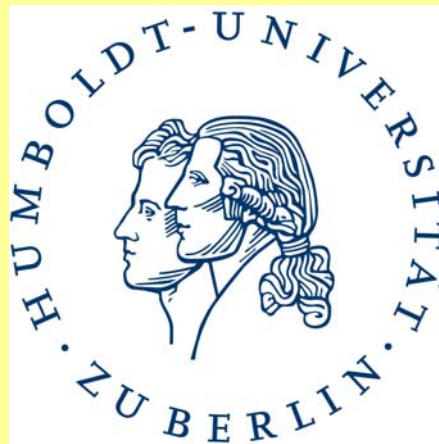


Polaron Transport in Organic Crystals: Theory and Modelling

Karsten Hannewald

*Institut für Physik & IRIS Adlershof
Humboldt-Universität zu Berlin (Germany)*



Coworkers & Sponsors

2001 – 2004: TU Eindhoven → Peter Bobbert
(Netherlands)



2005 – 2012: U Jena → Frank Ortmann &
(Germany) Friedhelm Bechstedt

- Lars Matthes & Falk Tandetzky (2D & 1D systems)
- Marcel Hieckel & Martin Krause (rubrene & durene)
- Robert Maul & Benjamin Höffling (amino acids)
- Björn Oetzel & Martin Preuss (quantum transport)
- Ralf Hambach & Uwe Treske (nanotubes & ribbons)



since 2012: HU Berlin (Germany) → Claudia Draxl



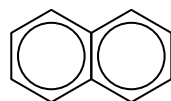
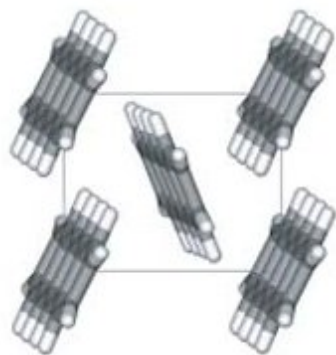
Organic Molecular Crystals as Benchmark Systems



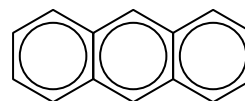
Niemax, Tripathi & Pflaum
[APL 86, 122105 (2005)]

= crystals of organic molecules → **well-ordered** systems
→ ideal to study **intrinsic transport** properties

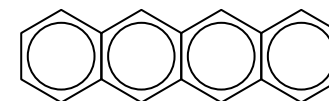
Herringbone Stacking



Naphthalene

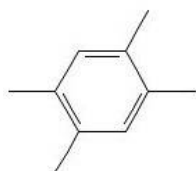


Anthracene



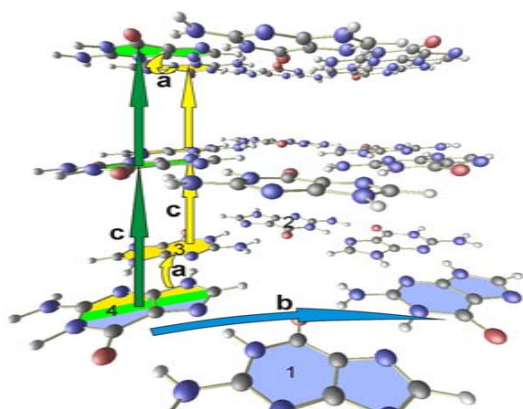
Tetracene

Hannewald et al., Phys. Rev. B 69, 075211 & 075212 (2004)
Appl. Phys. Lett. 85, 1535 (2004)
New J. Phys. 12, 023011 (2010)

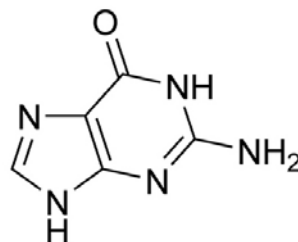


Durene

Ortmann, Hannewald & Bechstedt
Phys. Rev. B 75, 195219 (2007)
Appl. Phys. Lett. 93, 222105 (2008)



Layered Stacking



Guanine

Ortmann, Hannewald & Bechstedt
J. Phys. Chem. B 112, 1540 (2008)
J. Phys. Chem. B 113, 7367 (2009)

Peculiarities of Organic Molecular Crystals

Quite different than inorganic semiconductors!

- weak intermolecular van der Waals bonds
 - small electronic bandwidths $< 1\text{eV}$
 - strong electron-lattice interaction
- **polarons = electrons + phonon cloud**



Moreover: **Many important material parameters difficult to measure!**

→ bandwidths, effective masses, electron-phonon couplings ?

→ Transport: Theory & Ab-initio modelling play essential role!

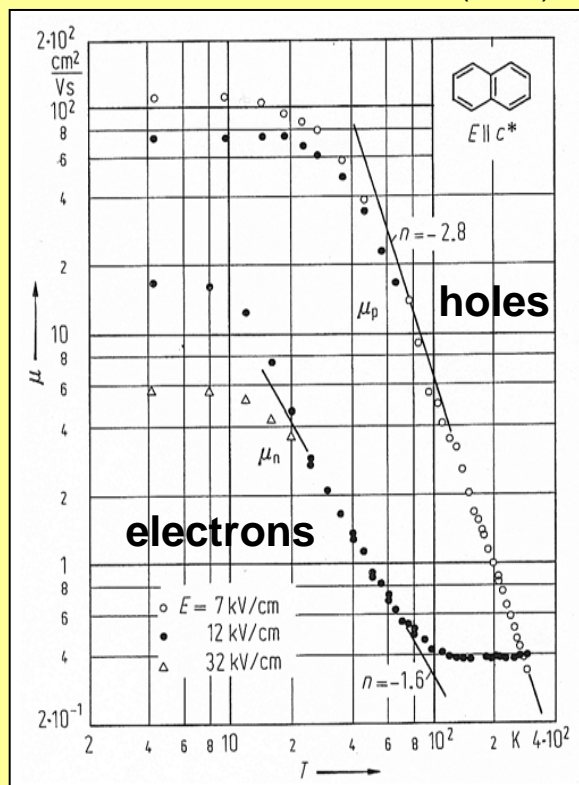
Open Questions for Charge Transport

- band transport or hopping ?
- temperature dependence ?
- electrons vs. holes ?

- mobility anisotropy & relation to stacking motif ?
- visualization of transport ?

Time-of-Flight Experiments

Warta & Karl, PRB 32, 1172 (1985)



Field-Effect Transistor Expts.

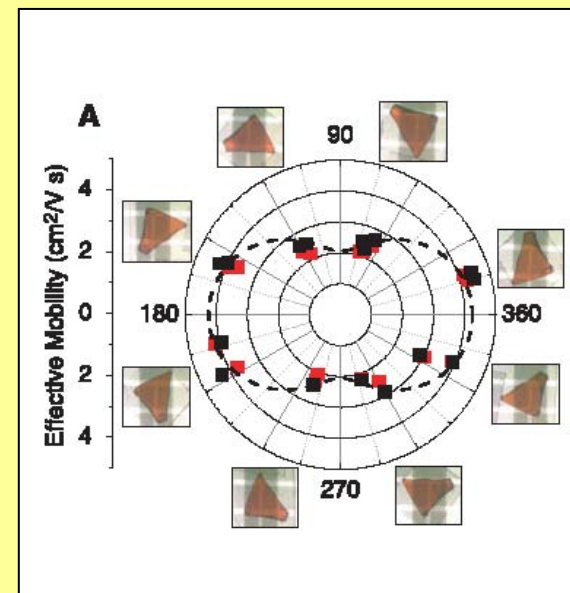
("stamp technique")

Sundar et al., Science 303, 1644 (2004)
Podzorov et al., PRL 93, 086602 (2004)

"There are still great challenges for theoreticians."

Norbert Karl
[Synth. Met. 133 & 134, 649 (2003)]

Goal: First-Principles Theory of Mobilities



Goal: First-Principles Theory of Conductivity

Drude formula for mobility looks simple:

$$\mu = e_0 \tau / m^*$$

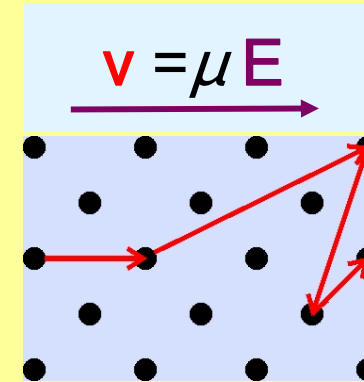
m^* ... effective mass

τ ... scattering time

Temperature dependences?

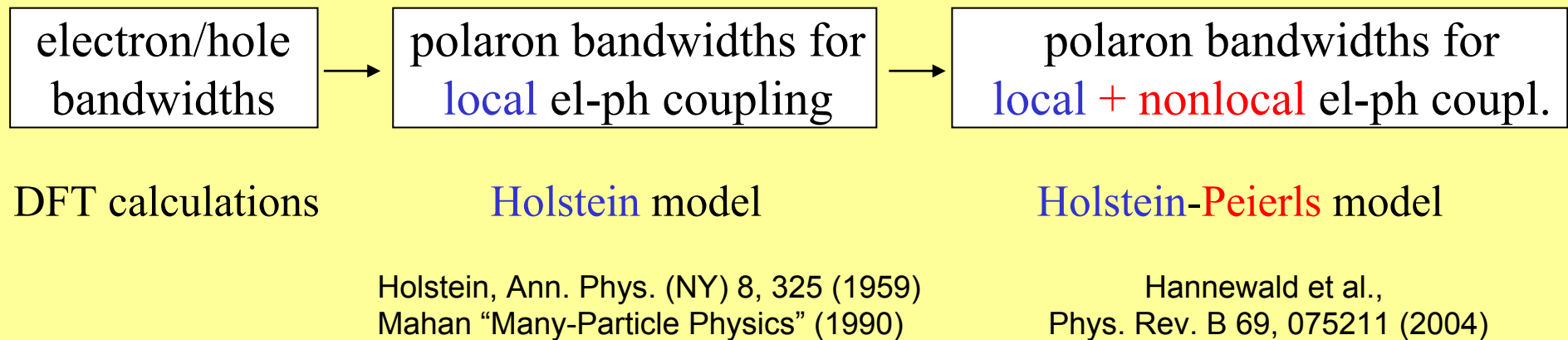
Step 1:
Polaron
band structure
(bandwidth $\sim 1/m^*$)

Step 2:
Mobility theory incl.
electron-phonon
scattering



**Needed: Microscopic models incl. electron-phonon coupling
supplemented by ab-initio material parameters**

Polaron Band Narrowing: Theory & Modelling



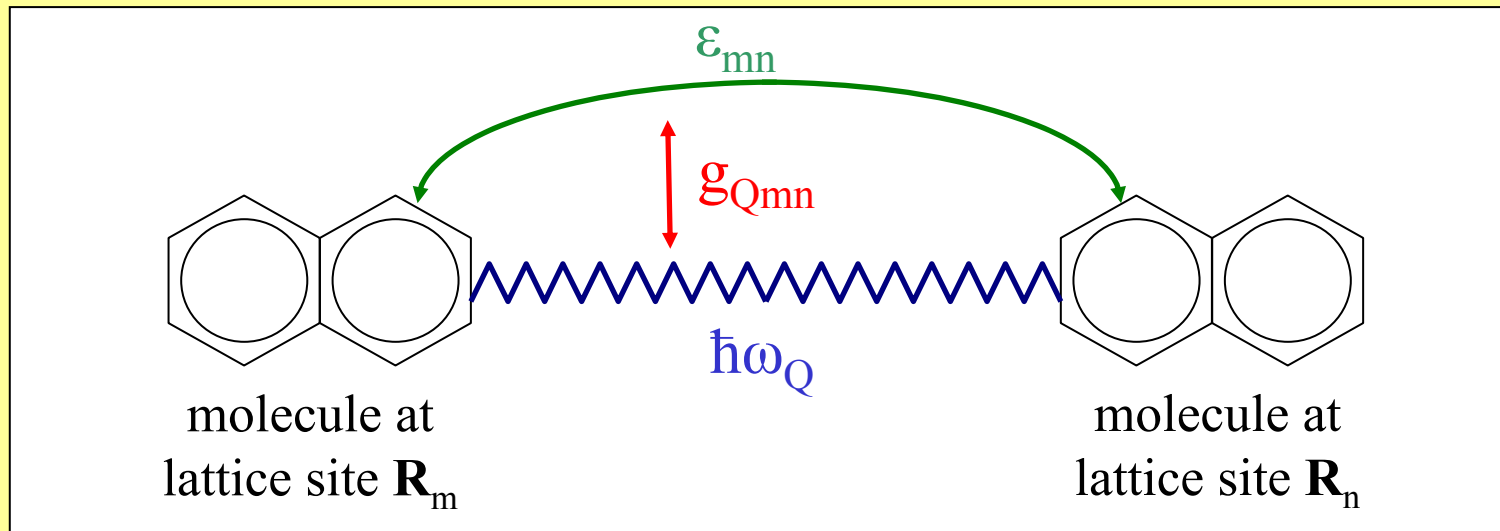
Hamiltonian for Holstein-Peierls Model

$$H = \sum_{mn} \epsilon_{mn} a_m^\dagger a_n + \sum_{Q=(q,\lambda)} \hbar\omega_Q (b_Q^\dagger b_Q + 1/2) + \sum_{Qmn} \hbar\omega_Q g_{Qmn} (b_{-Q}^\dagger + b_Q) a_m^\dagger a_n$$

$m=n$: on-site energies ϵ_{mm}
 $m \neq n$: transfer integrals ϵ_{mn}

for electrons: conduction band (LUMO)
 for holes: valence band (HOMO)

$m=n$: local coupling (Holstein)
 $m \neq n$: nonlocal coupling (Peierls)



Transition into Polaron Picture

Idea: Perform nonlocal canonical (Lang-Firsov) transformation!

$$f \rightarrow F = e^S f e^{S^\dagger}, \quad S = \sum_{mn} C_{mn} a_m^\dagger a_n, \quad C_{mn} = \sum_Q g_{Qmn} (b_{-Q} - b_Q^\dagger)$$

Advantages: • unitary transformation (does not change eigenvalues)
• nonperturbative w.r.t. electron-phonon coupling!

$$\Rightarrow \quad \text{H} = \sum_{mn} \tilde{\varepsilon}_{mn} A_m^\dagger A_n + \sum_Q \hbar \omega_Q (B_Q^\dagger B_Q + 1/2)$$

polarons **(displaced) phonons**

↑
polaron energies & transfer integrals

(after Fourier transformation into k-space → polaron bandstructure $\tilde{\varepsilon}_{\mathbf{k}}$)

Polaron Transfer Integrals

$$\tilde{\epsilon}_{mn} = (\epsilon_{mn} - \Delta_{mn}) e^{-\sum_{\lambda} (\frac{1}{2} + N_{\lambda}) (G_{\lambda mm} + G_{\lambda mn})}$$

- exponential reduction of transfer integrals \Rightarrow narrower bands
- temperature dependence via phonon occupations $N_{\lambda} = [e^{\hbar\omega_{\lambda}/k_B T} - 1]^{-1}$
- electron-phonon coupling in all orders
- effective coupling constants $G_{\lambda mm} = g_{\lambda mm}^2 + \frac{1}{2} \sum_{m \neq k} g_{\lambda mk}^2$ (Holstein + Peierls)

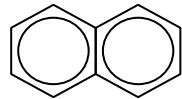
Key result: Once ϵ_{mn} , $g_{\lambda mn}$, and ω_{λ} are known, quantitative studies of temperature-dependent polaron band narrowing are possible!

[Hannewald et al., Phys. Rev. B 69, 075211 (2004); J. Phys.: Cond. Matt. 16, 2023 (2004)]

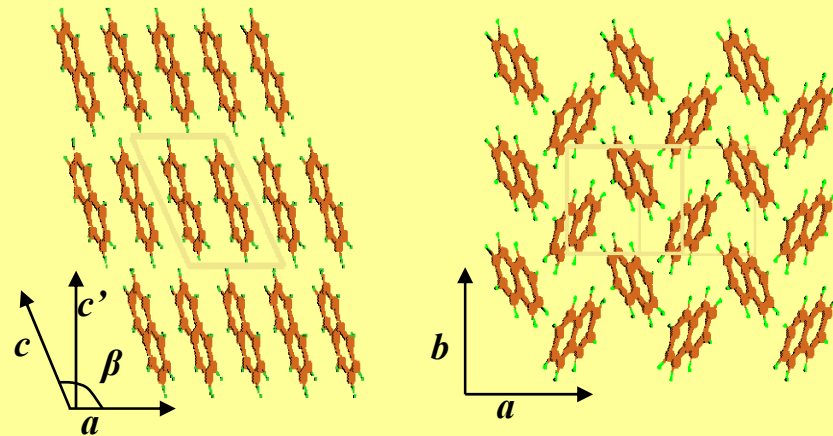
How to Obtain Material Parameters?

- **Step 1: Crystal geometry (R_m) & phonons (ω_λ)**
→ **ab-initio DFT-LDA calculations, VASP code**
- **Step 2: Transfer integrals (ϵ_{mn}) for HOMO & LUMO**
→ **ab-initio band-structure calculations & fit to tight-binding model**
- **Step 3: Electron-phonon coupling constants ($g_{\lambda mn} \sim \Delta\epsilon_{mn}$)**
→ **repeat step 2, but for the displaced (phonon-excited) geometry**

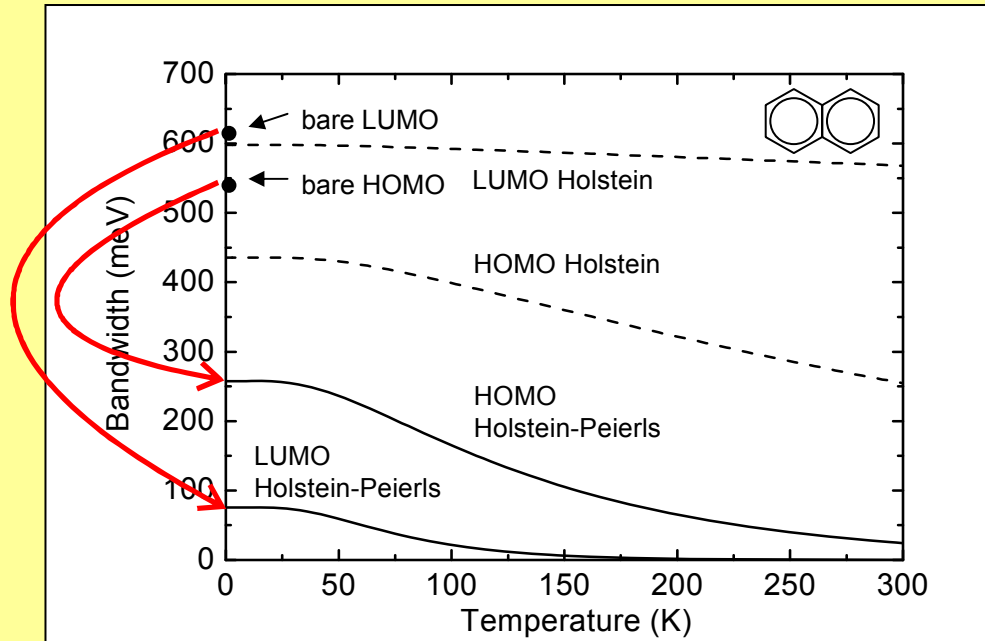
Naphthalene



- **monoclinic crystal**
- **two molecules per unit cell**
- **herringbone stacking**



Strong Band Narrowing in Naphthalene Crystals



Naphthalene, Anthracene & Tetracene:
Hannewald et al., Phys. Rev. B 69, 075211 (2004)

Durene Crystals:
Ortmann, Hannewald & Bechstedt,
Appl. Phys. Lett. 93, 222105 (2008)

Guanine Crystals:
Ortmann, Hannewald & Bechstedt,
J. Phys. Chem. B 113, 7367 (2009)

Experiments? → Very difficult to measure but recent progress using ARPES:

Pentacene: 240 meV (at 120 K) → 190 meV (at 300 K) [N. Koch et al., PRL 96, 156803 (2006)]
(HOMO) 250 meV (at 75 K) → 200 meV (at 300 K) [R. Hatch et al., PRL 104, 047601 (2010)]

⇒ Go beyond bandwidth calculations & develop mobility theory!

Mobility for Narrow Bands (“Small Polarons”): Theory & Modelling

DFT calculations

bare electron
& hole bands

Holstein model

polaron bands with
local el-ph

Holstein-Peierls model

polaron bands with
local + nonlocal el-ph

mobilities with
local el-ph

mobilities with
local + nonlocal el-ph

Holstein, Ann. Phys. (NY) 8, 325 (1959)
Mahan “Many-Particle Physics” (1990)

Hannewald & Bobbert,
Phys. Rev. B 69, 075212 (2004)
Appl. Phys. Lett. 85, 1535 (2004)

Kubo Formulism for Electrical Conductivity

- Linear response theory for mobility:

$$\mu_\alpha \sim T^{-1} \int_{-\infty}^{\infty} dt \langle j_\alpha(t) j_\alpha(0) \rangle_H$$

- Current $\mathbf{j} = d\mathbf{P}/dt = 1/i\hbar [\mathbf{P}, H]$ with polarization $\mathbf{P} = e_0 \sum_m \mathbf{R}_m a_m^+ a_m$

$$\begin{aligned} \text{current} &= \text{electronic current} &+& \text{phonon-assisted current (new)} \\ \mathbf{j} &= \mathbf{j}^{(I)} &+& \mathbf{j}^{(II)} \\ &= e_0/i\hbar \left\{ \sum_{mn} (\mathbf{R}_m - \mathbf{R}_n) \epsilon_{mn} a_m^+ a_n + \sum_{Qmn} (\mathbf{R}_m - \mathbf{R}_n) \hbar \omega_Q g_{Qmn} (b_{-Q} + b_Q) a_m^+ a_n \right\} \end{aligned}$$

hopping term for nonlocal coupling!

- Idea: Evaluate Kubo formula by means of canonical transformation!

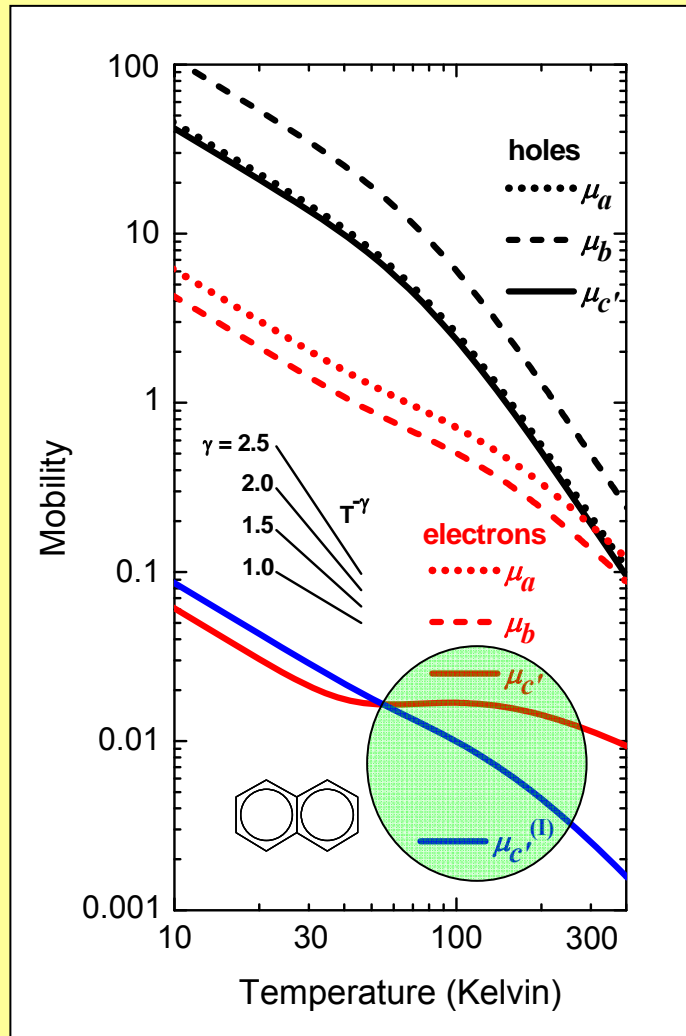
Key result: Once \mathbf{R}_m , ϵ_{mn} , $g_{\lambda mn}$, and ω_λ are known, quantitative predictions for anisotropy & T-dependence of mobilities $\mu = \mu^{(I)} + \mu^{(II)}$ possible!

[Hannewald & Bobbert, Phys. Rev. B 69, 075212 (2004)]

Naphthalene: Theory Describes Experiments Well

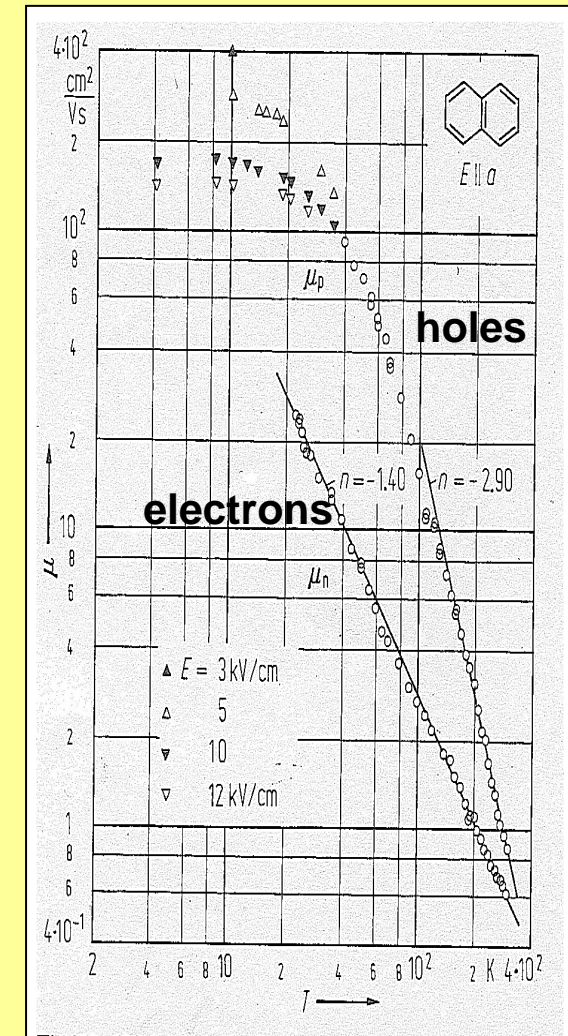
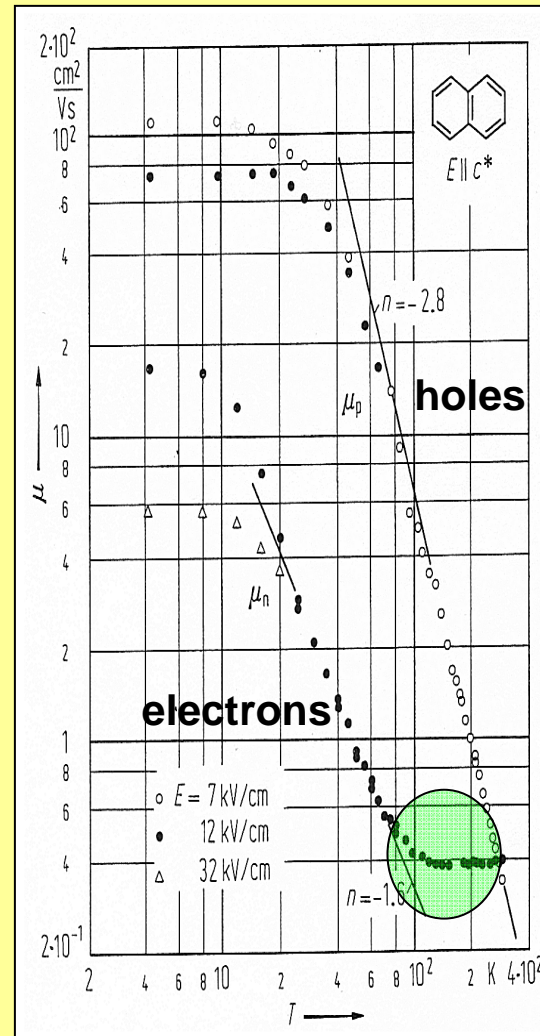
Ab-Initio Theory

Hannewald & Bobbert [APL 85, 1535 (2004)]

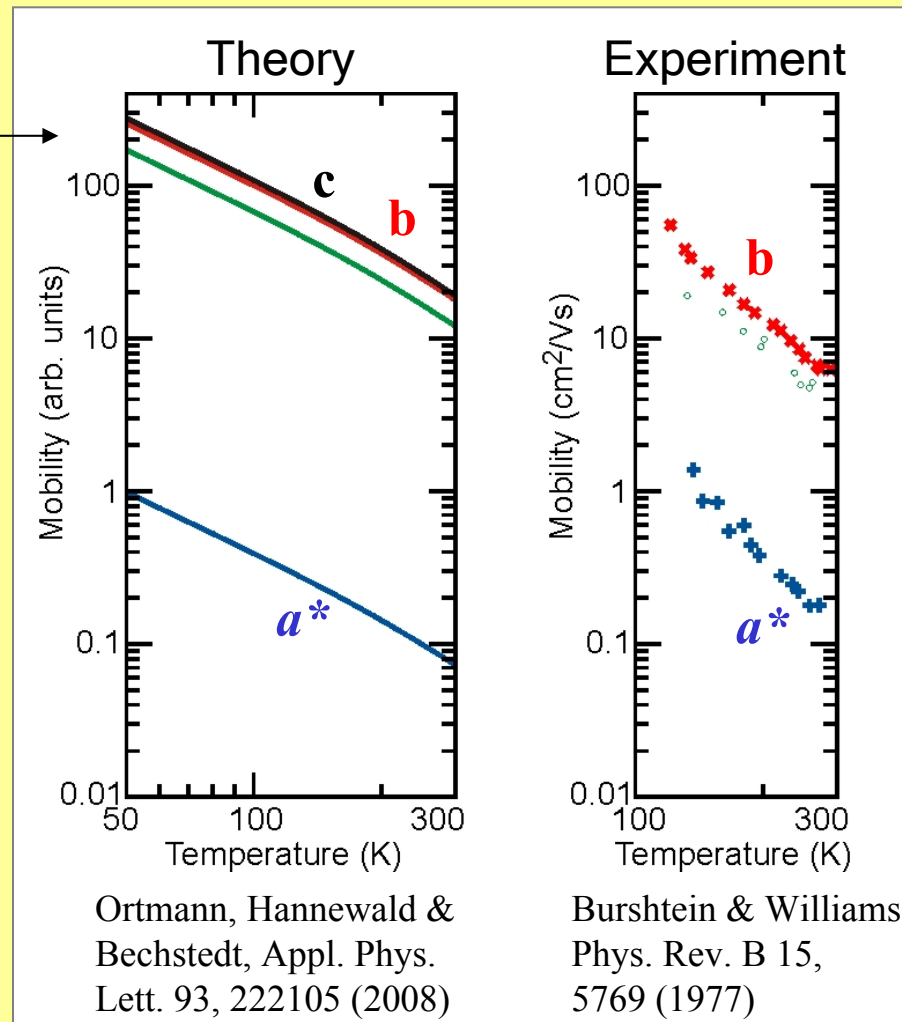
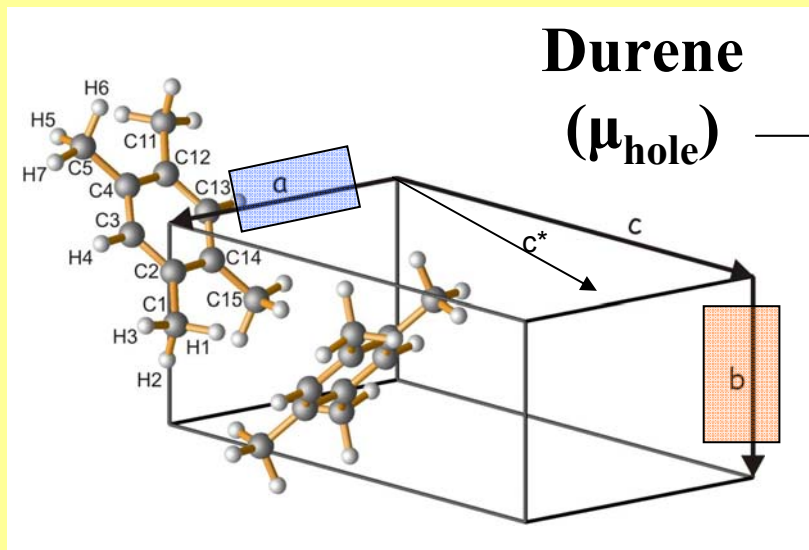


Experiment

Warta & Karl [Phys. Rev. B 32, 1172 (1985)]



Mobility Predictions for Other Materials



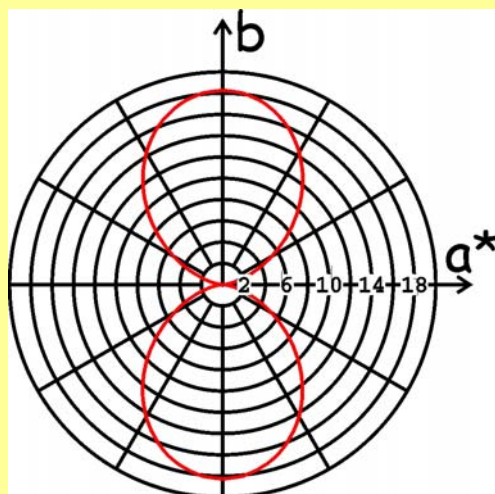
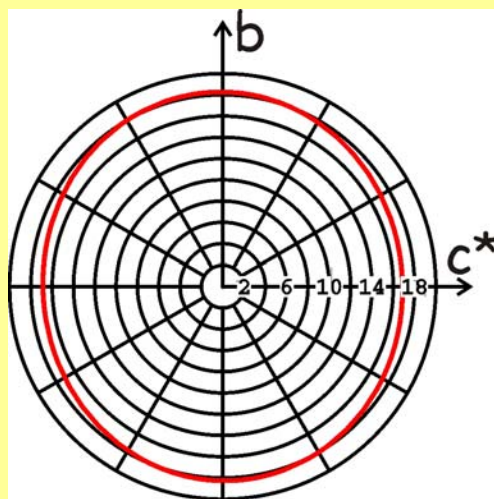
Naphthalene:
Hannewald & Bobbert,
Appl. Phys. Lett. 85, 1535 (2004)

Anthracene & Tetracene:
Hannewald & Bobbert,
AIP Conf. Proc. 772, 1101 (2005)

Guanine:
Ortmann, Hannewald & Bechstedt,
J. Phys. Chem. B 113, 7367 (2009)

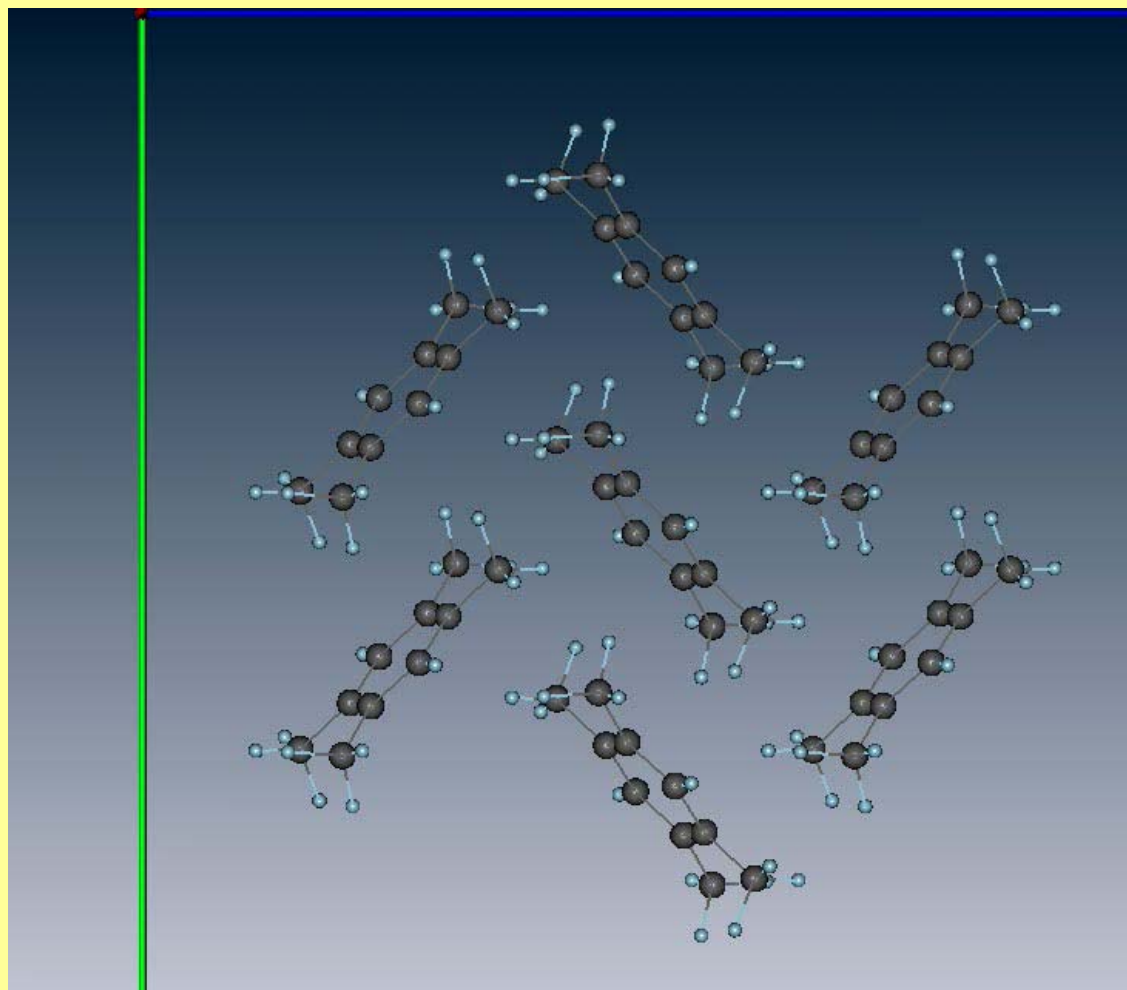
Anisotropic Hole Transport in Durene: Visualization

Mobility Tensor



HOMO Wave Function Overlap

Movie: http://ftp.aip.org/epaps/appl_phys_lett/E-APPLAB-93-052847/254195_0_vid_0_k71b6k.mpeg

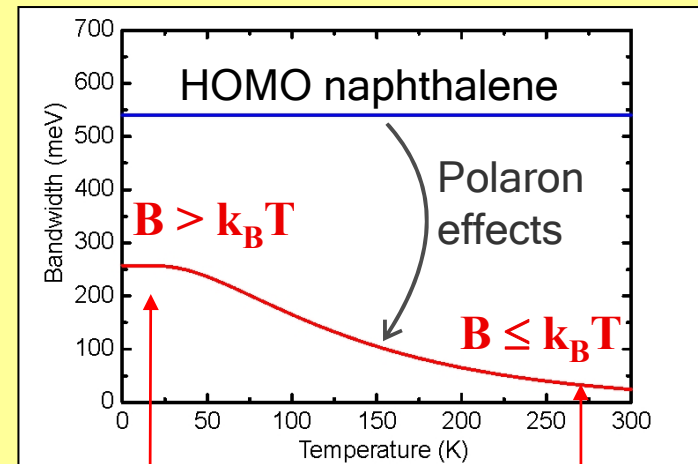
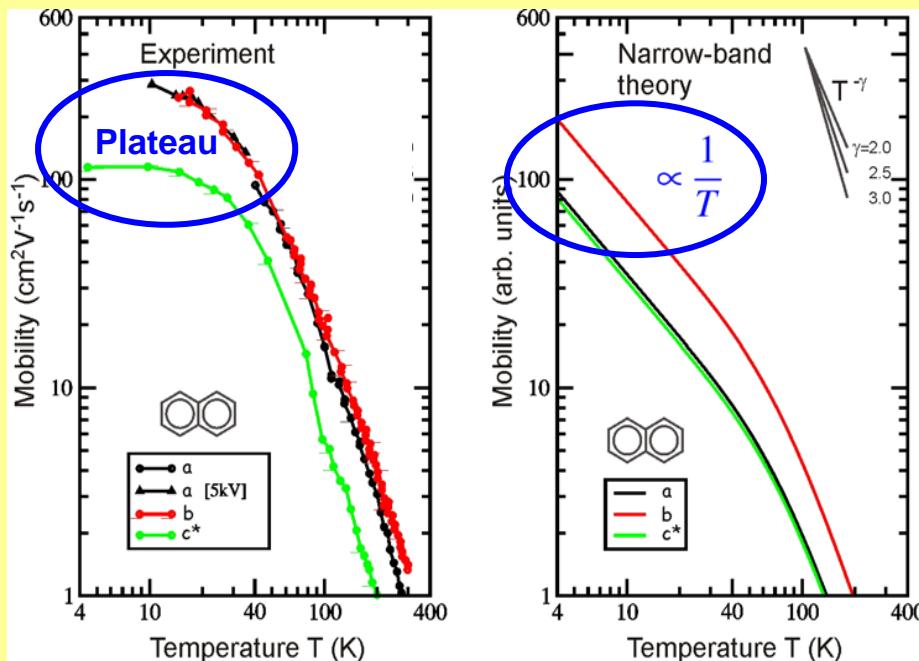


So Far: Our Approach Works Very Well ...

- novel combination of analytical theory & numerical analysis
- formulas for polaron bandwidths & mobilities (incl. el-ph coupling in all orders)
- important effects included: **3D anisotropy, temperature, band narrowing & hopping**
- material parameters from ab-initio calculations → **No fits to experiment!**

... But There is a Problem at Very Low T

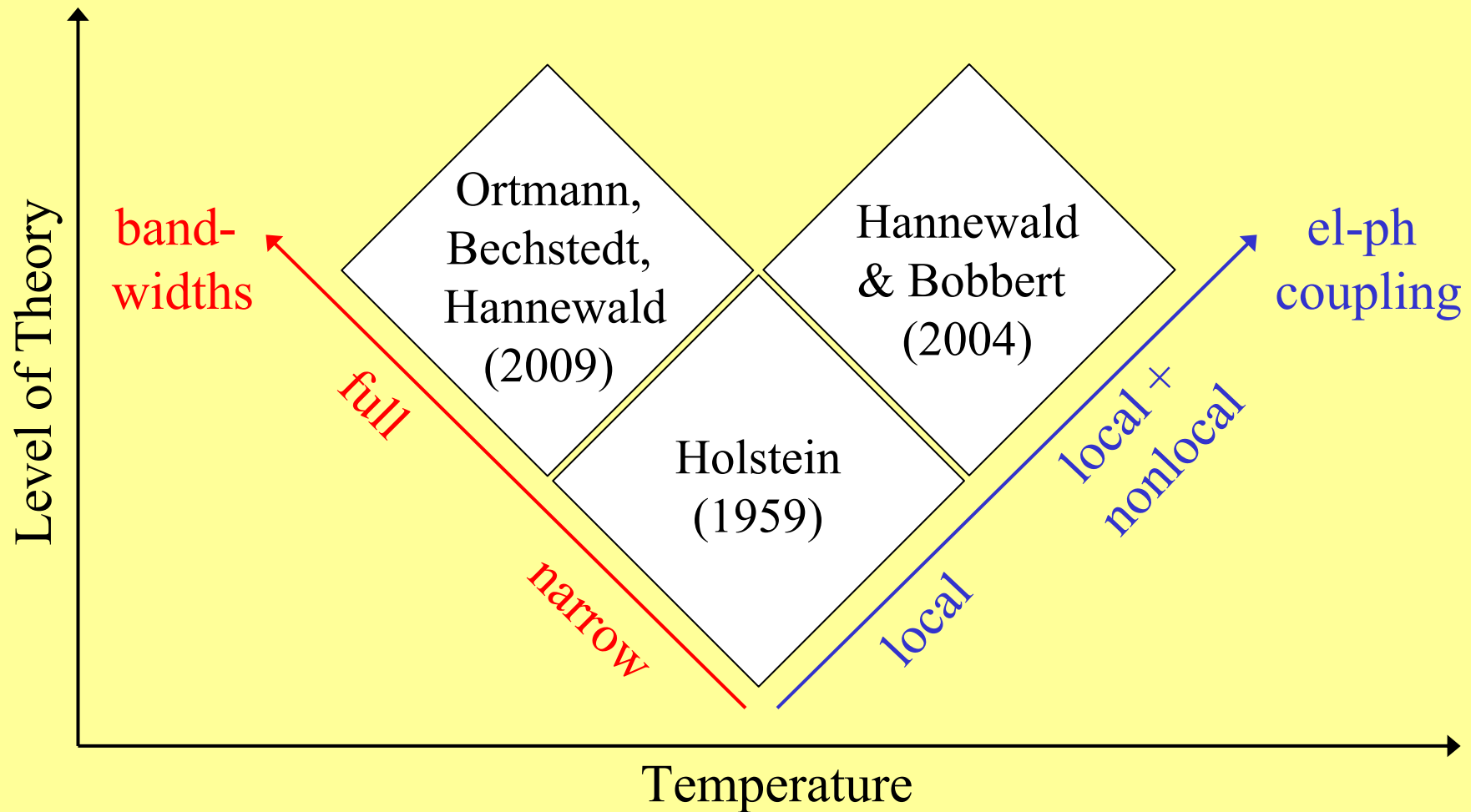
→ **Goal: Mobility theory for arbitrary polaron bandwidths!**



$T=0$ K
wide bands
("large polarons")

$T=300$ K
narrow bands
("small polarons")

General Mobility Theory: → Beyond Narrow Bands & Small Polarons



Mobility from Kubo Formula

$$\mu_{\alpha\beta} = \frac{1}{e_0 N 2k_B T} \int_{-\infty}^{\infty} dt \langle j_{\alpha}(t) j_{\beta}(0) \rangle_H$$

$$H = H_{el} + H_{el-ph} + H_{ph}$$

Problem: Diagonalization of H necessary, but not exactly possible

Step 1 : Polaron Transformation

$$\tilde{H} \rightarrow \tilde{H}_{pol} + \tilde{H}_{ph} = \sum_{M,N} a_M^{\dagger} \tilde{\epsilon}_{MNA} a_N + \sum_{\mathbf{Q}} \hbar \omega_{\mathbf{Q}} \left(b_{\mathbf{Q}}^{\dagger} b_{\mathbf{Q}} + \frac{1}{2} \right)$$

$$\begin{aligned} & \langle j_{\alpha}(t) j_{\beta}(0) \rangle_H \\ &= \left(\frac{e_0}{i\hbar} \right)^2 \sum_{LMNP} \underbrace{\langle e^{\frac{i}{\hbar} \tilde{H}_{pol}} a_L^{\dagger} a_M e^{-\frac{i}{\hbar} \tilde{H}_{pol}} a_N^{\dagger} a_P \rangle_{\tilde{H}_{pol}}}_{\text{polaron correlator} \rightarrow ?} \underbrace{\langle e^{C_L(t)} [R_{\alpha}, \epsilon]_{LM} e^{-C_M(t)} e^{C_N} [R_{\beta}, \epsilon]_{NP} e^{-C_P} \rangle_{\tilde{H}_{ph}}}_{\text{solve analytically as before}} \end{aligned}$$

polaron correlator $\rightarrow ?$

solve analytically as before

Step 2 : Diagonalization of

$$\tilde{H}_{pol} = \sum_L \tilde{\epsilon}_{LL} a_L^\dagger a_L + \sum_{L \neq M} \tilde{\epsilon}_{LM} a_L^\dagger a_M$$

Before: Narrow-Band Theory
= approximate diagonaliz. in real space

$$\tilde{H}_{pol} \rightarrow \tilde{H}'_{pol} = \sum_L \tilde{\epsilon}_{LL} a_L^\dagger a_L$$

$$\langle a_L^\dagger a_M a_N^\dagger a_P \rangle_{\tilde{H}'_{pol}} \rightarrow n_L (1 - n_M)$$

$$n_L = n_M = \text{constant}$$

Now: Generalized Theory
= exact diagonalization in k-space

$$\tilde{H}_{pol} = \sum_{\mathbf{k}} \tilde{\epsilon}_{\mathbf{k}} a_{\mathbf{k}}^\dagger a_{\mathbf{k}}$$

$$\langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2} a_{\mathbf{k}_3}^\dagger a_{\mathbf{k}_4} \rangle_{\tilde{H}_{pol}} \rightarrow n_{\mathbf{k}_1} (1 - n_{\mathbf{k}_2})$$

$n_{\mathbf{k}}$ = Fermi distribution of polarons

Major improvement: **correct statistics + correct T dependence**

Key Result: Generalized Mobility Formula

Ortmann, Bechstedt & Hannewald, Phys. Rev. B 79, 235206 (2009)

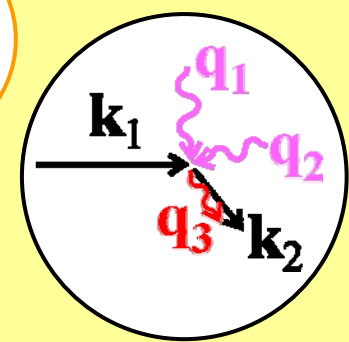
$$\mu_{\alpha\beta} = \underbrace{-\frac{e_0}{2N_c \hbar^2 k_B T} \sum_{LMN} R_{L\alpha} R_{N\beta} \tilde{\epsilon}_L \tilde{\epsilon}_N}_{\text{anisotropy}} \frac{1}{N_\Omega} \sum_{\mathbf{k}_1 \mathbf{k}_2} \underbrace{e^{-i\mathbf{k}_1(\mathbf{R}_M + \mathbf{R}_N)}}_{\text{momentum}} \underbrace{e^{i\mathbf{k}_2(\mathbf{R}_M - \mathbf{R}_L)}}_{\text{momentum}} \underbrace{n_{\mathbf{k}_1} (1 - n_{\mathbf{k}_2})}_{\text{occupation}}$$

$$\times \int_{-\infty}^{\infty} dt e^{\frac{i}{\hbar} [\tilde{\epsilon}_{\mathbf{k}_1} - \tilde{\epsilon}_{\mathbf{k}_2}]} \exp \left\{ + \sum_{\mathbf{Q}} [N_{\mathbf{Q}} e^{i\omega_{\mathbf{Q}} t} + (1 + N_{\mathbf{Q}}) e^{-i\omega_{\mathbf{Q}} t}] (g_{\mathbf{Q}})_{0LON}^2 e^{-i\mathbf{Q}\mathbf{R}_M} \right\}$$

energy conservation (incl. phonon absorption & emission)
momentum conservation

$\sum_{\mathbf{k}_1 \mathbf{k}_2}$	initial state \mathbf{k}_1	\rightarrow	final state \mathbf{k}_2
	occupied $n_{\mathbf{k}_1}$	\rightarrow	empty $(1 - n_{\mathbf{k}_2})$
$\sum_{\mathbf{M}}$	momentum \mathbf{k}_1	\rightarrow	momentum $\mathbf{k}_2 + \sum_i \mathbf{q}_i$
$\int_{-\infty}^{\infty} dt$	energy $\tilde{\epsilon}_{\mathbf{k}_1}$	\rightarrow	energy $\tilde{\epsilon}_{\mathbf{k}_2} \pm \sum_i \hbar \omega_{\mathbf{q}_i}$

Pauli blocking



→ Microscopic equivalent of Drude formula!

Polaron Band Transport & Hopping Included

coherent (band) transport:

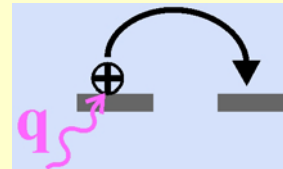
$$\mu_{\alpha\beta}^{(coh)} = \frac{\sqrt{\pi} e_0 \tau}{2N_c k_B T} \sum_{\mathbf{k}} n_{\mathbf{k}} (1 - n_{\mathbf{k}}) \tilde{v}_{\alpha}(\mathbf{k}) \tilde{v}_{\beta}(\mathbf{k})$$

→ like Boltzmann equation but with polaron velocities:

$$\tilde{v}_{\alpha}(\mathbf{k}) = \frac{1}{\hbar} \frac{\partial \tilde{\epsilon}(\mathbf{k})}{\partial k_{\alpha}}$$

→ for low T: $\mu \rightarrow \text{const}$ because $n_{\mathbf{k}}(1 - n_{\mathbf{k}}) \propto k_B T$

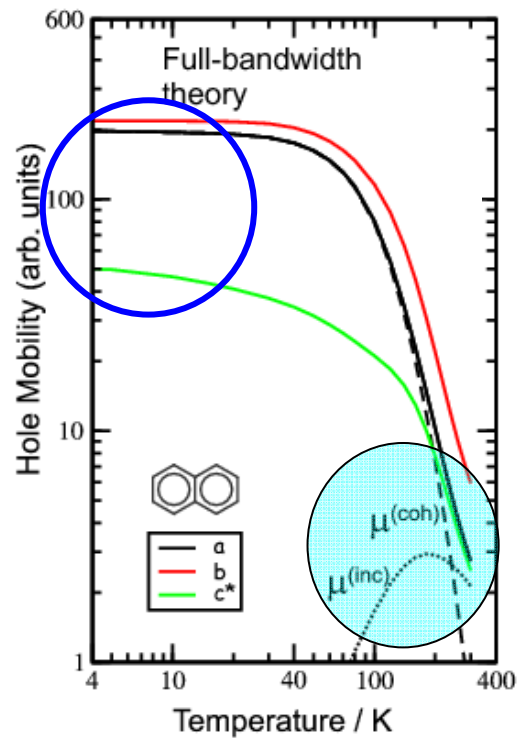
incoherent (phonon-assisted) hopping:



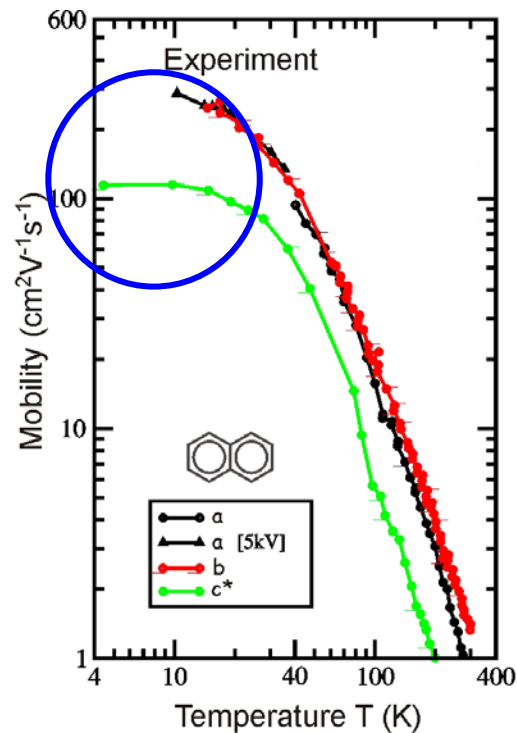
→ high-T limit covers narrow-band approximation & Marcus theory

Ortmann, Bechstedt & Hannewald
Phys. Rev. B 79, 235206 (2009)
J. Phys.: Cond. Matt. 22, 465802 (2010)

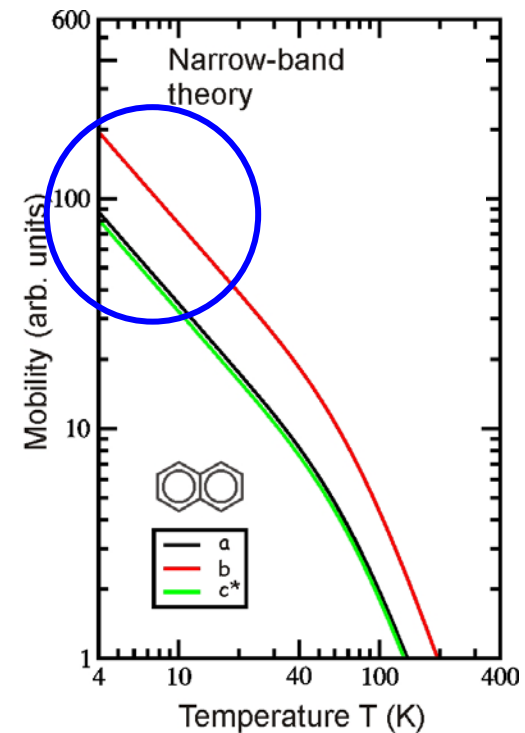
Improved Low-Temperature Mobilities (Example: Naphthalene Holes)



Ortmann, Bechstedt & Hannewald
New J. Phys. **12**, 023011 (2010)



N. Karl, in Landolt-Börnstein
Group III, **Vol.17**, p.106



Hannewald & Bobbert
APL **85**, 1535 (2004)

Summary

Novel theories of polaron bandstructures & mobilities

- beyond Holstein model (**nonlocal** electron-phonon coupling, **arbitrary** bandwidths)
- explicit formulas for **temperature dependence & anisotropy**
- electron-phonon interaction in **all** orders
- coherent **band transport** & incoherent phonon-assisted **hopping**

Application to real 3D crystals (naphthalene, durene, ...)

- **ab-initio** calculation of all material parameters
- temperatur-dependent **band narrowing** predicted
- **very good agreement** with exp. mobility data (temperature dependence & anisotropy)
- intuitive visualization of relevant **transport channels**

→ **Deeper understanding of charge transport through organic molecular crystals**



Review:
Phys. Stat. Sol. B
248, 511 (2011)