Polaronic Signatures in the Static (and Dynamical) Conductivities of Organic Crystals

Karsten Hannewald

European Theoretical Spectroscopy Facility (ETSF) &
Friedrich-Schiller-Universität Jena/Germany

Deutsche Forschungsgemeinschaft DFG

seit 1558

ETSF European Theoretical Spectroscopy Facility

Coworkers & Sponsors

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

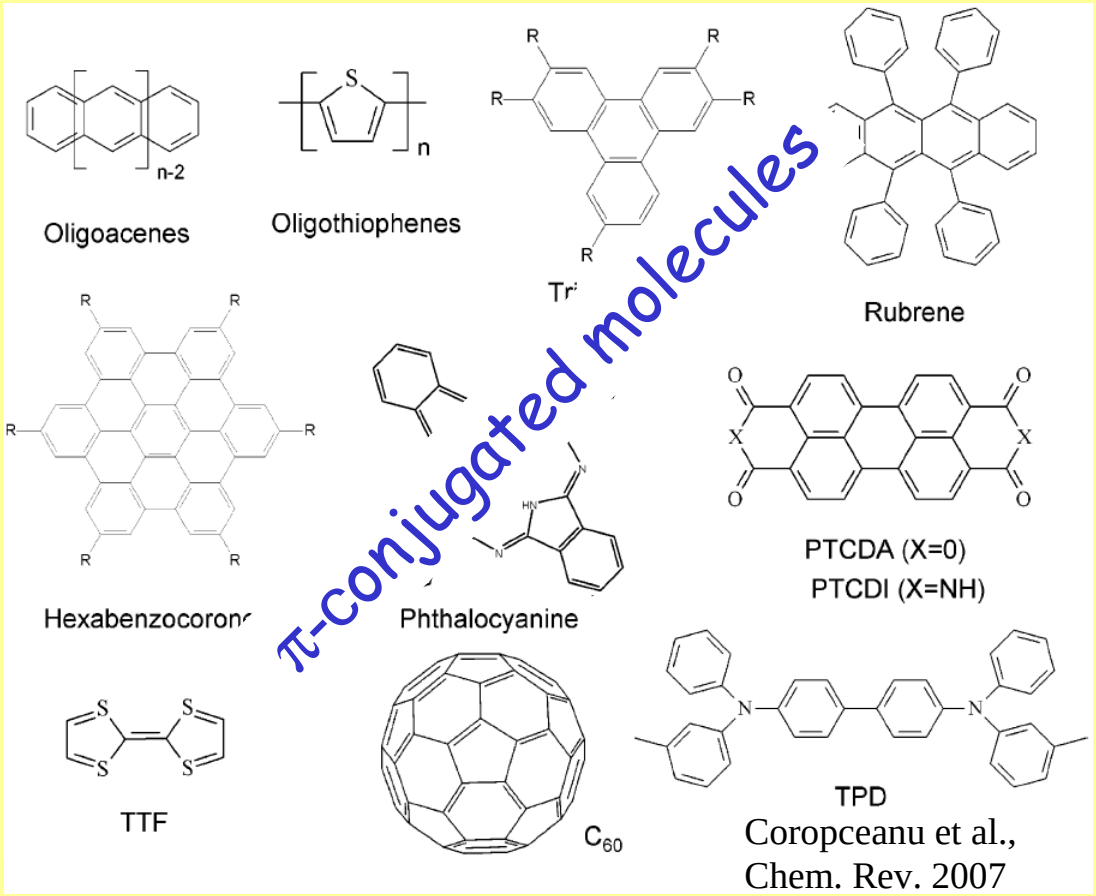
since 2005: U Jena → Frank Ortmann, André Fischer (Germany) & Friedhelm Bechstedt

- 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)

very soon: HU Berlin (Germany) → Claudia Draxl

Organic Electronics

- semiconducting polymers
  via doping (Nobel Prize 2000)
- many molecules available
  → easy tailoring of properties
  (e.g., via sidegroups)
- easy solubility & processability
- flexible substrates
- cheap production
  (spin coating, printing, roll-to-roll)



→ **Applications:**

OFETs, OLEDs, OPVs

organic electronics | ligthing & displays | solar cells & modules

Example: rollable OLED display (Sony, SID-2010)

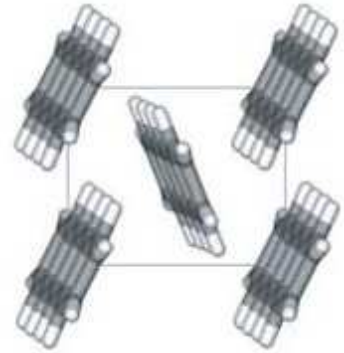
Organic Molecular Crystals as Benchmark Systems

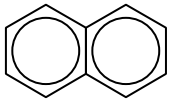
Niemax, Tripathi & Pflaum
[APL 86, 122105 (2005)]

= crystals of organic molecules → well-ordered systems

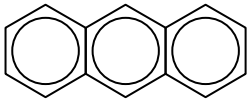
→ ideal to study intrinsic transport properties

Herringbone Stacking

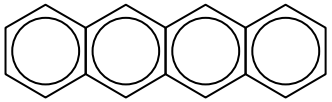




Naphthalene

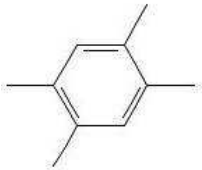


Anthracene



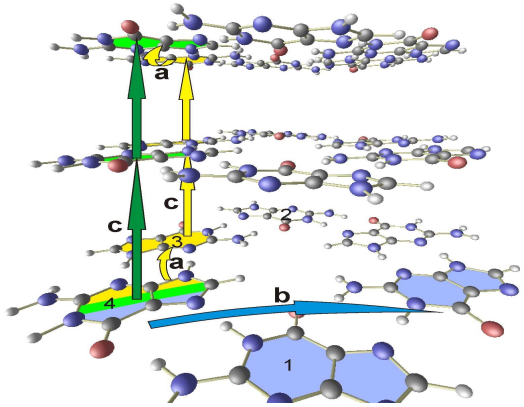
Tetracene

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

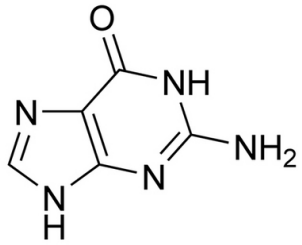


Durene

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



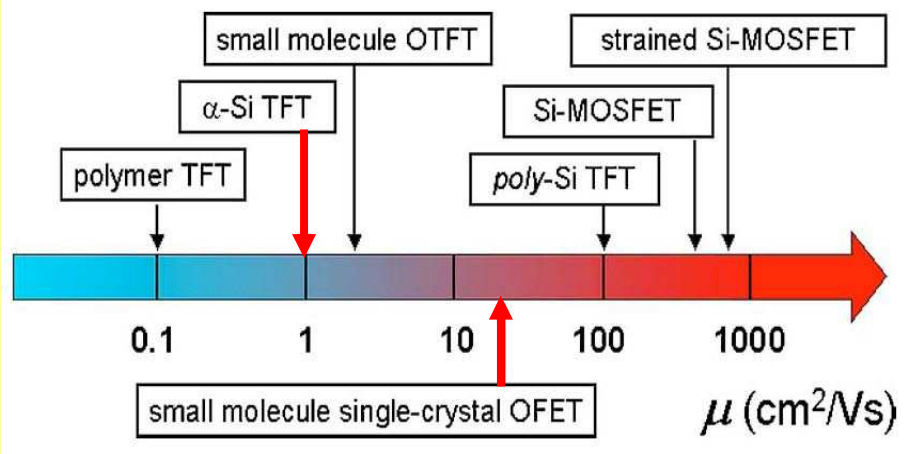
Layered Stacking



Guanine

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

Search for High-Mobility Organic Crystals



[from Gershenson et al., Rev. Mod. Phys. 78, 973 (2006)]

- Naphthalene (T=10K): $\mu \approx 300$ cm^2/Vs (Warta & Karl, 1985)
- Pentacene (T=300K): $\mu \approx 35$ cm^2/Vs (Jurchescu et al., 2004)
- Rubrene (T=300K) : $\mu \approx 20$ cm^2/Vs (Podzorov et al., 2004)
- Durene (T=300K) : $\mu \approx 20$ cm^2/Vs (Pflaum et al., 2008, private comm.)
  [$\mu \approx 5$ cm^2/Vs (Burshtein & Williams, 1977)]

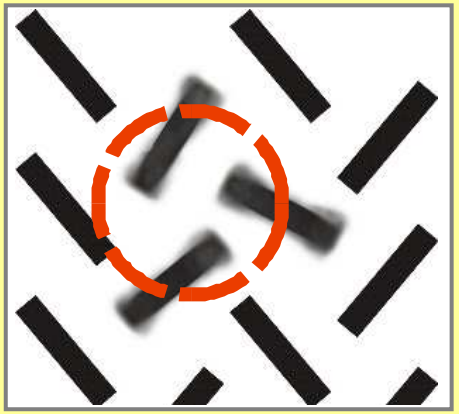
→ in technologically relevant regime!

Peculiarities of Organic Molecular Crystals

Quite different than inorganic semiconductors!

- weak intermolecular van der Waals bonds
- small electronic bandwidths < 1eV
- 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!

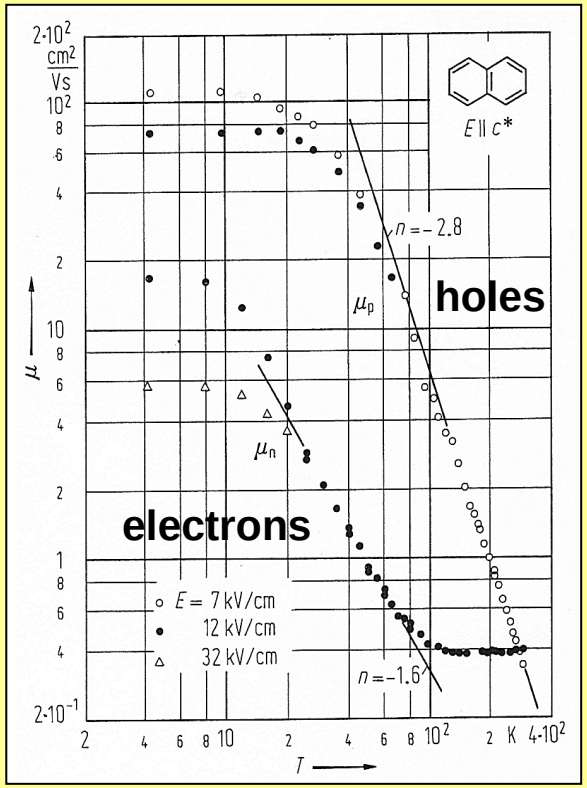
Open Questions for Charge Transport

- 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)



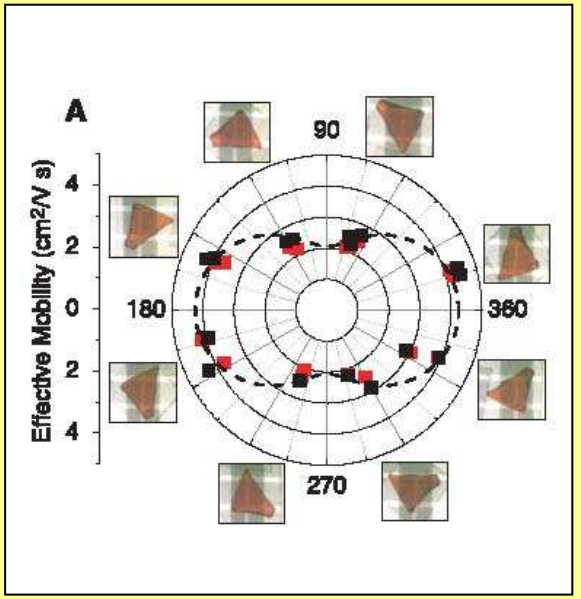
"There are still great challenges for theoreticians."

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

Goal: First-Principles Theory of Mobilities

Field-Effect Transistor Expts.
("stamp technique")

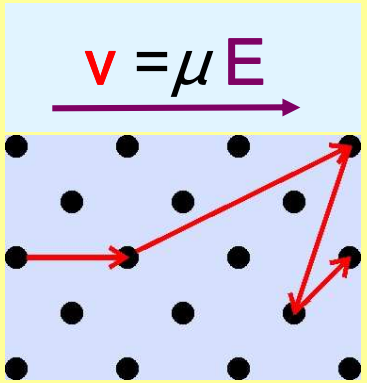
Sundar et al., Science 303, 1644 (2004)
Podzorov et al., PRL 93, 086602 (2004)



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 ~ $1/m^*$)

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

electron/hole bandwidths →	polaron bandwidths for local el-ph coupling →	polaron bandwidths for local + nonlocal el-ph coupl.
DFT calculations	Holstein model	Holstein-Peierls model
	Holstein, Ann. Phys. (NY) 8, 325 (1959) Mahan "Many-Particle Physics" (1990)	Hannewald et al., Phys. Rev. B 69, 075211 (2004)

Hamiltonian for Holstein-Peierls Model

electrons **phonons** **electron-phonon coupling**

$$H = \sum_{mn} \varepsilon_{mn} a^{+}_{m} a_{n} + \sum_{Q=(q,\lambda)} \hbar\omega_{Q} \left(b^{+}_{Q} b_{Q} + \tfrac{1}{2}\right) + \sum_{Qmn} \hbar\omega_{Q} g_{Qmn} \left(b_{-Q} + b^{+}_{Q}\right) a^{+}_{m} a_{n}$$

m=n: on-site energies ε_{mm}

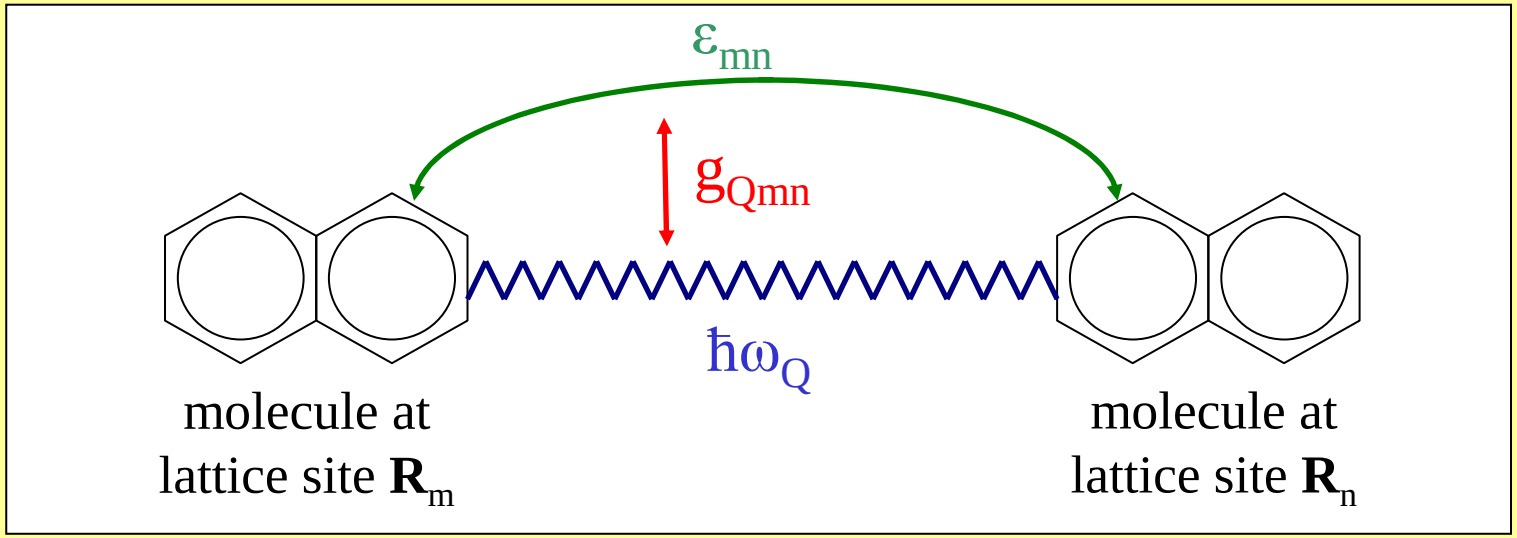
m≠n: transfer integrals ε_{mn}

m=n: local coupling (Holstein)

m≠n: nonlocal coupling (Peierls)

for electrons: conduction band (LUMO)

for holes: valence band (HOMO)



Transition into Polaron Picture

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

$$f \rightarrow F = e^{S}\, f\, e^{S^{+}}\,, \quad S = \sum_{mn} C_{mn} a^{+}_{m} a_{n}\,, \quad C_{mn} = \sum_{Q} g_{Qmn}(b_{-Q} - b^{+}_{Q})$$

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

$\Rightarrow$

$$H = \sum_{mn} \tilde{\varepsilon}_{mn} A^{+}_{m} A_{n} + \sum_{Q} \hbar\omega_{Q} \left(B^{+}_{Q} B_{Q} + \tfrac{1}{2}\right)$$

polarons **(displaced) phonons**

polaron energies & transfer integrals

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

Polaron Transfer Integrals

$$\tilde{\varepsilon}_{mn} = (\varepsilon_{mn} - \Delta_{mn})\, e^{-\sum_\lambda (\frac{1}{2} + N_\lambda)(G_{\lambda mm} + G_{\lambda nn})}$$

- 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 $G_{\lambda mm} = g^2_{\lambda mm} + \frac{1}{2} \sum_{m \neq k} g^2_{\lambda mk}$ (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?

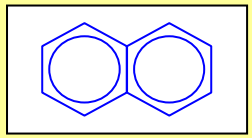
⇒ **Three-step strategy:**

(i) Crystal geometry (R_m) & phonons (ω_λ)

(ii) On-site energies (ε_{mm}) & transfer integrals (ε_{mn})

(iii) Electron-phonon coupling constants ($g_{\lambda mm}$)

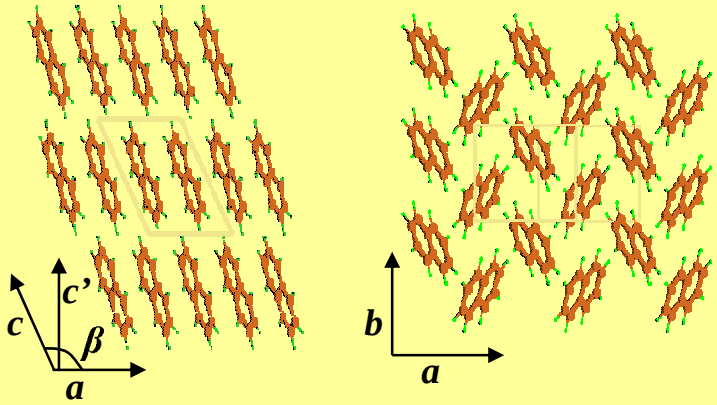
⇒ **Application to naphthalene crystals**



(i) Crystal Geometry (R_m) & Phonons (ω_λ)

- **Determine crystal equilibrium structure**
  → **ab-initio DFT-LDA, VASP code**

Naphthalene: monoclinic, two molecules per unit cell, herringbone stacking



	ab-initio	exp.
a (Å)	7.68	8.24
b (Å)	5.76	6.00
c (Å)	8.35	8.66
β (°)	125.6	122.9

- **Determine intermolecular Γ-point phonons**
  → **direct method, rigid molecules**

here only 3 optical modes

mode	ab-initio	exp.
$\hbar\omega_1$ (meV)	10.6	8.8
$\hbar\omega_2$ (meV)	14.1	11.1
$\hbar\omega_3$ (meV)	17.5	15.3

(ii) On-Site Energies (ε_{mm}) & Transfer Integrals (ε_{mn})

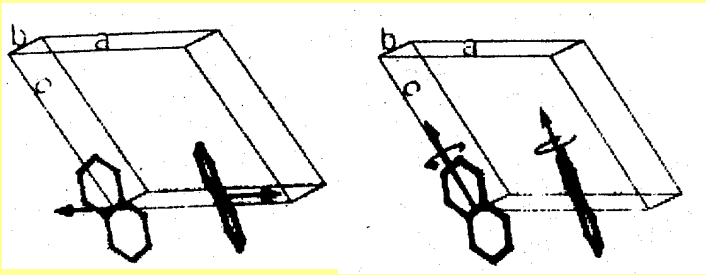
- Determine ab-initio band structure $\Rightarrow \varepsilon(k)$ for electrons (LUMO) and holes (HOMO)
- Fit to tight-binding model incl. several nearest-neighbour transfer integrals

  Here: $\mathbf{R_m - R_n = 0, \pm a, \pm b, \pm c, \pm\frac{1}{2}(a \pm b), \pm(a+c), \pm\frac{1}{2}(a \pm b + 2c)}$

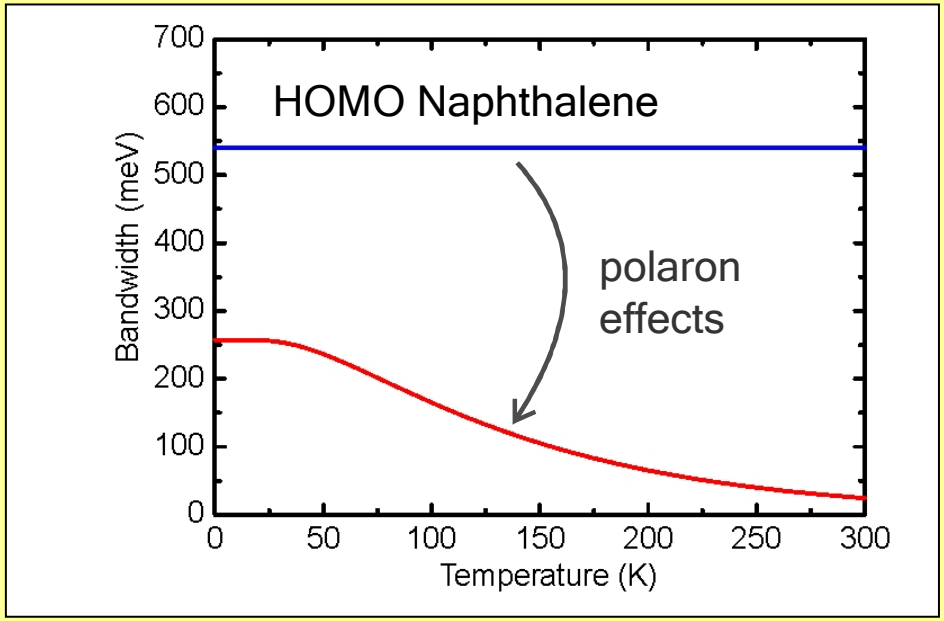
$\Rightarrow$ Obtain ε_{mm} and ε_{mn} for HOMO and LUMO!

(iii) Electron-Phonon Coupling Constants ($g_{\lambda mn}$)

- Displace molecules according to eigenvector e_λ of phonon mode λ
- Repeat ab-initio band structure calculation
- Fit to full tight-binding Hamiltonian
- Compare to previous fit $\Rightarrow$ Obtain $g_{\lambda mn} \sim \Delta\varepsilon_{mn}$



Strong Band Narrowing in Naphthalene Crystals



Napthalene, 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

Holstein model

Holstein-Peierls model

bare electron & hole bands → polaron bands with local el-ph → polaron bands with local + nonlocal el-ph

polaron bands with local el-ph → mobilities with local el-ph

polaron bands with local + nonlocal el-ph → mobilities with local + nonlocal el-ph

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

(known)

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

(new)

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 $\mathbf{P} = e_0 \Sigma_m \mathbf{R}_m a^+_m a_m$

current = **electronic current** + **phonon-assisted current** (new)

$$\mathbf{j} = \mathbf{j}^{(I)} + \mathbf{j}^{(II)}$$

$$= e_0/i\hbar \left\{ \sum_{mn} (R_m - R_n) \varepsilon_{mn} a^+_m a_n + \sum_{Qmn} (R_m - R_n) \hbar\omega_Q g_{Qmn} (b_{-Q} + b^+_Q) a^+_m a_n \right\}$$

hopping term for **nonlocal** coupling!

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

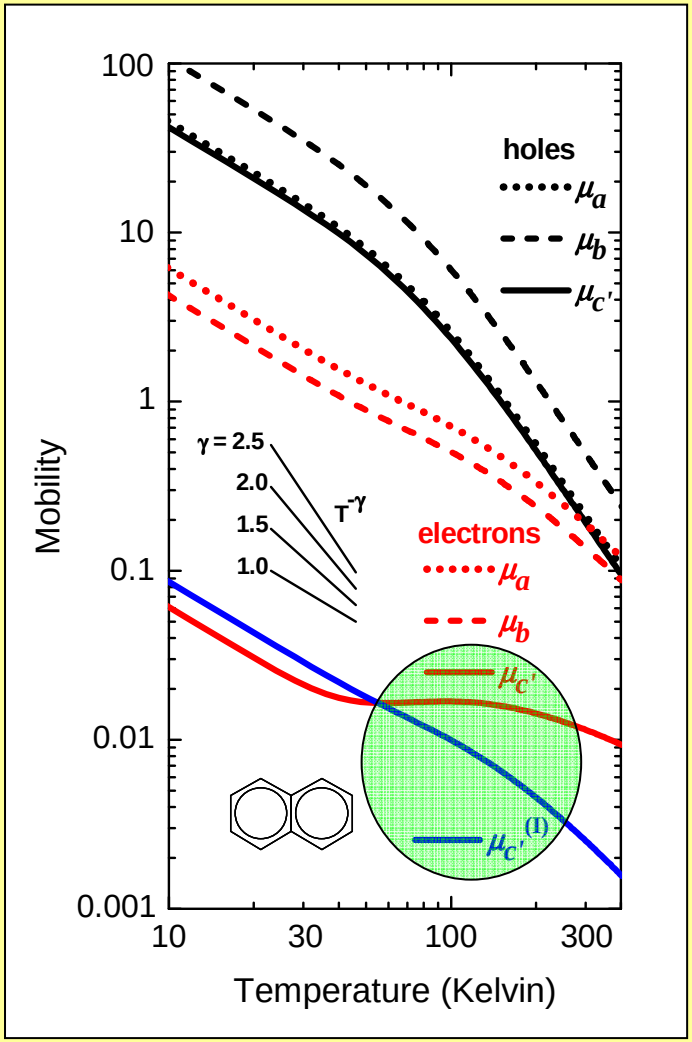
Key result: Once R_m, ε_{mn}, $g_{\lambda mn}$, and ω_λ are known, quantitative predictions for anisotropy & T-dependence of mobilities $\mu = \mu^{(I)} + \mu^{(II)}$ possible!

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

Naphthalene: Theory Describes Experiments Well

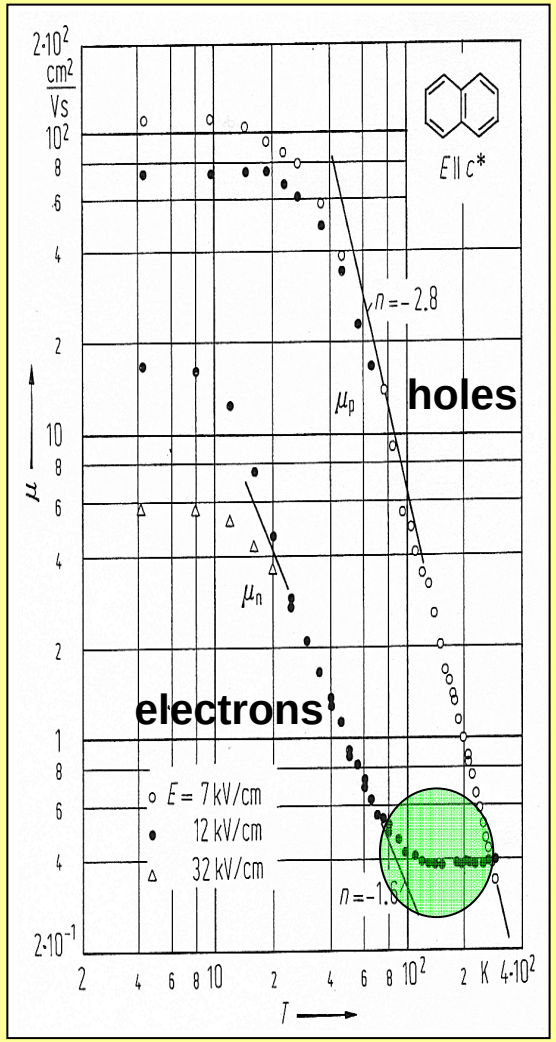
Ab-Initio Theory

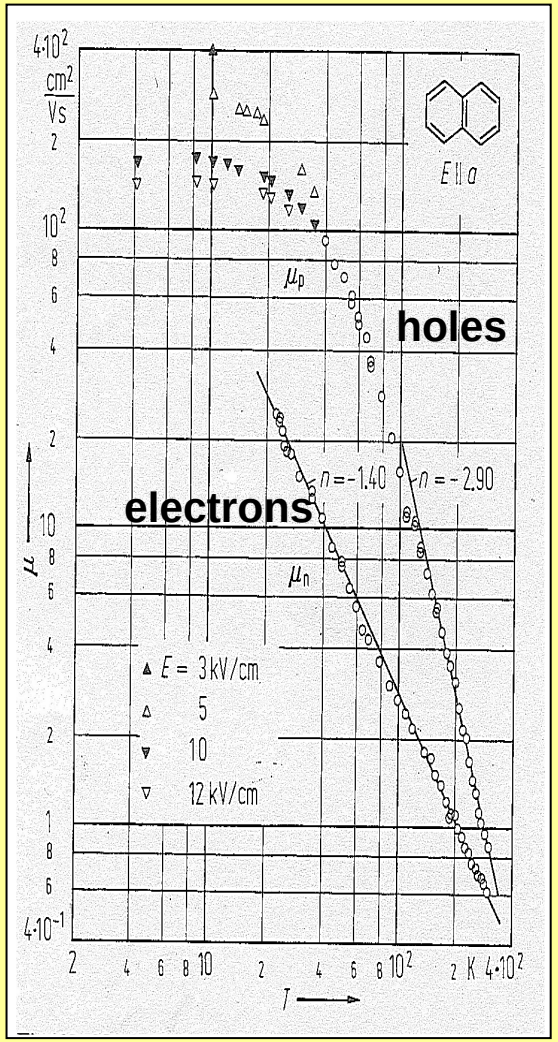
Hannewald & Bobbert [APL 85, 1535 (2004)]



Experiment

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



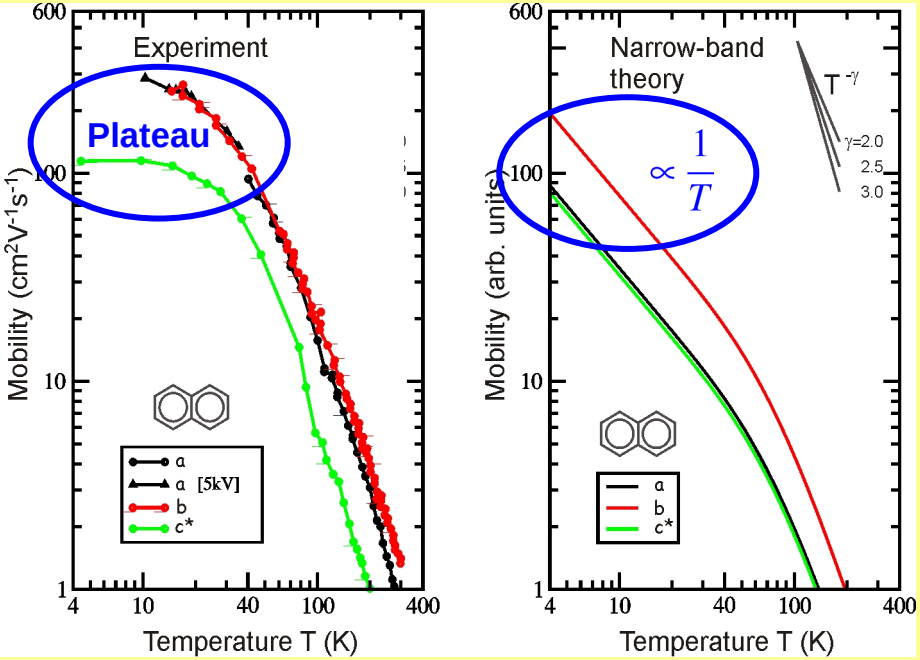


So Far: Our Approach Works Very Well …

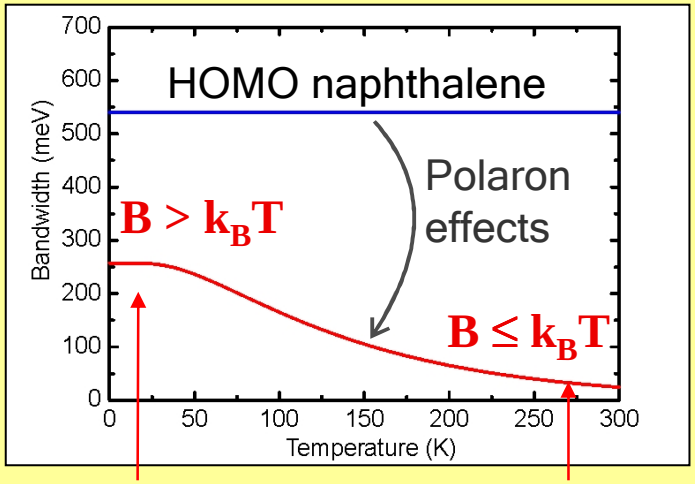
→ novel combination of analytical theory & numerical analysis

- formulas for polaron bandwidths and 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



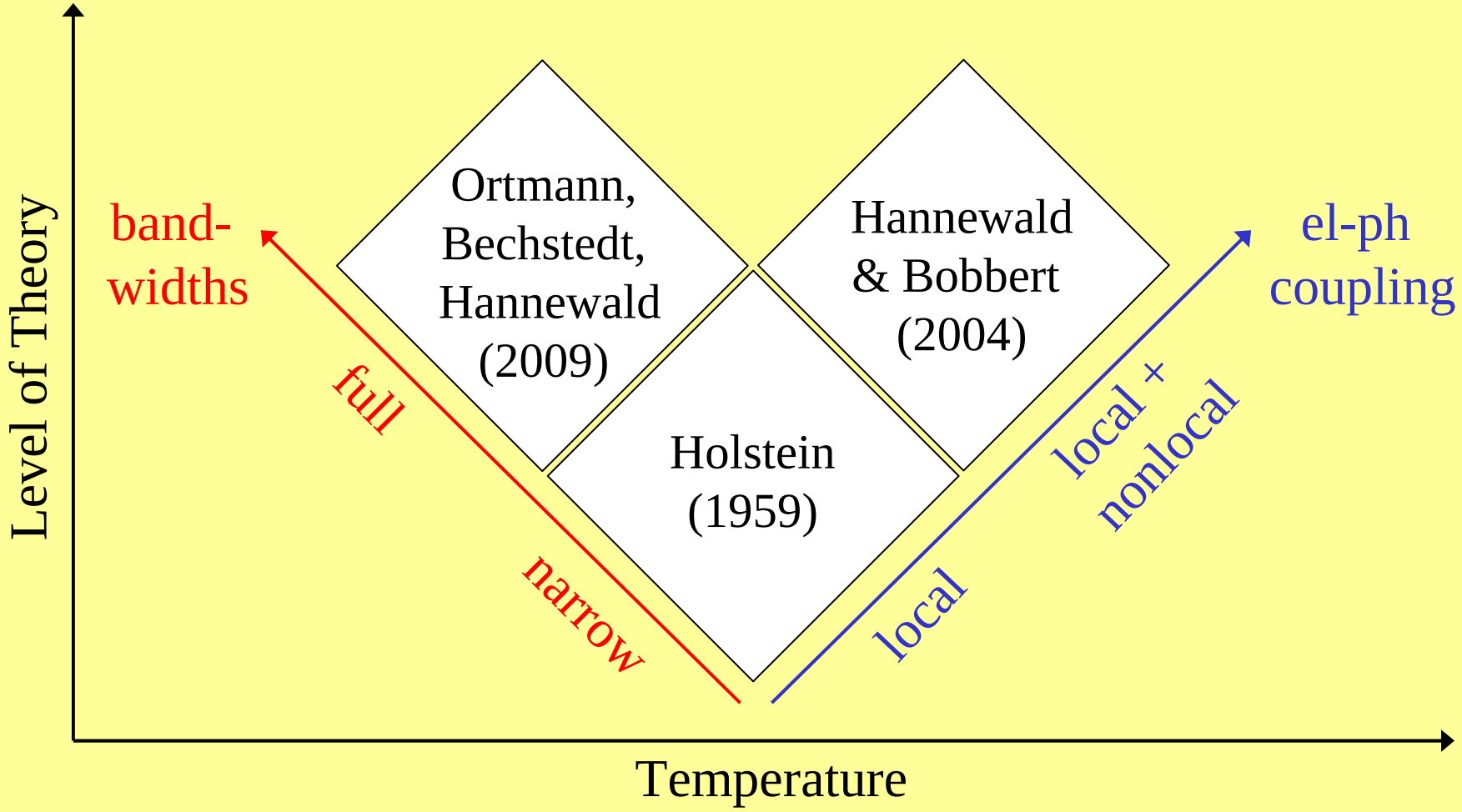
→ Goal: Mobility Theory for Arbitrary Polaron Bandwidths!



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

$$\widetilde{H} \to \widetilde{H}_{pol} + \widetilde{H}_{ph} = \sum_{M,N} a_M^\dagger \widetilde{\varepsilon}_{MN} a_N + \sum_{\mathbf{Q}} \hbar\omega_{\mathbf{Q}} \left(b_{\mathbf{Q}}^\dagger b_{\mathbf{Q}} + \frac{1}{2} \right)$$

$$\langle j_\alpha(t) j_\beta(0) \rangle_H = \left(\frac{e_0}{i\hbar} \right)^2 \sum_{LMNP} \left\langle e^{\frac{it}{\hbar}\widetilde{H}_{pol}} a_L^\dagger a_M e^{-\frac{it}{\hbar}\widetilde{H}_{pol}} a_N^\dagger a_P \right\rangle_{\widetilde{H}_{pol}} \left\langle e^{C_L(t)} [R_\alpha, \varepsilon]_{LM} e^{-C_M(t)} e^{C_N} [R_\beta, \varepsilon]_{NP} e^{-C_P} \right\rangle_{\widetilde{H}_{ph}}$$

polaron correlator → ?

solve analytically as before

Step 2 : Diagonalization of $\widetilde{H}_{pol} = \sum_{L} \widetilde{\varepsilon}_{LL} a_L^{\dagger} a_L + \sum_{L \neq M} \widetilde{\varepsilon}_{LM} a_L^{\dagger} a_M$

Before: Narrow-Band Theory

= approximate diagonaliz. in real space

$$\widetilde{H}_{pol} \rightarrow \widetilde{H}'_{pol} = \sum_{L} \widetilde{\varepsilon}_{LL} a_L^{\dagger} a_L$$

$$\left\langle a_L^{+} a_M a_N^{+} a_P \right\rangle_{\widetilde{H}'_{pol}} \rightarrow n_L (1 - n_M)$$

n_L = n_M = constant

Now: Generalized Theory

= exact diagonalization in k-space

$$\widetilde{H}_{pol} = \sum_{\mathbf{k}} \widetilde{\varepsilon}_{\mathbf{k}} a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}}$$

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

$n_{\mathbf{k}}$ = 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); J. Phys.: Cond. Matt. 22, 465802 (2010)

anisotropy | momentum | occupation

$$\mu_{\alpha\beta} = -\frac{e_0}{2N_c\hbar^2 k_B T}\sum_{LMN} R_{L\alpha}R_{N\beta}\tilde{\varepsilon}_L\tilde{\varepsilon}_N\frac{1}{N_\Omega}\sum_{\mathbf{k}_1\mathbf{k}_2} e^{-i\mathbf{k}_1(\mathbf{R}_M+\mathbf{R}_N)}e^{i\mathbf{k}_2(\mathbf{R}_M-\mathbf{R}_L)}n_{\mathbf{k}_1}(1-n_{\mathbf{k}_2})$$
$$\times\int_{-\infty}^{\infty}dt\, e^{\frac{it}{\hbar}\left[\tilde{\varepsilon}_{\mathbf{k}_1}-\tilde{\varepsilon}_{\mathbf{k}_2}\right]}\exp\left\{+\sum_{\mathbf{Q}}\left[N_{\mathbf{Q}}e^{i\omega_{\mathbf{Q}}t}+(1+N_{\mathbf{Q}})e^{-i\omega_{\mathbf{Q}}t}\right](g_{\mathbf{Q}})^2_{0L0N}e^{-i\mathbf{Q}\mathbf{R}_M}\right\}$$

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

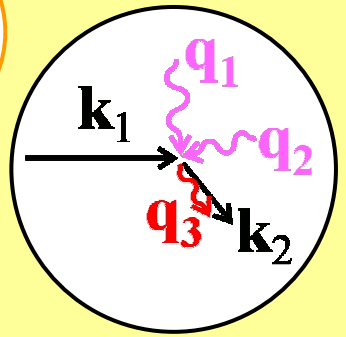
$\sum_{\mathbf{k}_1\mathbf{k}_2}$ initial state $\mathbf{k}_1$ → final state $\mathbf{k}_2$

occupied n_{k1} → empty $(1-n_{k2})$

Pauli blocking

Σ_M : momentum $\mathbf{k}_1$ → momentum $\mathbf{k}_2 + \Sigma_i \mathbf{q}_i$

$\int_{-\infty}^{\infty}dt$: energy $\tilde{\varepsilon}_{\mathbf{k}_1}$ → energy $\tilde{\varepsilon}_{\mathbf{k}_2} \pm \Sigma_i \hbar\omega_{qi}$



→ Microscopic equivalent of Drude formula!

Polaron Band Transport & Hopping Included

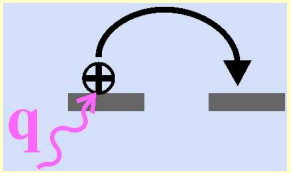
coherent (band) transport:

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

→ like Boltzmann equation but with polaron velocities: $\tilde{v}_\alpha(\mathbf{k}) = \frac{1}{\hbar} \frac{\partial \tilde{\varepsilon}(\mathbf{k})}{\partial k_\alpha}$

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

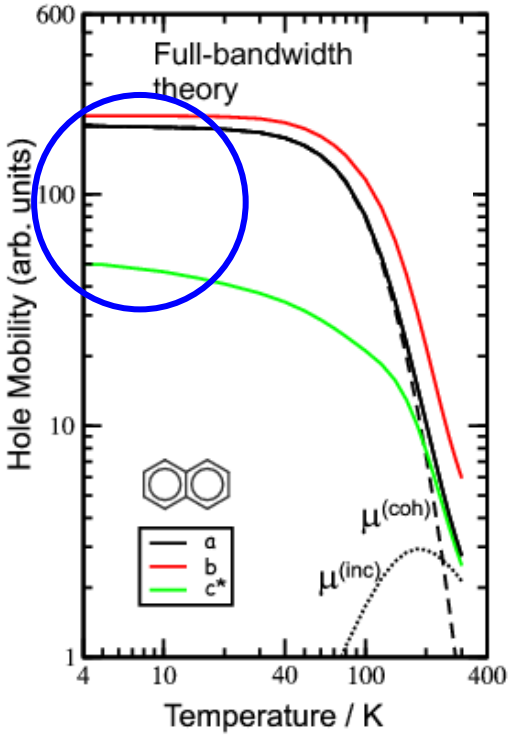
incoherent (phonon-assisted) hopping:



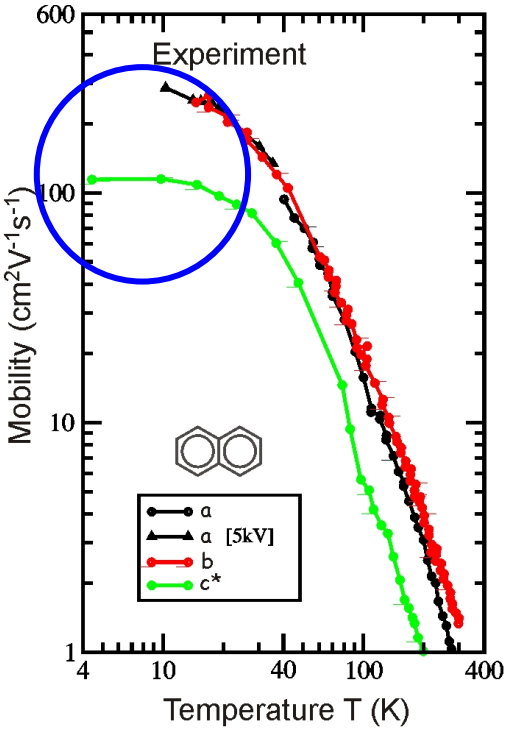
→ high-T limit covers narrow-band approximation & Marcus theory

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

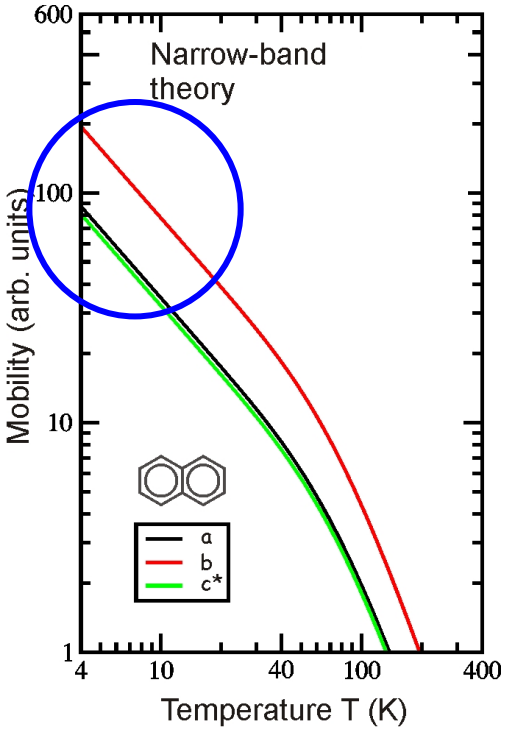
Improved Low-Temperature Mobilities (Example: Naphthalene Holes)



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)

Discussion: Important Challenges

Theoretical challenges

- Unification of theories (nonlocal el-ph coupling + arbitrary bandwidths)
- Microscopic description of additional static disorder
- High electric fields (→ go beyond Kubo formulism)
- Frequency-dependent conductivity $\sigma(\omega)$
- Optics (→ exciton-phonon replica [BSE for polarons])

First ideas: A. Fischer et al.,
Talk DPG spring meeting 2012
[unpublished results, slides not included here]

Numerical challenges

- Efficient (automized) calculation of ab-initio material parameters
- Better ab-initio material parameters (→ beyond LDA, dispersive phonons)