Multiscale bottom-up simulations of charge and energy transport in disordered organic semiconductors

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Acknowledgments

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Outline

1. Compound design in organic electronics
   - fundamentals, aims, and limitations
   - photoelectric processes in organic photovoltaic cells

2. Multiscale workflow for microscopic charge transport simulations
   - multiscale “challenge”
   - Ménage à trois: density-functional theory, classical Molecular Dynamics, kinetic Monte-Carlo

3. Stochastic Graph Model with Weighted Edges
   1. Stochastic model of vertices (hopping sites)
   2. Stochastic model of edges (connected hopping sites)
   3. Weighting of edges
      1. Simulation of correlated site energies
      2. Simulation of transfer integral

4. Outlook
Organic Light Emitting Diodes

**solution processability**
- spin-coating
- inkjet-printing

**tunability**
- electronic structure (charge transport, optical properties)
- morphology control (crystallization, self-assembly) via side groups

**development**
- life time of OLEDs
- efficiency of OPV cells

structure-processing-property relationships for “rational compound design”
Relevant photoelectric processes in OPV

1. **Exciton formation**
   - Absorption properties of materials

2. **Exciton diffusion**
   - Migration of local excitons

3. **Exciton separation**
   - Charge transfer excitons at interface

4. **Charge carrier dynamics**
   - Transport of free charges

[+ geminate/non-geminate recombination]
Compound design: experiments

NMR, WAXS: averaged quantities, no distribution functions
Is the improvement due to electronic structure or morphology?
Theoretical Challenges

- a. Large-scale morphology (topology of the charge percolating network)
- b. Local mutual orientations/positions of molecules
- c. Electronic structure (reorganization energy, driving force, electronic coupling)
Workflow of charge transport simulations

Marcus type hopping rate:

\[
\omega_{ij} = \frac{J_{ij}^2}{\hbar} \sqrt{\frac{\pi}{\lambda_{ij} k_B T}} \exp \left[ - \frac{(\Delta E_{ij} - \lambda_{ij})^2}{4 \lambda_{ij} k_B T} \right]
\]
Microscopic Simulations of Charge Transport in Disordered Organic Semiconductors

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Supporting Information

ABSTRACT: Charge carrier dynamics in an organic semiconductor can often be described in terms of charge hopping between localized states. The hopping rates depend on electronic coupling elements, reorganization energies, and driving forces, which vary as a function of position and orientation of the molecules. The exact evaluation of these contributions in a molecular assembly is computationally prohibitive. Various, often semiempirical, approximations are employed instead. In this work, we review some of these approaches and introduce a software toolkit which implements them. The purpose of the toolkit is to simplify the workflow for charge transport simulations, provide a uniform error control for the methods and a flexible platform for their development, and eventually allow in silico prescreening of organic semiconductors for specific applications. All implemented methods are illustrated by studying charge transport in amorphous films of tris-(8-hydroxyquinoline)aluminum, a common organic semiconductor.
Tris(8-hydroxyquinolinato)aluminium (Alq3)

Green light emitter
Hole and electron conductor
Pronounced Poole-Frenkel behavior

Dipole moment: 4 Debye
Changes the direction in ions

Phase: amorphous
Isomer: meridional

Hole reorganization energy: 0.23 eV

J. J. Kwiatkowski, J. Nelson, H. Li and J. L. Bredas, W. Wenzel, and C. Lennartz,
Simulating charge transport in tris(8-hydroxyquinoline) aluminium (Alq3),
Phys. Chem. Chem. Phys. 10, 1852, 2008

Yuki Nagata and Christian Lennartz
Atomistic simulation on charge mobility of amorphous tris(8-hydroxyquinoline)
aluminium (Alq3): Origin of Poole-Frenkel-type behavior,
J. Chem. Phys. 129, 034709, 2008
Alq3: Force Field and Morphology

21 unknown angle and dihedral potentials
[scans and fits using B3LYP/6-311+g(d,p)]
partial charges - CHELPG
van der Waals parameters – OPLSaa
Ligands - rigid

Box of 512 molecules

\[ \rho = 1.5 \text{ g/cm}^3 \]

\[ T_g = 448 \text{ K} \]

A. Lukyanov, C. Lennartz, D. Andrienko, Phys. Stat. Sol. A, 2009
Alq3: Electronic coupling elements

\[ J_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle \]

\[ \phi_{ij} \] - frontier orbitals
\[ \hat{H} \] - dimer Hamiltonian

- depend on positions, orientations
- distributions are not Gaussian
- span several orders of magnitude
- semiempirical and DFT methods agree

**ZINDO**: J. Kirkpatrick, Int. J. Quantum Chem. 108, 51 (2008)

**DFT**: E. F. Valeev, V. Coropceanu, D. A. da Silva Filho, S. Salman, J.-L. Bredas, J. Am. Chem. Soc. 128, 9882 (2006)
B. Baumeier, J. Kirkpatrick, D. Andrienko, Phys. Chem. Chem. Phys. 12, 11103 (2010)
Transfer integrals = connectivity
• transfer integrals reflect topological connectivity in the system
• energetic disorder weights the “quality” of the connection
Site energy: electrostatics and polarization

Coulomb interaction (with bulk screening)

\[ E_{i}^{\text{el}} = \frac{1}{4\pi\varepsilon_0} \sum_{a_i} \sum_{b_k} \left( q_{a_i}^c - q_{a_i}^n \right) \frac{q_{b_k}^n}{\varepsilon_s r_{a_i b_k}} \]

Phenomenological distance-dependence

\[ \epsilon(r) = \epsilon_\infty - (\epsilon_\infty - 1) \left( 1 + s r + \frac{1}{2} s^2 r^2 \right) e^{-s r} \]

Explicit polarization via polarizable force-fields

\[ \vec{\mu}_{a_i}^{(k+1)} = \omega \vec{F}_{a_i}^{(k)} \alpha_{a_i} + (1 - \omega) \vec{\mu}_{a_i}^{(k)} \]

Screening: Y. Nagata, C. Lennartz, J. Chem. Phys. 2008, 129, 034709.
Thole model: B. Thole, Chem. Phys. 1981, 59, 341–350.
Master Equation

State-based description

\[ \frac{\partial P_\alpha}{\partial t} = \sum_\beta P_\beta \Omega_{\beta\alpha} - \sum_\beta P_\alpha \Omega_{\alpha\beta} \]

\( P_\alpha \) - occupation probability of a state

Site-occupation based description

mean-field

\[ \frac{\partial p_i}{\partial t} = \sum_j p_j (1 - p_i) \omega_{ji} - p_i (1 - p_j) \omega_{ij} \]

\( p_i \) - occupation probability of a site

state-to-site: J. Cottaar, P.A. Bobbert, Phys. Rev. B 74, 115204 (2006).

kmc: A.P.J. Jansen, An Introduction To Monte Carlo Simulations Of Surface Reactions, cond-mat/0303028
Kinetic Monte Carlo

KMC explicitly simulates the dynamics of charge carriers by constructing a Markov chain in state space.

Can find both stationary and transient solutions of the master equation.

Only states with a direct link to the current state are needed at each step.

Extensions to multiple charge carriers (without the mean-field approximation), site-occupation dependent rates, and different types of interacting particles and processes, are straightforward.
Energetic disorder reduces the value of mobility by six orders of magnitude.

The Poole-Frenkel behavior for small fields can only be observed if correlated disorder is taken into account.

For a system with such large energetic disorder the absolute values of (non-dispersive) mobility are systematically overestimated due to significant finite size effects.
Alq3: Occupation probabilities and currents

occupation probabilities
4096 molecules

current filaments
512 molecules

All sites are sampled (can be also checked using detailed balance)
Currents have preferred pathways (correlated disorder) – current filaments

current filaments: J.J.M. van der Holst, M.A. Uijttewaal, B. Ramachandran, R. Coehoorn, P.A. Bobbert, G.A. de Wijs, R.A. de Groot, Phys. Rev. B 79, 085203 (2009).
Alq3: Finite size effects

Boxes of molecules

512 = 8 × 8 × 8
2197 = 13 × 13 × 13
4096 = 16 × 16 × 16
13824 = 24 × 24 × 24

Mobility does not converge with the increase of the box size?

finite size effects: A. Lukyanov, D. Andrienko, Phys. Rev. B, 2010
Dispersive versus non-dispersive transport

Mean energy of a charge carrier

\[ E_N = \left\langle Z_N^{-1} \sum_{n=1}^{N} \epsilon_n e^{-\beta \epsilon_n} \right\rangle \]

\( \epsilon_n \) - Gaussian distributed

\[ E_{\infty}/\sigma = -\sigma/k_B T \]

Dispersive to non-dispersive transport

\[ (\sigma/k_B T)^2 = -5.7 + 1.05 \ln N \]

10,000 molecules max (ZINDO level)
30 × 30 × 30 lattice
Sampling of full DOS is not possible

A. Lukyanov, D. Andrienko, Phys. Rev. B, 2010
Advantages and Limitations

✓ Parameter-free direct link between chemical structure, processing, and property
✓ Allows microscopic understanding of the fundamental physical processes
✓ Formulation of design rules

❖ Computationally extremely demanding
❖ Treatable system sizes limited to 15-20nm length (10000 molecules)
❖ Systematic dependence of mobility on system size

Wait for bigger/faster computers?

Stochastic modeling!

Volker Schmidt  Ole Stenzel

Bulk heterojunction

Domains ~ 10nm
Device > 100nm
Stochastic model of vertices (hopping sites)

- Hopping sites generated by microscopic model are interpreted as realization of point-process model
- Rather regular, but still random structure
- No clustering of points

- $g(r)$ proportional to the relative frequency of point pairs with distance $r$
- Hard-core distance (minimum distance) between points, since $g(r) = 0$ for $0 < r < 0.6\text{nm}$
- Rather regular point process, since has only three (narrow) oscillations.
Goal: Simulation of point process with **high intensity** and **large distances**

Soft-core model

- Step 1: Homogeneous Poisson point process. No interaction of points
- Step 2: Each point $S_n$ is assigned a random radius $R_n \sim F$, where $F$ is a continuous distribution function on $[0, \infty)$
- Steps 3 & 4: Delete all points that are contained in a larger sphere
- Finally: Each point $S_n$ has a distance to its nearest neighbor point larger than $R_n$
- Maximum intensity (average number of points per unit volume) of soft-core process is limited.

Therefore: iterative soft-core model
Iterative soft-core model

- Step 1: soft-core model
- Step 2: second, independent realization of a soft-core process in the complementary phase (blue circles).
- Step 3 & 4: delete all points that interfere with previous realization
- Step 5: repeat steps 2-4 until desired intensity is reached
- Finally: Only consider points (without the radii)
Model validation

Hopping sites by microscopic model

Hopping sites by point-process model
Model validation

- Comparing structural characteristics for the configuration of hopping sites generated by microscopic model and by iterative soft-core model
- Excellent agreement

**Diagram:**
- Pair-correlation function
- Nearest-neighbor-distance distribution function
- Spherical contact distribution function

**Legend:**
- Black: microscopic model
- Red: iterative soft-core model
Stochastic graph model: connecting vertices

Points $S_i$ and $S_j$ are connected according to a Bernoulli experiment, with probability $p$ depending on their distance.

Probability of two hopping sites being connected

Black: microscopic model
Red: fitted function
Model of correlated site-energies: Moving-average approach

- Edge weight is given by: 
  \[ \omega_{ij} = \frac{2\pi}{h} \frac{J_{ij}^2}{\sqrt{4\pi k_B T}} \exp\left( -\frac{(\Delta E_{ij} - \lambda_{ij})^2}{4\lambda_{ij} k_B T} \right) \]

- Site energies \( E_i, E_j \) are normally distributed 
  \( E_i \sim N(\mu, \sigma^2) \), but have a spatial correlation

- Every point \( S_i \) assigned the triple \( (S_i, R_i^{(a)}, R_i^{(b)}) \), where
  \[ R_i^{(a)} \sim N\left( \frac{\mu}{L} (1 - \omega), \frac{\sigma^2}{L} (1 - \omega) \right) \] and \[ R_i^{(b)} \sim N(\mu \omega, \sigma^2 \omega) \] for some \( L > 0, \omega \in [0,1] \)

- For every point \( S_i \), let 
  \( \left( (S_i^{(1)}, R_i^{(1,a)}, R_i^{(1,b)}), (S_i^{(2)}, R_i^{(2,a)}, R_i^{(2,b)}), \ldots, (S_i^{(L)}, R_i^{(L,a)}, R_i^{(L,b)}) \right) \) be its \( L \) nearest neighbors with corresponding marks (including the point itself)

- Define energy \( E_i \) (of site \( S_i \)) by 
  \[ E_i = \sum_{n=1}^{L} R_i^{(n,a)} + R_i^{(b)} \]
• Transfer integral $J_{ij}$ depends on the distance between the hopping sites $S_i, S_j$
• $\log(J_{ij}^2) \sim N(\mu, \sigma^2)$
• $\mu, \sigma^2$ depend on the distance between the points.
Validation: Example of fit

- \( \log(J_{ij}^2) \sim N(\mu, \sigma^2) \)
- Estimation of \( \mu = \mu(\text{distance}) \) from microscopic model
- Estimation of \( \sigma^2 = \sigma^2(\text{distance}) \) from microscopic model
- Fitting of parametric curves \( \mu_1(\cdot), \sigma_1^2(\cdot) \)
- Two hopping sites with distance \( d \) are assigned a squared transfer integral by \( J_{ij}^2 = \exp(X_{ij}) \) with \( X_{ij} \sim N(\mu(d), \sigma^2(d)) \)

![Graph of mean value \( \mu_1(\cdot) \)](image1)

![Graph of variance \( \sigma_1^2(\cdot) \)](image2)
Microscopic model

- Iterative soft-core model
  - graph vertices
- Bernoulli model
  - vertex connectivity
- Moving-averages
  - correlated site energies
- Normal distributions
  - transfer integral

Stochastic graph model

kMC

Graph representation:
- Force field
- Atomistic morphology
- Electronic coupling
- Electrostatics and polarization
- Master equation
- Current filaments

Graph statistics:
- rel frequency vs distance (nm)
- rel frequency vs number of edges
- rel frequency vs edge length (nm)
- rel frequency vs correlation
- rel frequency vs mean value
- rel frequency vs distance (nm)

Graph model outputs:
- without site-energies
- microscopic model
- stochastic graph model

Graph analysis:
- 300 400 500 600 700 800 900 1000
- $F_{1/2} (V/cm)^{1/2}$
- $10^{-5}$ $0.0001$ $0.001$ $\mu (cm^2/Vs)$
Outlook: bridging the gap

(1) microscopic simulation
   Acceptor material

bulk heterojunction

(1) microscopic simulation
   Donor material

(2) stochastic simulation
   Acceptor material

(3) dynamics in bulk morphology

(2) stochastic simulation
   Donor material