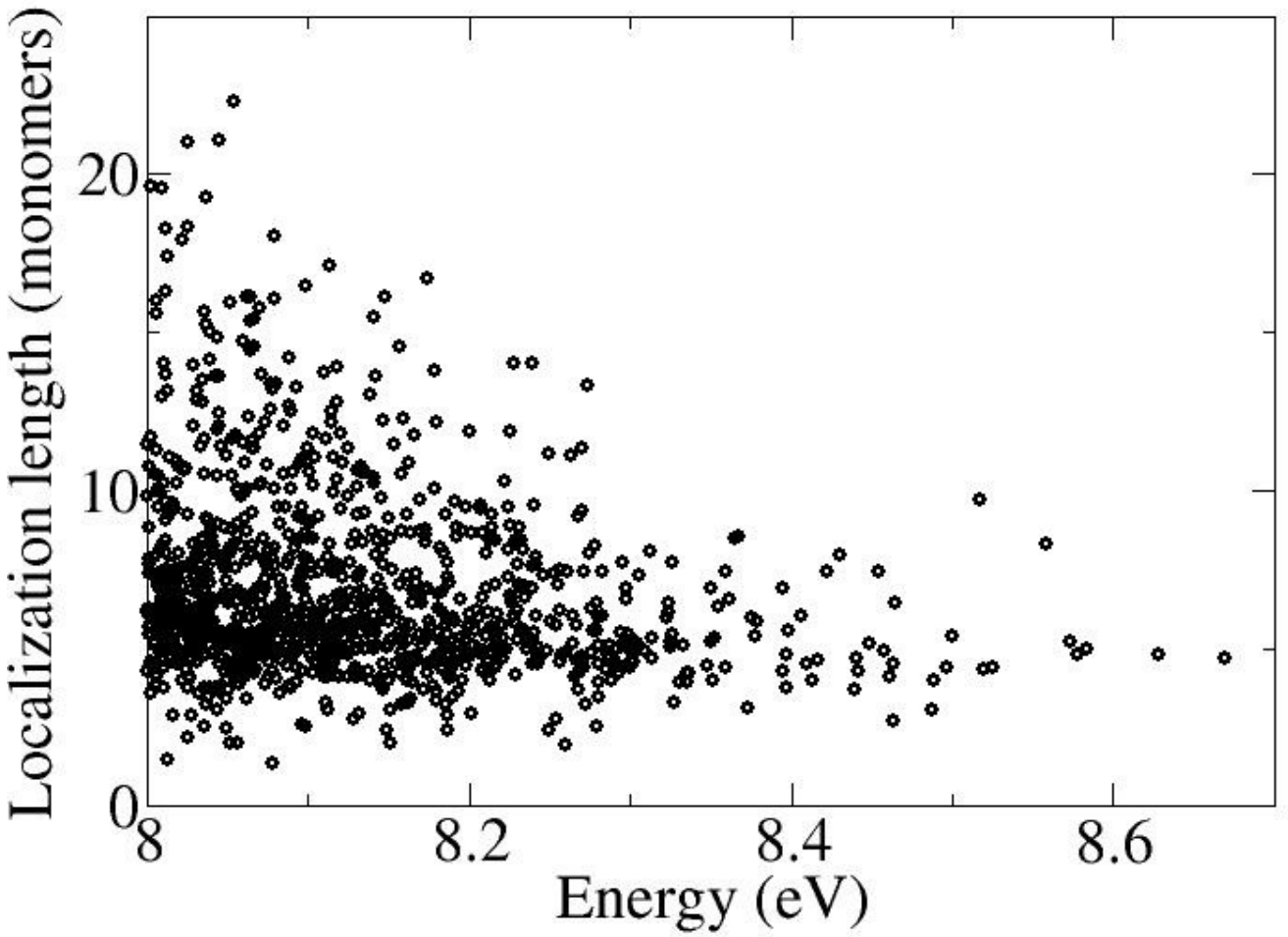
Wavefunction localization lengths

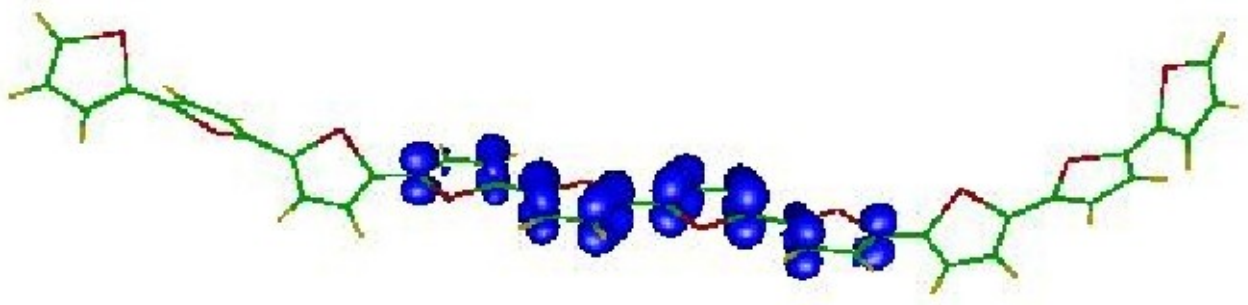
- No apparent mobility edge can be identified.



N. Vukmirović and L.-W. Wang, J. Phys. Chem. B (in press).

The origin of wavefunction localization (1)

- Two possible scenarios:

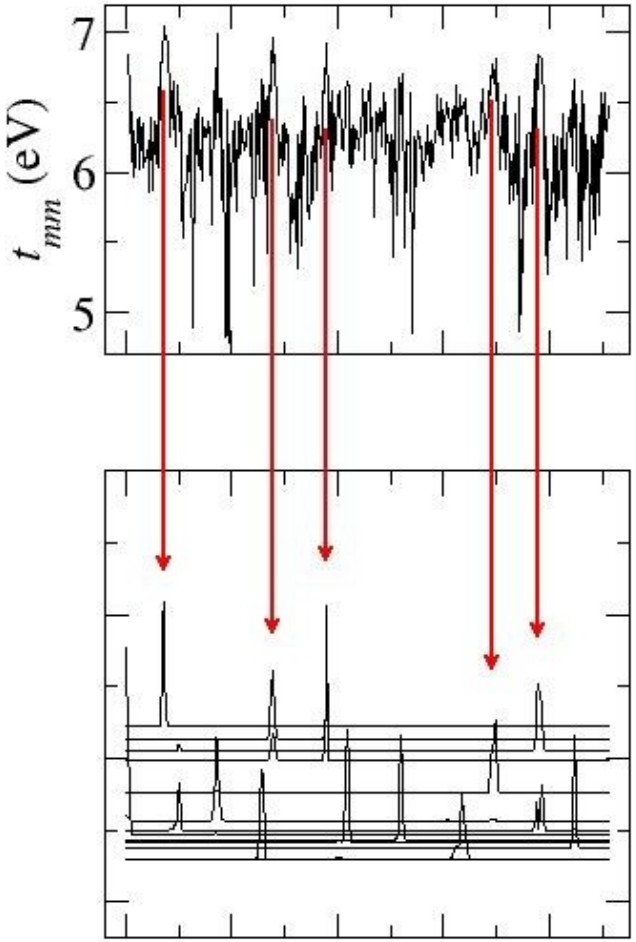


Conjugation break

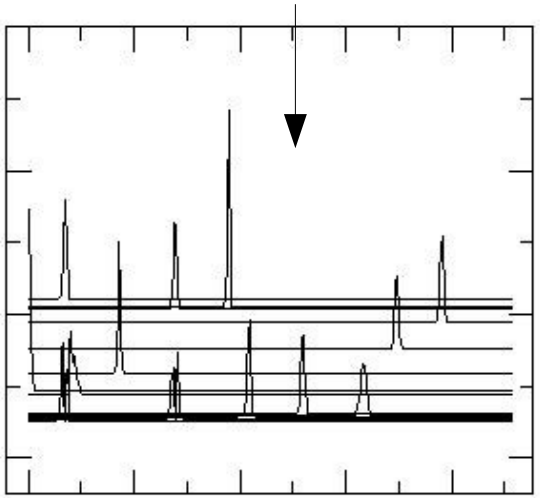
Disorder in onsite energies caused by long range electrostatic interaction

The origin of wavefunction localization (2)

- The disorder caused by electrostatic interactions localizes the wave functions



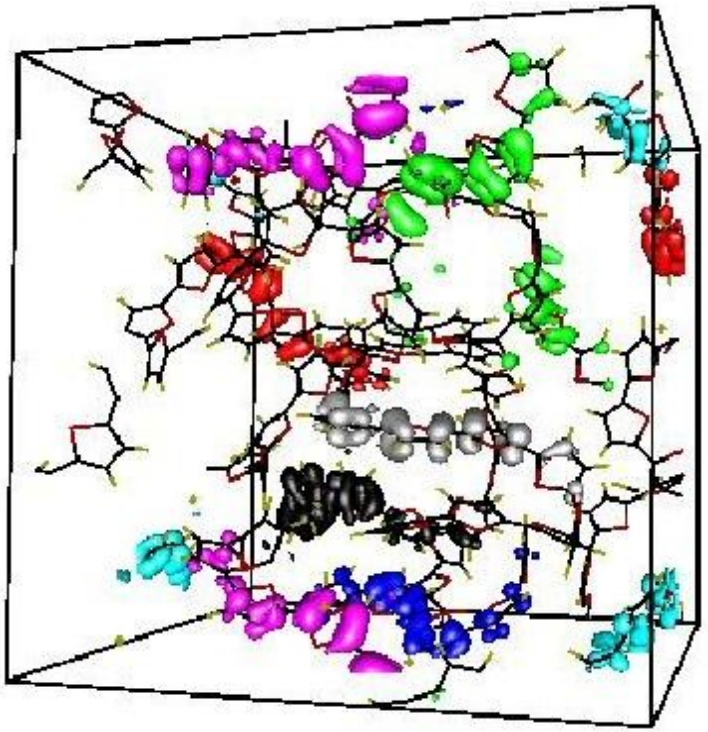
constant offsite
electronic coupling

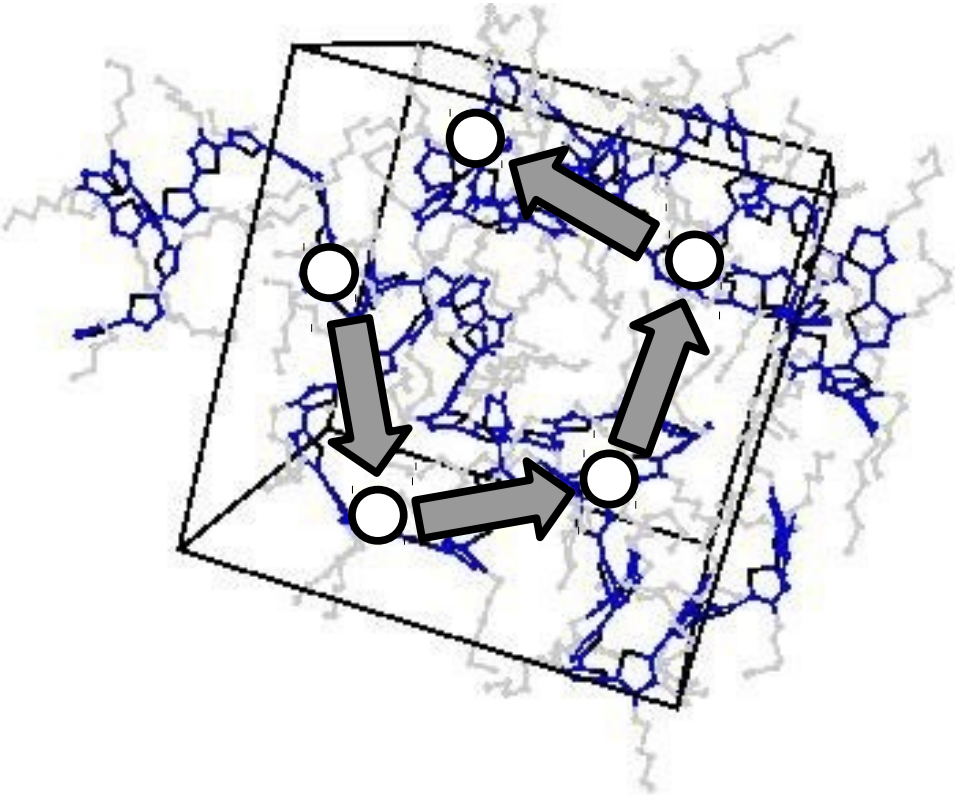


Electronic transport: Methods

Charge carrier transport in disordered conjugated polymers

- Disordered (amorphous) regions present in realistic polymers
- Phonon-assisted hopping between localised states.
- Large system calculations necessary.





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

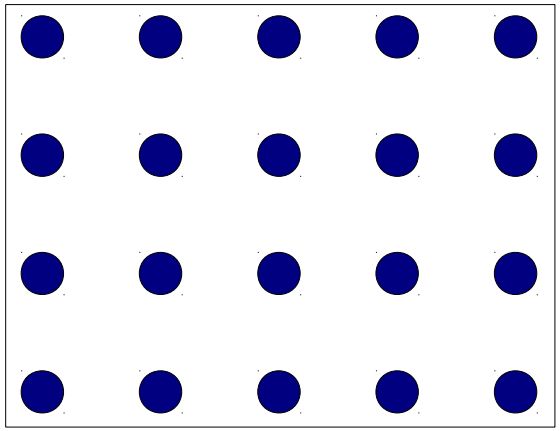
Previous approaches for transport

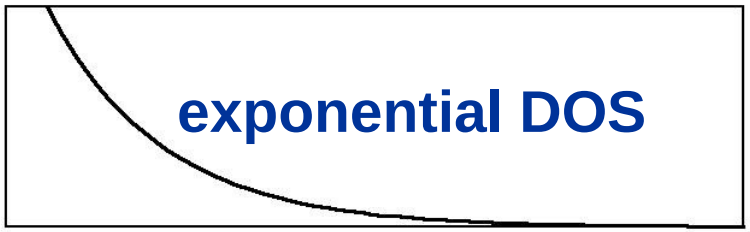
- Gaussian or exponential DOS
- Cubic lattice of sites
- Miller-Abrahams transition rates

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

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

- Several fitting parameters



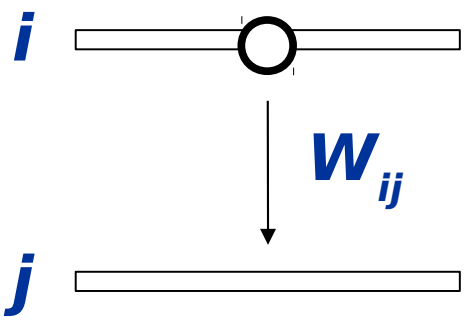


Energy

This approach

-Direct calculation of WFs and energies

-Transition rates calculated by considering interaction with all phonon modes



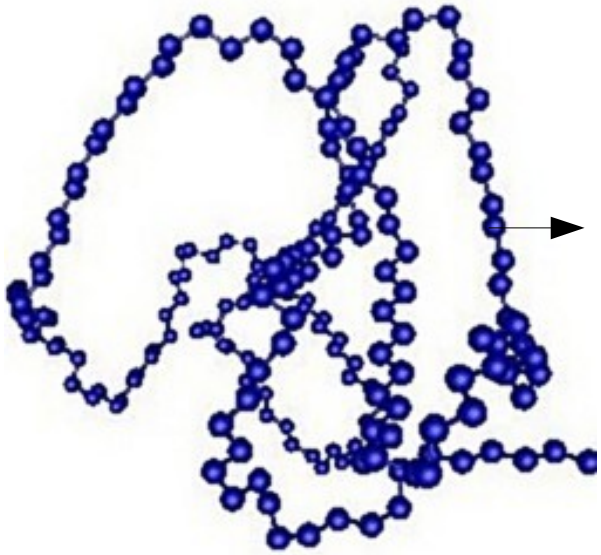
$$W_{ij} = \pi \sum_{\mu} \frac{|M_{ij,\mu}|^2}{\omega_\mu} [N(\hbar\omega_\mu)+1] \delta(E_i - E_j - \hbar\omega_\mu)$$

-Phonon modes from classical force field

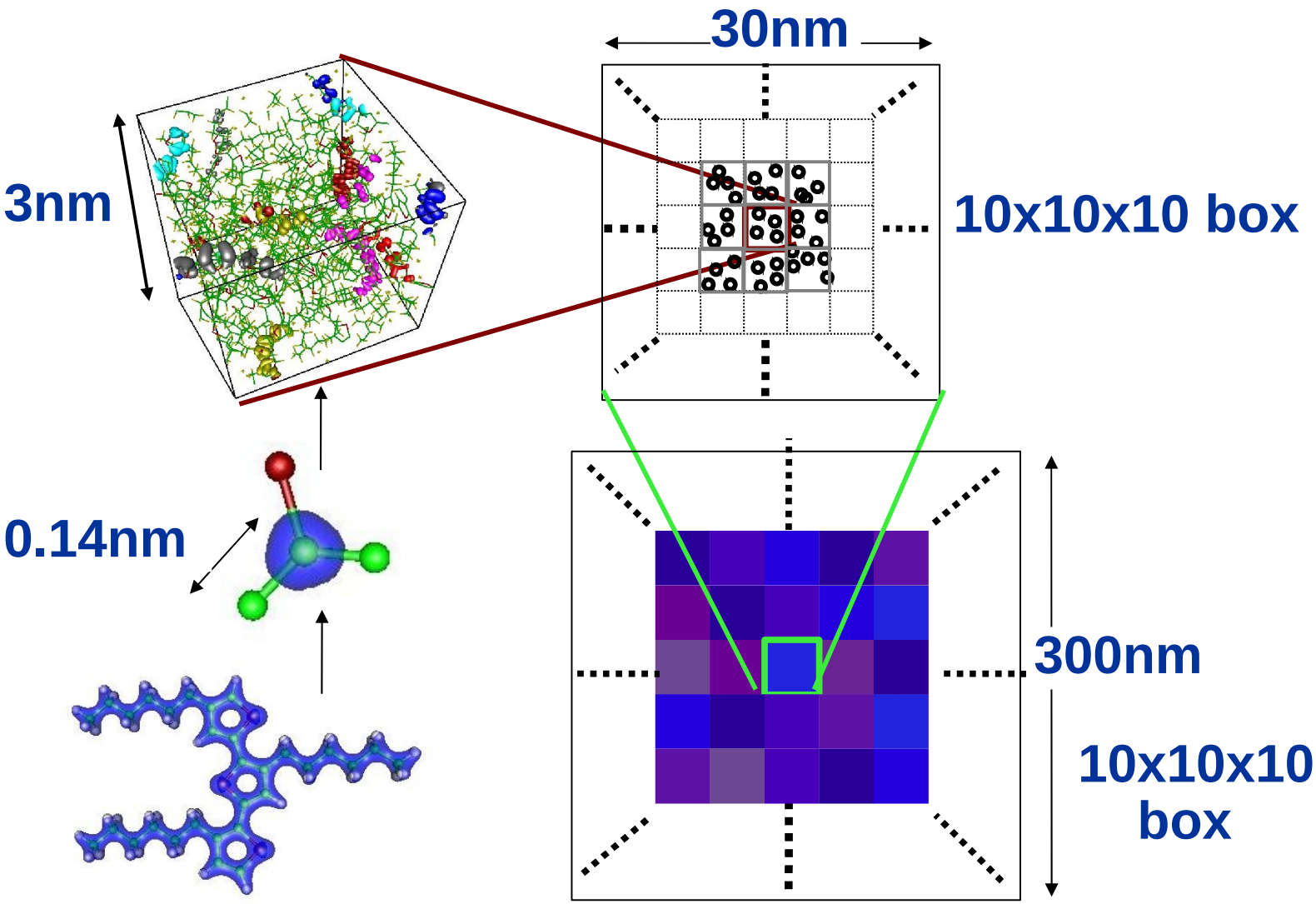
-Electron-phonon coupling constants from charge patching

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

-No fitting parameters



Multiscale method for carrier transport

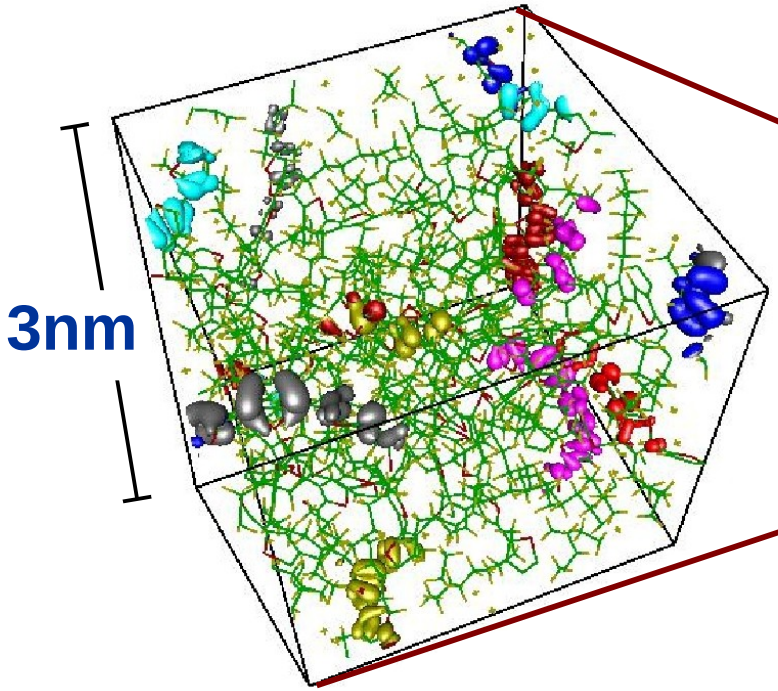


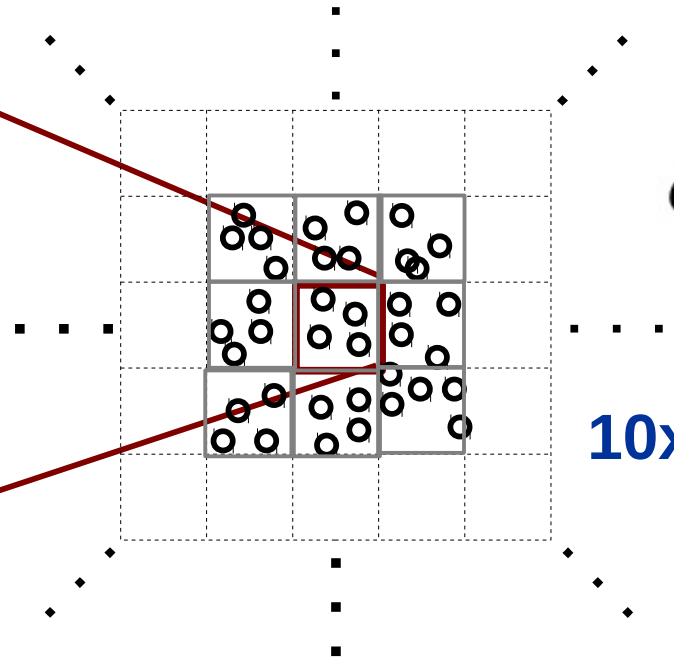
N. Vukmirović and L.-W. Wang, Nano Lett. 9, 3996 (2009)

SCIENTIFIC COMPUTING LABORATORY

From electronic structure toward mobility

- Supercell of (3nm)x(3nm)x(3nm) not large enough.
- Construction of a larger box from a number of calculations on a small box.
- Approximation of cross-boundary transition rates.
- Transport at low field = conductance network.



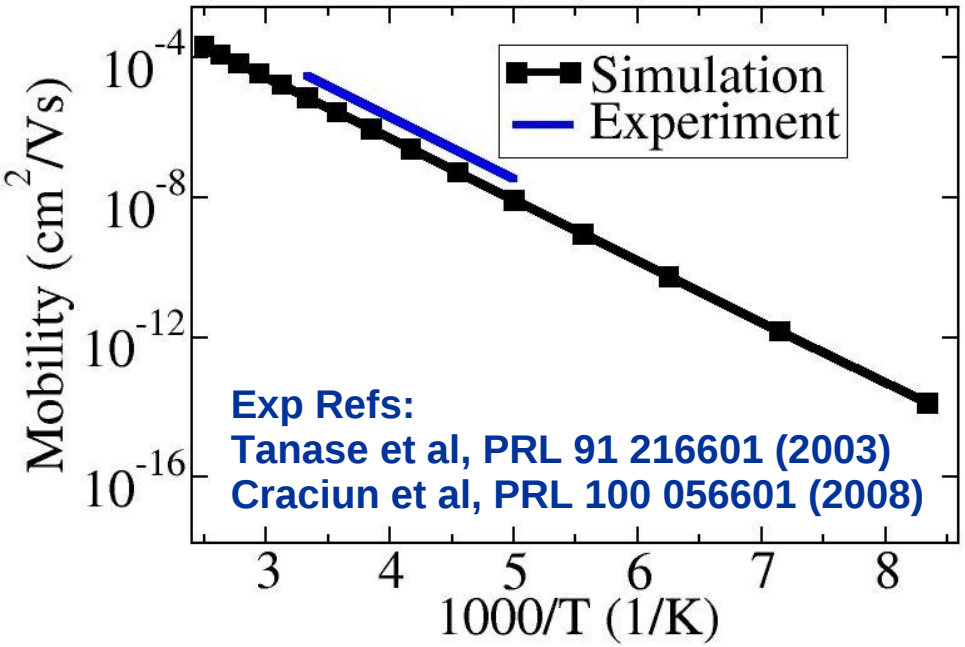


$$G_{ij} = \frac{e^2}{kT} n_i W_{ij}$$

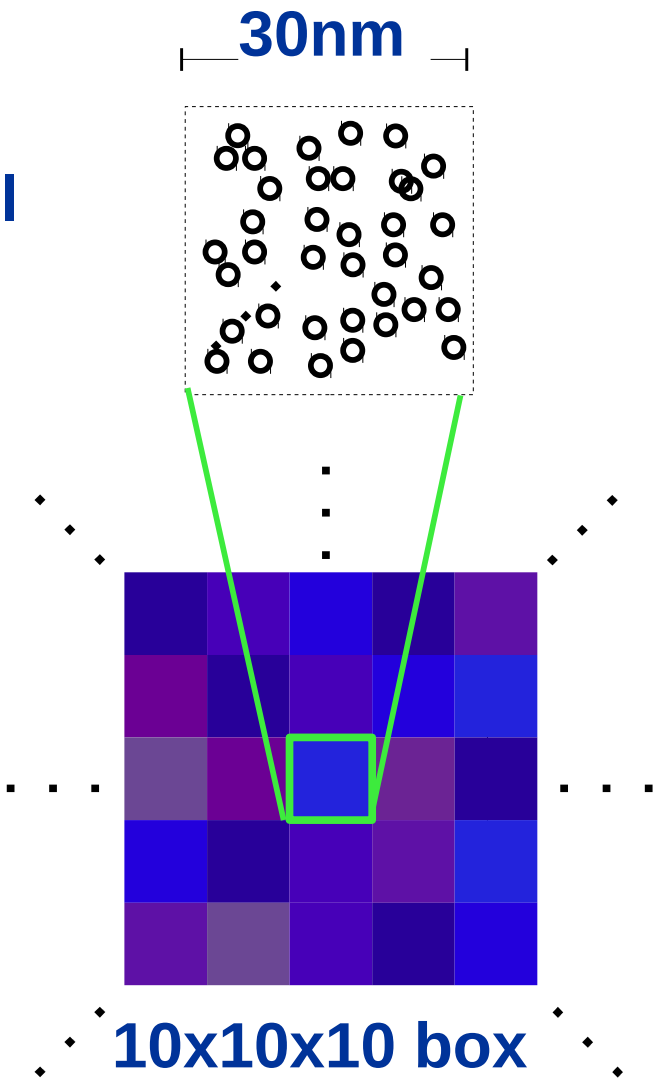
10x10x10 box

Mobility

- Fluctuations in the mobility for different realisations.
- Construction of a new box – each cell = uniform anisotropic conductor.
- Devices below 100nm have inherent fluctuations in transport.



Exp Refs:
Tanase et al, PRL 91 216601 (2003)
Craciun et al, PRL 100 056601 (2008)



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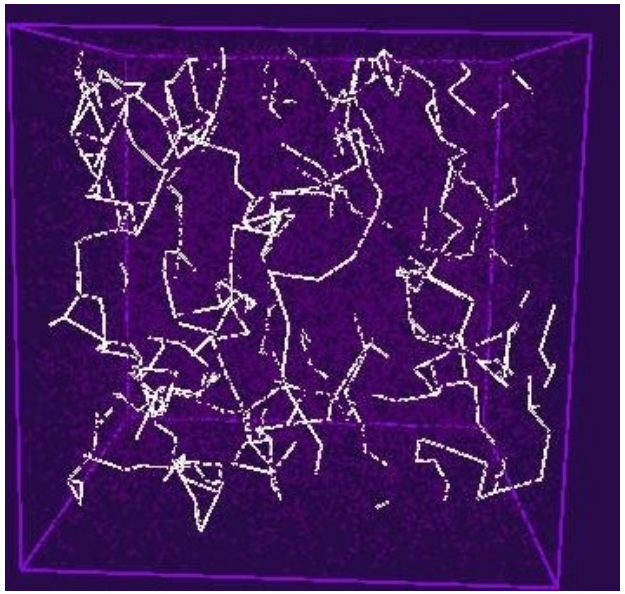
Electronic transport:
Results and lessons learned

Microscopic insight

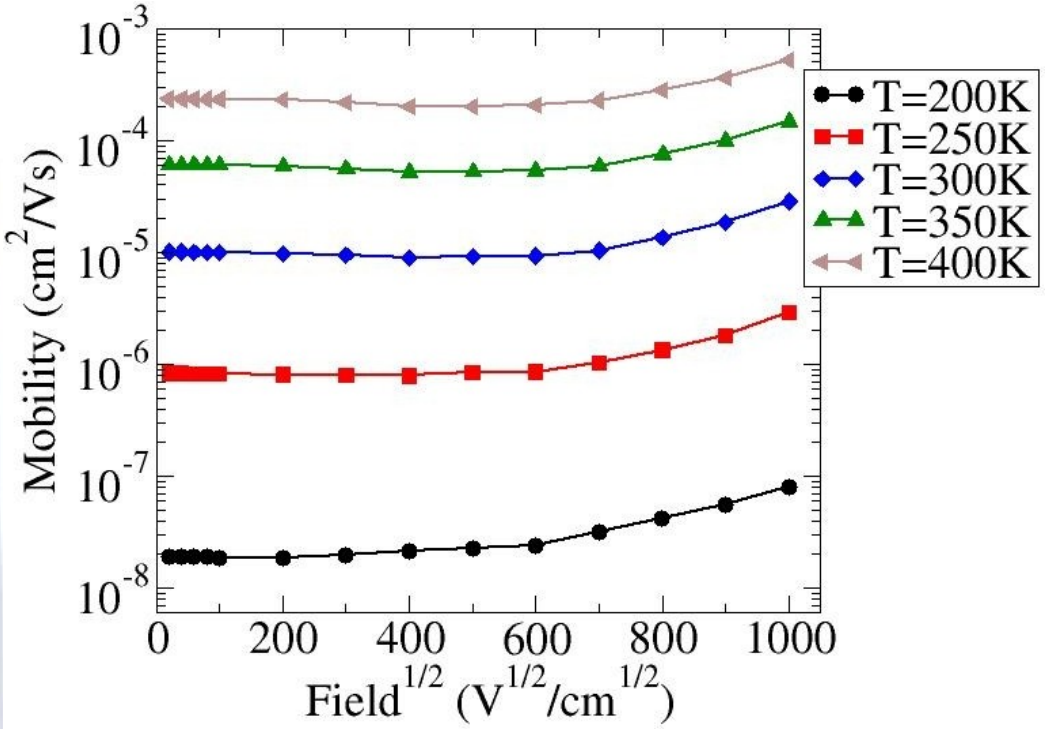
- Current paths resemble the lightning bolts.

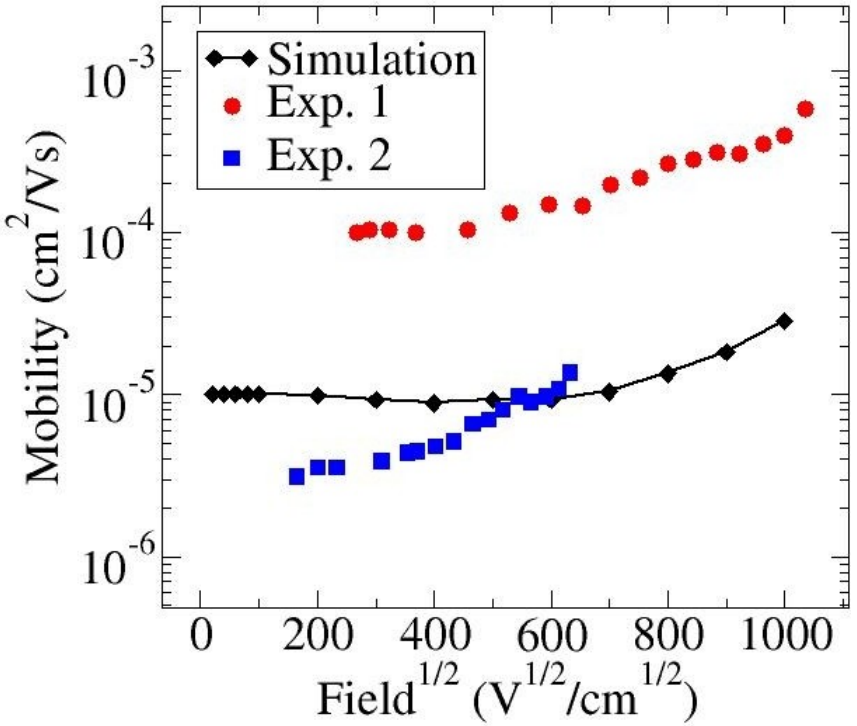


http://www.colourlovers.com/uploads/2008/02/sydney_lightning_bolts.jpg

Electric field dependence

- **Electric field dependence of mobility in disordered P3HT**





Exp. 1: S. S. Pandey et al, JJAP 39, L94 (2000).

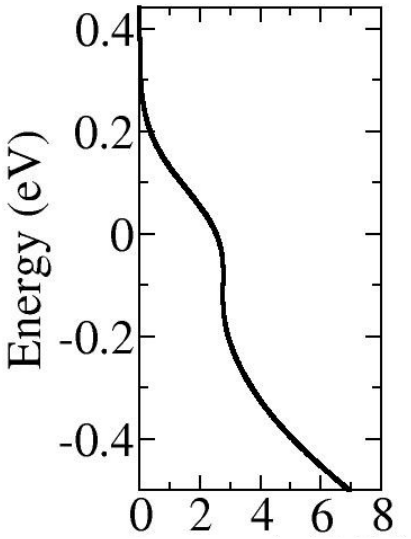
Exp. 2: K. Genevicius et al, Synth. Met. 137, 1407 (2003)

N. Vukmirović and L.-W. Wang, Phys. Rev. B 81, 035210 (2010)

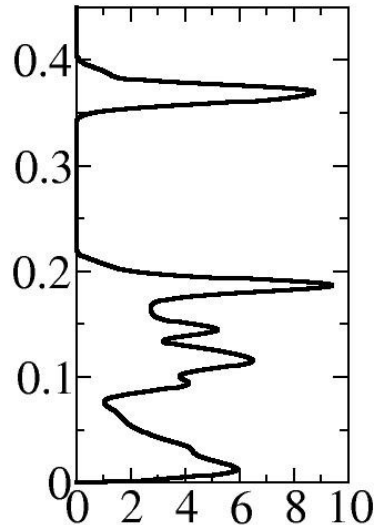
SCIENTIFIC COMPUTING LABORATORY

Is there a simpler model?

- How useful is the MA expression?
- Develop a simple model.
- What determines the transport:
  - electronic DOS?
  - phonon DOS?
  - details of WF overlaps?
  - details of phonon modes?



electronic DOS

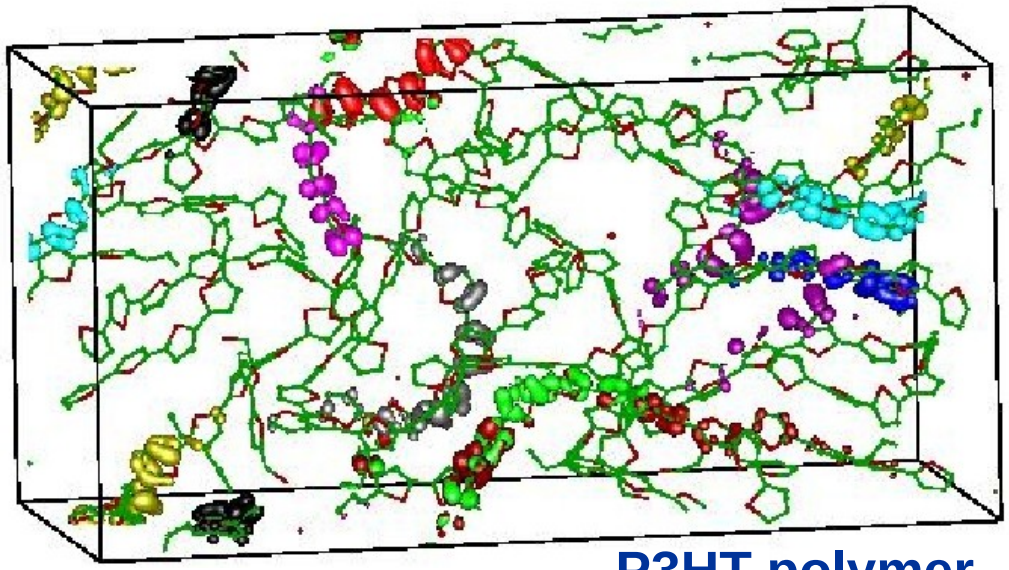


phonon DOS

Hopping rates

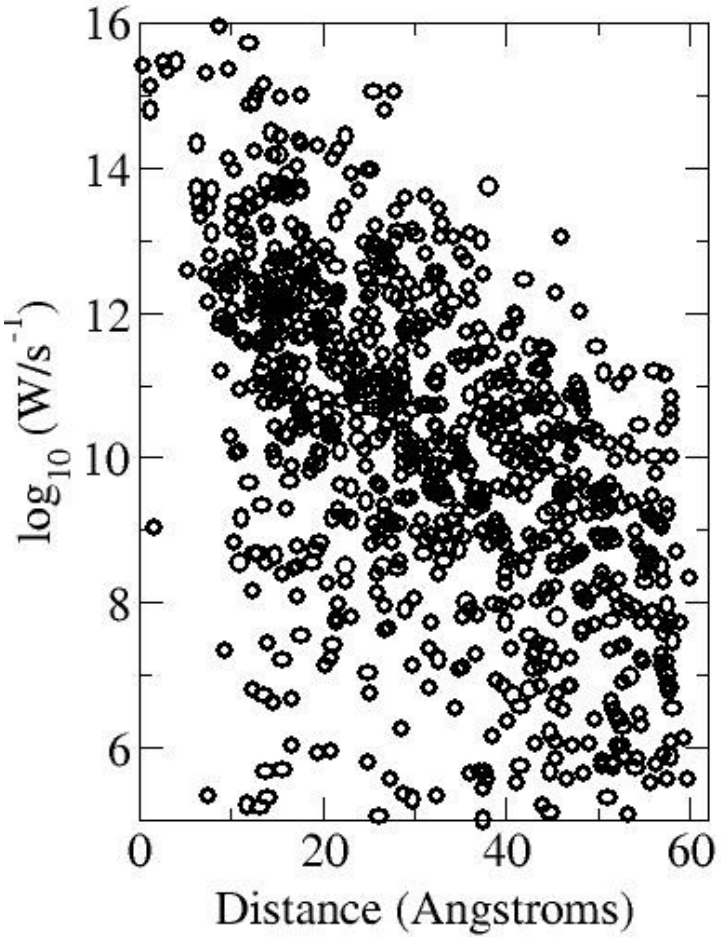
$$W_{ij} = \pi \sum_{\mu} \frac{|M_{ij,\mu}|^2}{\omega_{\mu}} [N(\hbar\omega_{\mu}) + 1] \delta(E_i - E_j - \hbar\omega_{\mu})$$

$$W_{ij} = W_0 \exp(-R_{ij}/a)$$

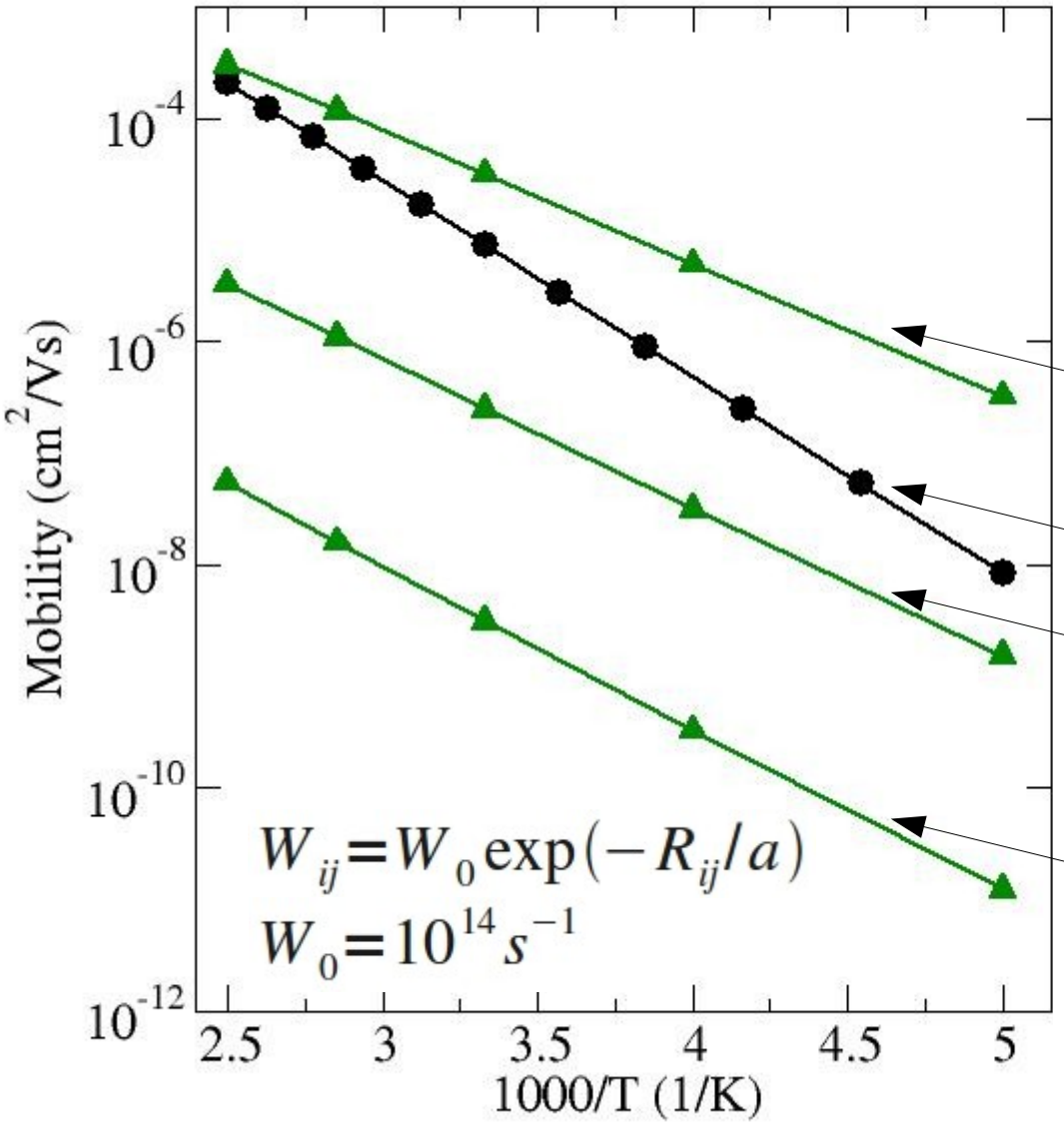


P3HT polymer

top hole states



Mobility



- Different slope of the temperature dependence in the MA model and the full simulation.

MA model, a=3.0Å

full model

MA model, a=2.0Å

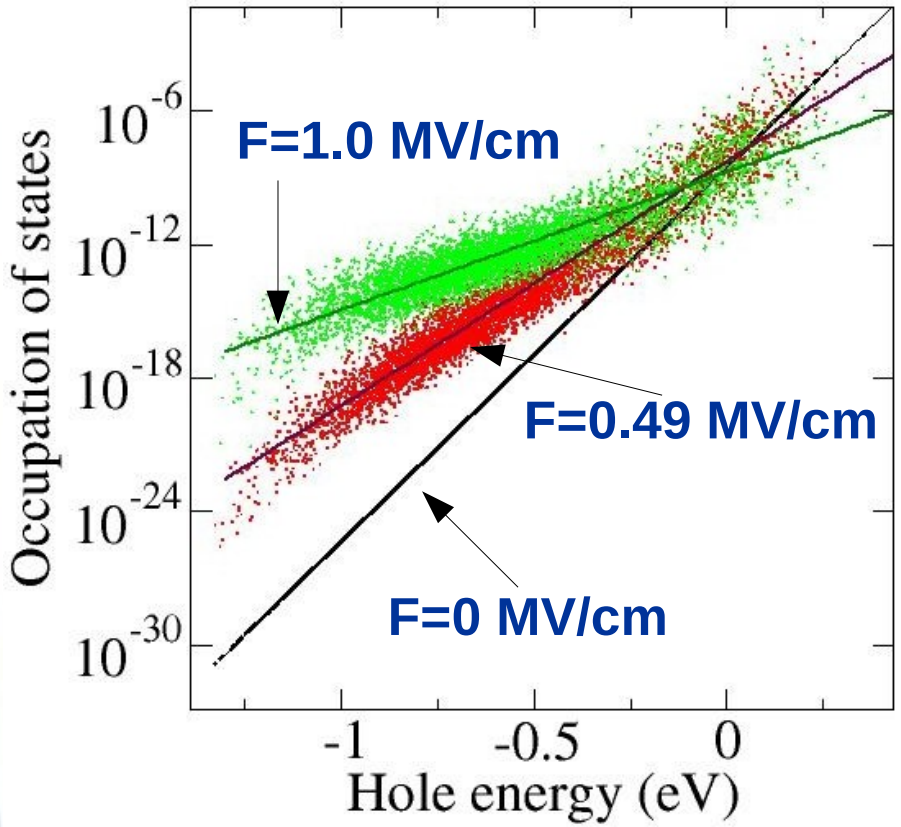
MA model, a=1.5Å

N. Vukmirović and L.-W. Wang, Appl. Phys. Lett. 97, 043305 (2010)

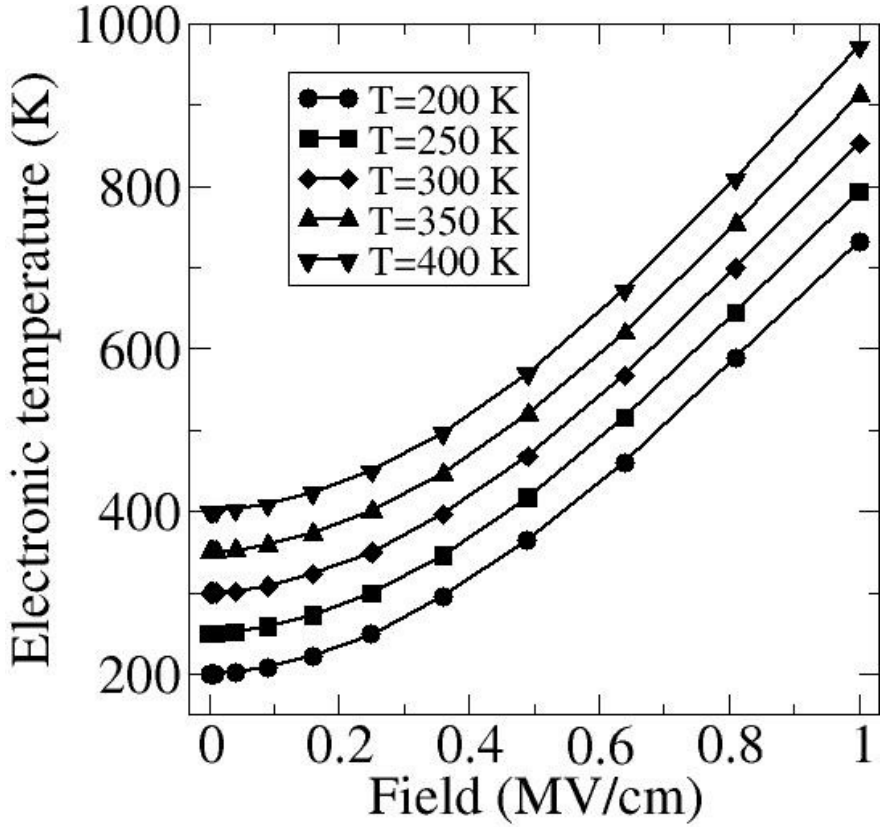
SCIENTIFIC COMPUTING LABORATORY

Electronic temperature in electric field

- Nonequilibrium carrier distribution in a finite electric field



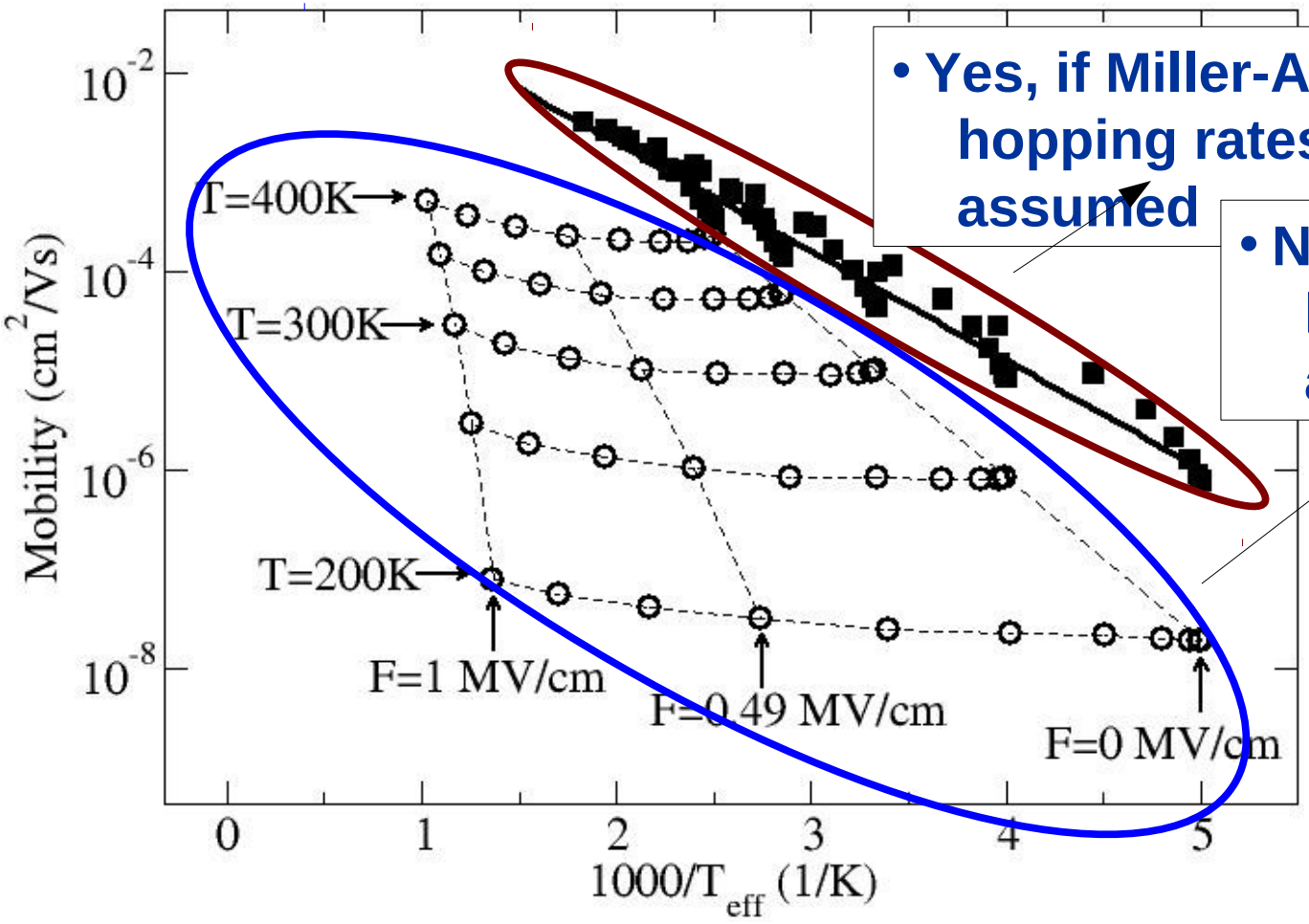
- Dependence of electronic temperature on electric field – full model



N. Vukmirović and L.-W. Wang, Phys. Rev. B 81, 035210 (2010)

Scientific Computing Laboratory

Is the concept of elec. temperature useful?



- Yes, if Miller-Abrahams hopping rates are assumed
- No, if realistic hopping rates are assumed
- Qualitatively different conclusions!

N. Vukmirović and L.-W. Wang, Phys. Rev. B 81, 035210 (2010)

Search for a simpler model

- **Full model – interaction with all phonon modes**

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

- **Model A – approximation:** $M_{ij} = \langle i | \frac{\partial H}{\partial v_\mu} | j \rangle \sim S_{ij} = \int d^3\boldsymbol{r} |\psi_i| \cdot |\psi_j|$

$$W_{ij} = \beta^2 S_{ij}^2 [N(E_{ij}) + 1] D_{ph}(E_{ij}) / E_{ij}$$

- **Model B:**

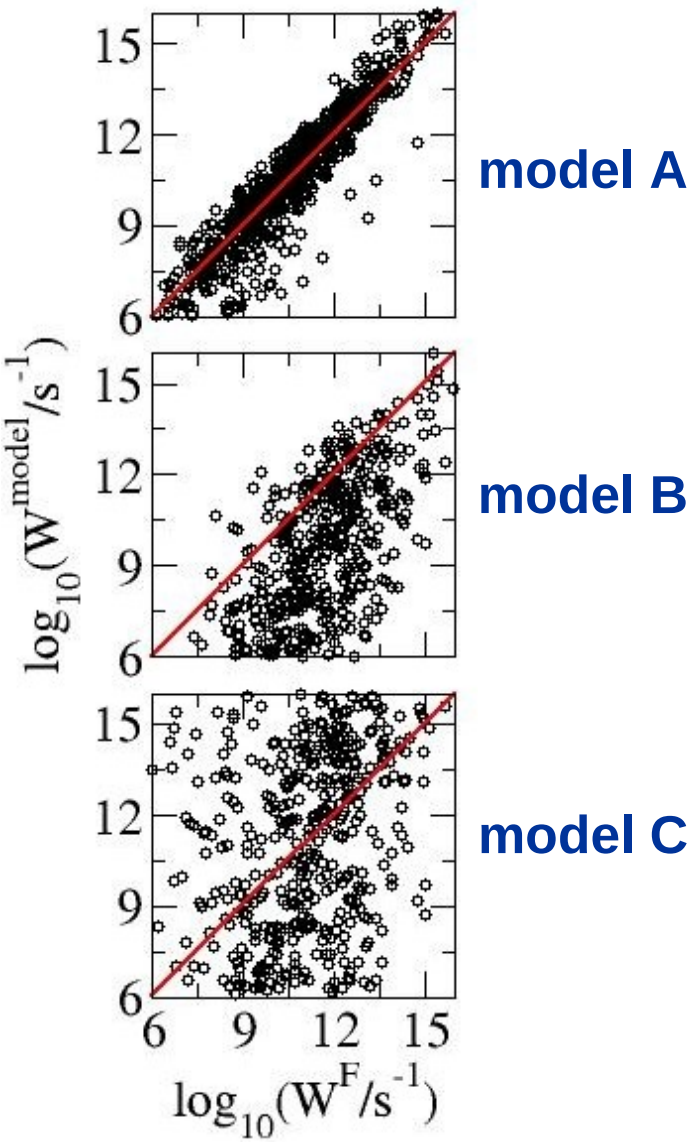
$$W_{ij} = \beta^2 \exp(-R_{ij}/a) [N(E_{ij}) + 1] D_{ph}(E_{ij}) / E_{ij}$$

- **Model C (Miller-Abrahams expression):**

$$W_{ij} = W_0 \exp(-R_{ij}/a)$$

- **Models A-C can fit the temperature dependence, but...**

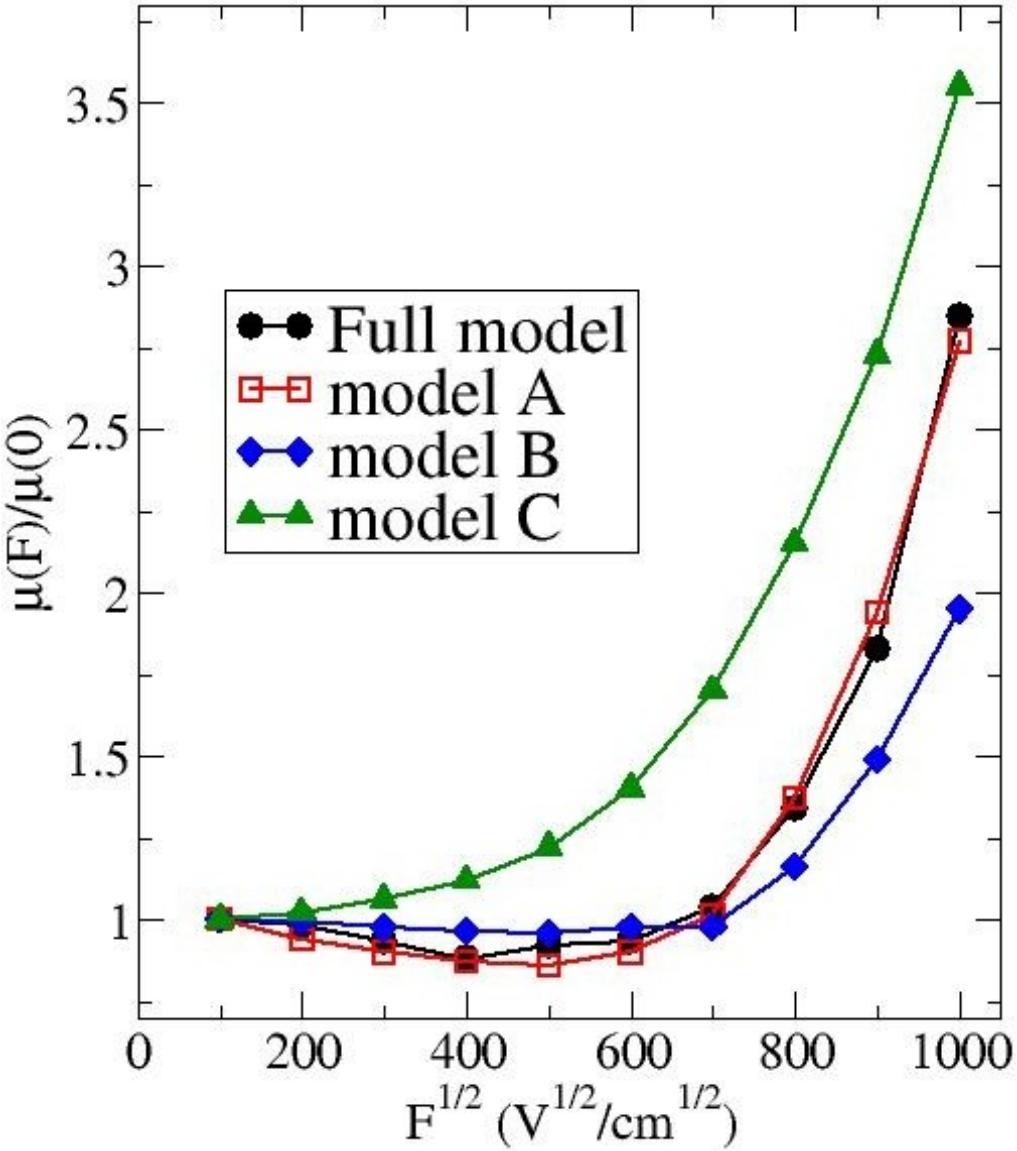
Test of different models



model A

model B

model C



N. Vukmirović and L.-W. Wang, Appl. Phys. Lett. 97, 043305 (2010)

SCIENTIFIC COMPUTING LABORATORY

So, what determines the transport?

$$W_{ij} = \beta^2 S_{ij}^2 [N(E_{ij}) + 1] D_{ph}(E_{ij}) / E_{ij}$$

transition energy

wavefunction moduli overlap

phonon occupation number

phonon DOS

- electronic DOS? • Yes.
- phonon DOS? • Yes.
- details of WF overlaps? • Yes.
- details of phonon modes? • No.

Take home messages

- Simulations that link the atomic structure of the material to its electrical properties
- Electronic structure
  - Exponential density of states in fully disordered polymers
  - Long range electrostatic interaction causes wavefunction localization, rather than breaks in conjugation
- Electronic transport
  - Electronic temperature in a finite electric field is not useful for the description of carrier transport.
  - Phonon DOS and details of WF overlaps are important.