

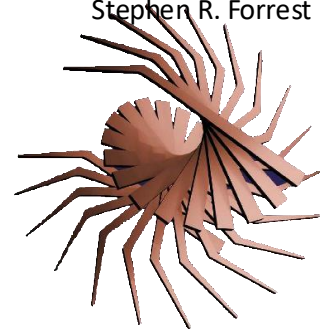
Electronic Properties of Organic Semiconductors

Electronic Properties 1

Energy Bands
Charge Transport and Mobility

Chapter 4.1 - 4.2

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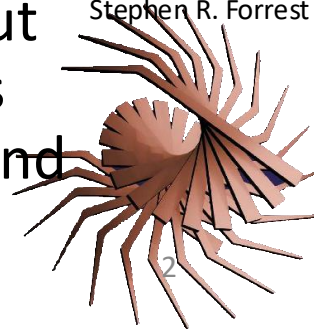


Objectives: Electronic Properties

“When talking about semiconductors, if you can’t draw a band diagram then you don’t know what you’re talking about”, ‘Kroemer’s Lemma’, Herbert Kroemer, ca. 1990.

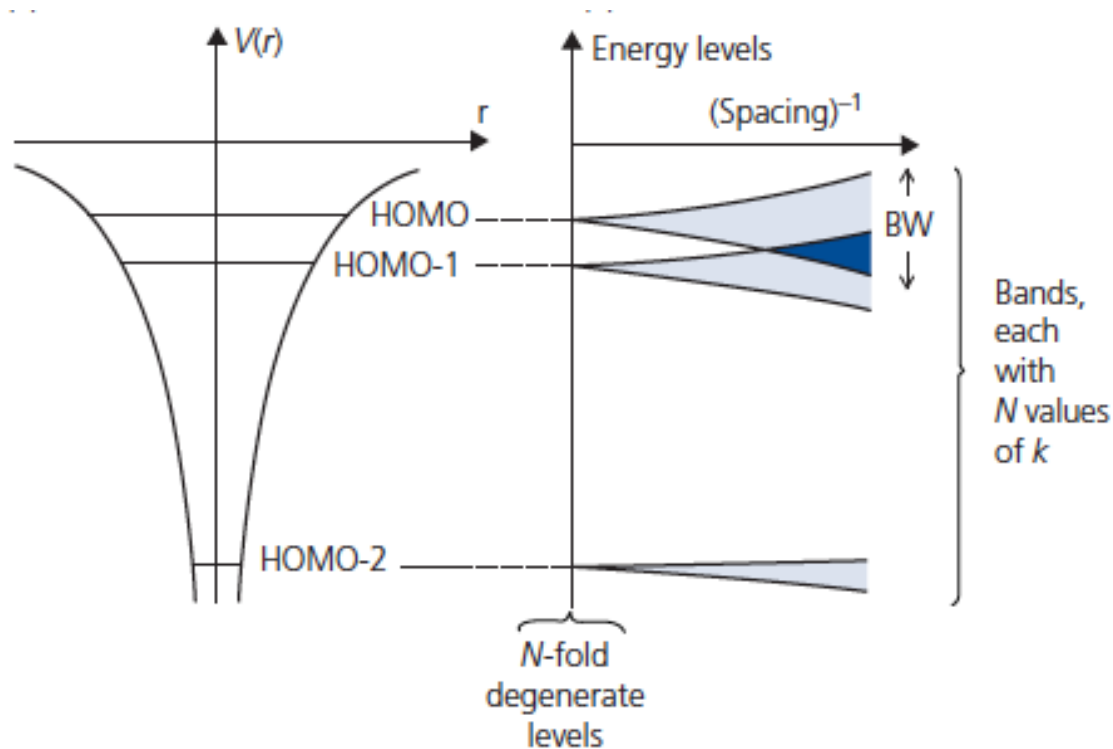
- Organic electronic devices can only be understood in the context of the conductive properties of materials
- In this discussion we introduce
 - Origins of electronic band structure
 - Concept of polarons (large and small)
 - Charge transfer
 - Conductivity, effective mass and mobility
 - Injection
 - Charge trapping
- At the end of this discussion, you will have learned about structure, optical and electronic properties: all the tools needed to fully understand and analyze all OE devices and phenomena

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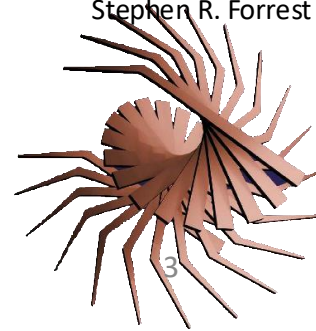


Transport Bands in Organics

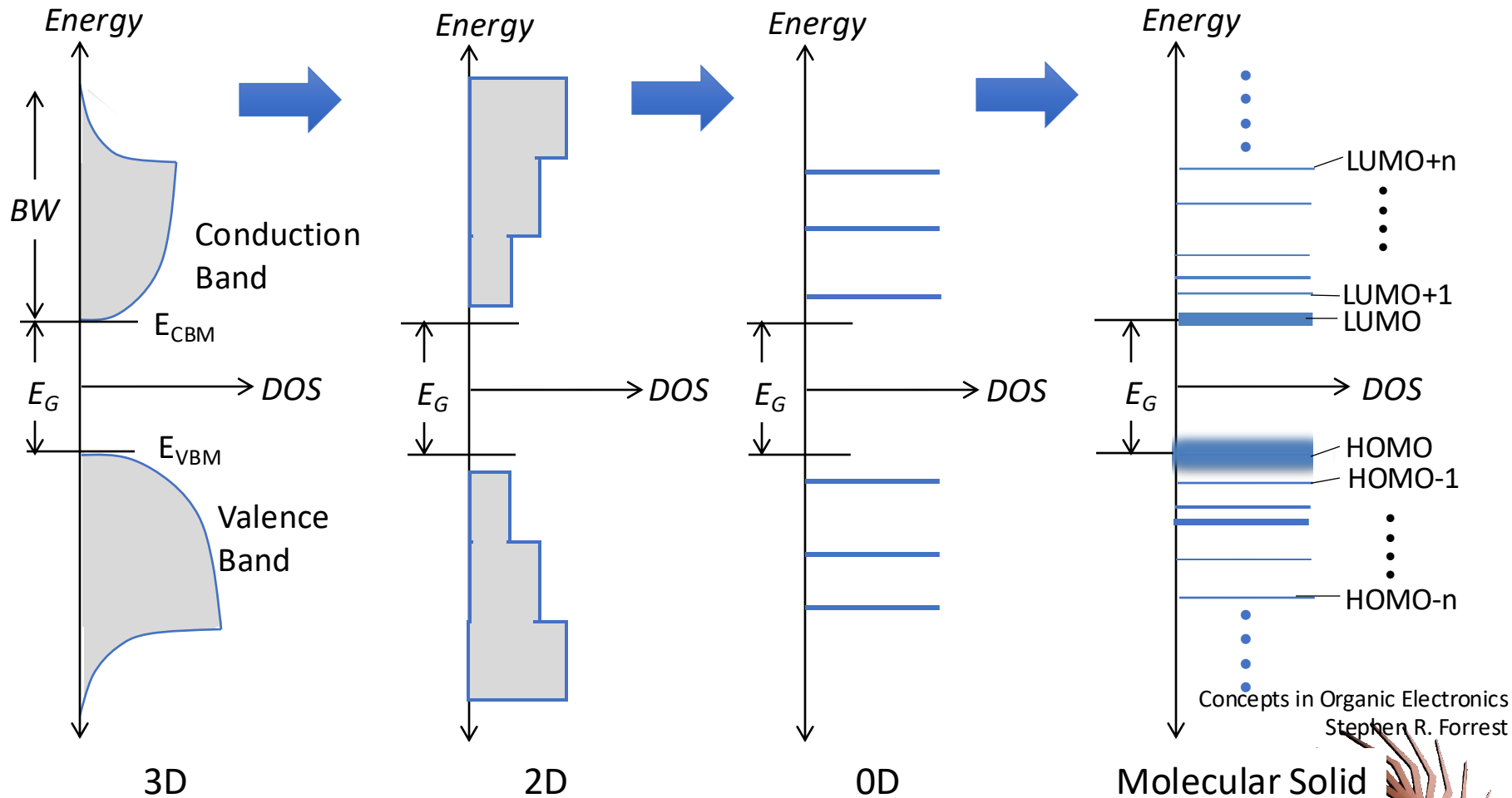
- **Tight binding** approximation is useful due to importance of only nearest neighbor interactions
- Recall case of dimers and larger aggregates on exciton spectrum. Close proximity of neighbors results in:
 - Coulomb repulsion
 - Pauli exclusion
 - Splitting leads to broadening of discrete energies into bands



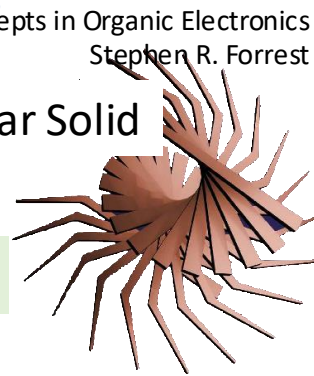
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The Density of States from 3D to 0D to Molecular Solids

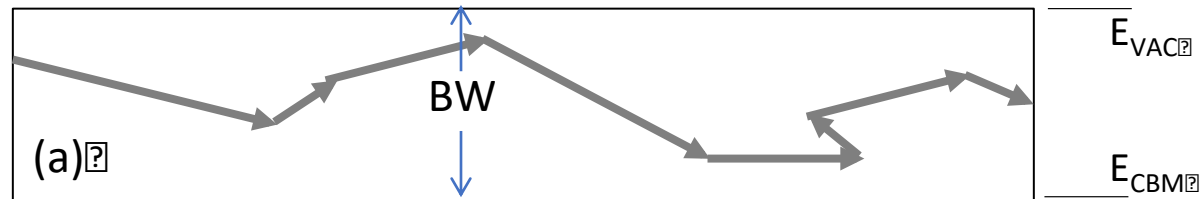


Molecular materials appear similar to 0D (quantum dot) solids



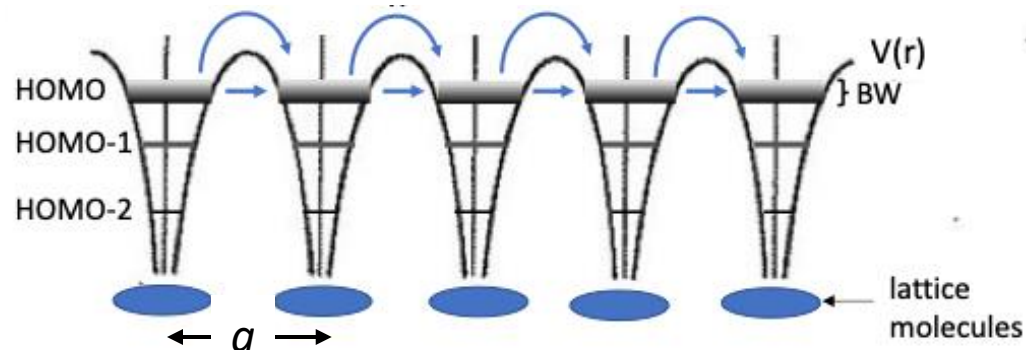
Modes of Conduction

Band transport



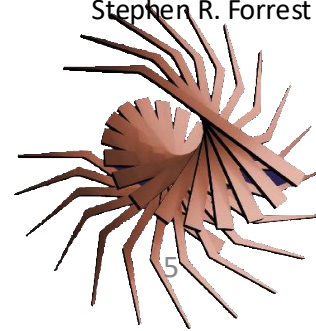
- Coherent
- Charge mean free path $\lambda \gg a$
- $BW > k_B T, \hbar \omega_0$

Thermally assisted hopping and tunneling transport



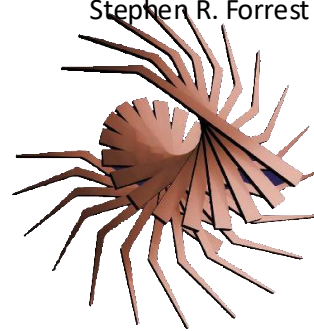
- Incoherent (each step independent of previous)
- Charge mean free path $\lambda \sim a$
- Tunneling between states of equal energy is band-like
- $BW < k_B T, \hbar \omega_0$

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Effective mass and charge velocity derives from band structure ($E(\mathbf{k})$)

- Charge velocity: $\mathbf{v}(\mathbf{k}) = \frac{1}{\hbar} \frac{\partial E(\mathbf{k})}{\partial \mathbf{k}}$
- Effective mass: $\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E(\mathbf{k})}{\partial k^2}$
- Momentum: $\mathbf{p} = m^* \mathbf{v}(\mathbf{k}) = \hbar \mathbf{k}$



Charge Mobility Describes Transport in Solids

- Charge mobility: μ (not the dipole moment!)
- Definition: “Constant” of proportionality between velocity and electric field:

$$\mathbf{v}(\mathbf{k}) = \tilde{\mu}_{\mathbf{k}} \mathbf{F}$$

- Tensor: dependent on crystal direction
- Generally field dependent: $\mu = \mu(\mathbf{F})$
- Depends on energy dispersion (i.e. band structure) via:

$$\mathbf{v}(\mathbf{k}) = \frac{1}{\hbar} \frac{\partial E(\mathbf{k})}{\partial \mathbf{k}}$$

- For band-like transport: $\mu = \frac{q\tau}{m^*}$

(τ = mean free scattering time of the charge in the crystal:

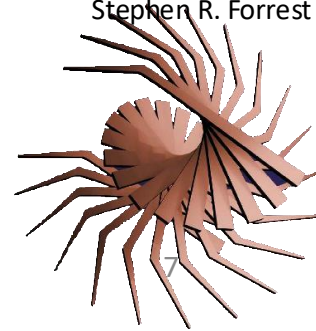
For thermally broadened bands: $\tau > \hbar / k_B T$)

- Ohms Law: $\mathbf{j} = q(n\mathbf{v}_e + p\mathbf{v}_h) = \vec{\sigma} \mathbf{F}$

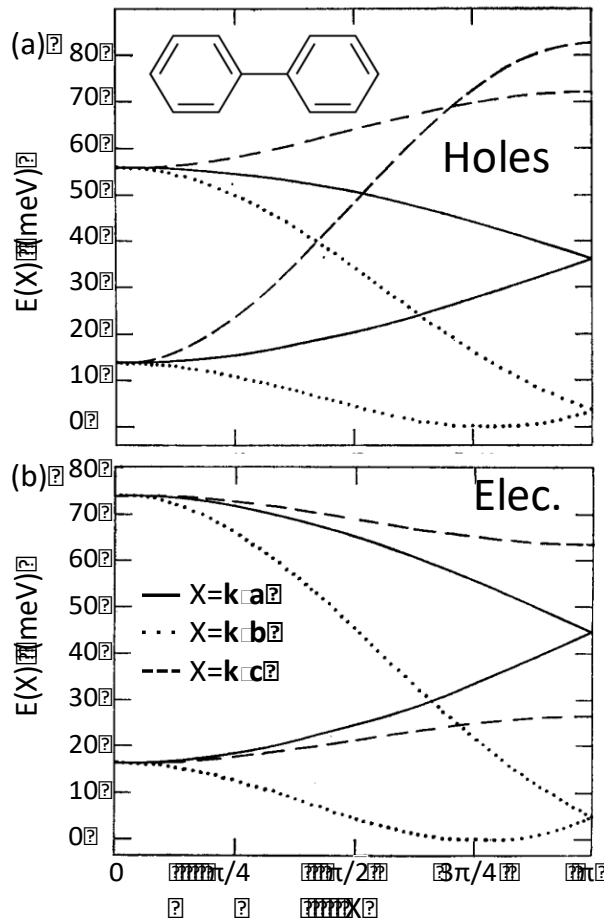
- or

$$\vec{\sigma} = q(n\tilde{\mu}_e + p\tilde{\mu}_p)$$

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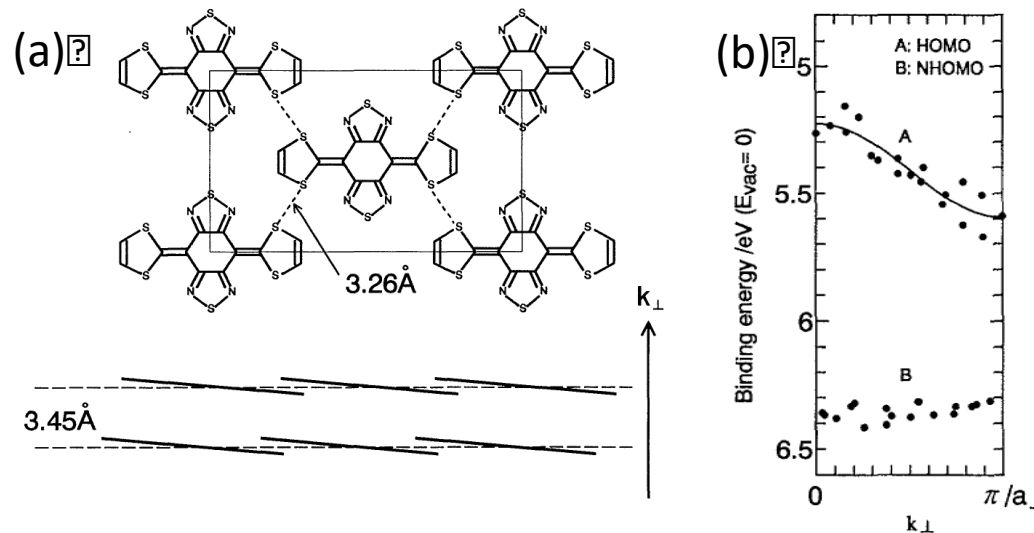
Calculated and Measured Band Structures



Calculated structure for biphenyl:

- Two molecules/cell give 2 branches *along each direction*
- Max. BW = ~ 70 meV for electrons & holes

Katz, J. I., et al. *J. Chem. Phys.*, **39**, 1683 (1963).



Hasegawa, S., et al. *J. Chem. Phys.*, **100**, 6969 (1994).

Measured structure for BTQBT:

- Technique: Angle-resolved UPS: ARUPS
- Minimum contact distance: 3.26 Å
- HOMO BW = 400 meV
- $m^* = 3.1 m_0$

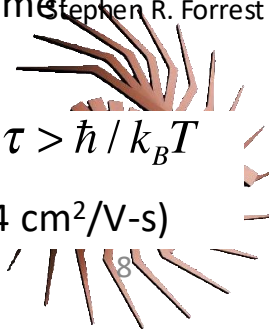
- Mobility vs. effective mass and mean free time

$$\mu_h = \frac{q\tau}{m_h^*}$$

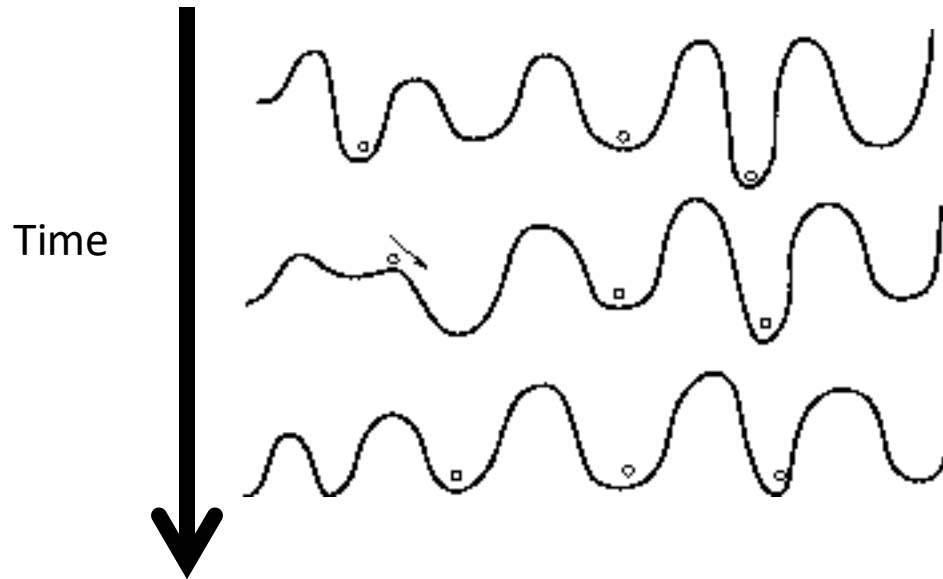
- But thermally broadened bands have $\tau > \hbar / k_B T$
- $\mu \sim 6.5 \text{ cm}^2/\text{V-s}$ (c.f. Hall measurement of $4 \text{ cm}^2/\text{V-s}$)

(NHOMO = next highest orbital)

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Hopping transport

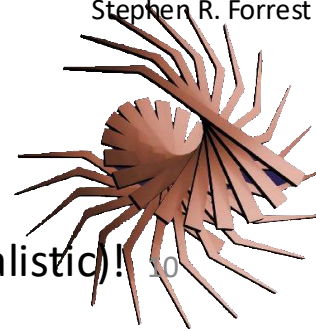


When there is strong electron-phonon (small polaron) coupling, we get another condition for band transport:

$$\mu > \frac{qa^2}{\hbar} \left(\frac{\hbar\omega_0}{k_B T} \right)$$

Optical phonon energy
(typ. ~ 100 meV)

$\mu \sim 20$ cm²/V-s at room temperature...very high (and probably unrealistic)!



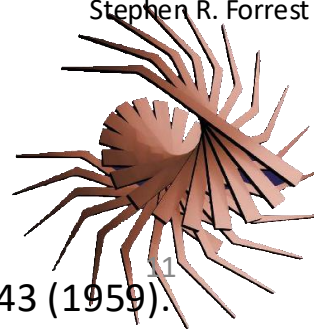
Band vs. Hopping Transport

- The charge diffusion length is: $L_q = \sqrt{D\tau} = \left[\frac{\mu\tau k_B T}{q} \right]^{\frac{1}{2}}$
- Band transport occurs when $L_q \gg a$.
- From uncertainty: $BW \cdot \tau > \hbar$
- Condition for band conduction $\Rightarrow \mu > \frac{qa^2}{\hbar} \left(\frac{BW}{k_B T} \right)$

(Ex. Room temperature, let $BW=25$ meV, $a=5\text{\AA}$. Then $\mu > 5$ cm²/V-s)

- Hopping due to short range interaction involving only nearest neighbor molecules
 - Incoherent diffusive process
 - Electron is heavy since it self traps: it polarizes the neighborhood and must carry that energy along with it.
 - Since only nearest neighbors are affected = **small polaron**
 - Ionic materials, where the interaction goes as $\sim 1/r$ = **large polaron**

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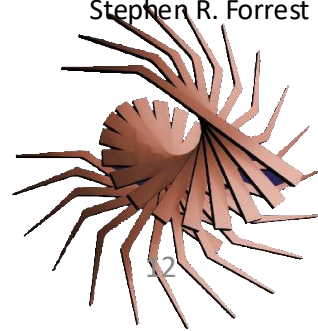


Mobility and Charge Diffusion

- Near equilibrium, the Einstein relationship connects these quantities:

$$\frac{D}{\mu} = \frac{k_B T}{q}$$

- Charge diffusion length: $L_q = \sqrt{D\tau}$



The theory of μ

- **Goal:** To find μ , include disorder expressed by the density of states: $\rho(\epsilon)$.
- We first need to find the rates, k_{ij} in the presence of disorder.

• Model 1: Miller-Abrahams theory

- Developed for impurity band conduction in semiconductors
- Valid for weak electron-phonon coupling (g_m, g_{nm} small)

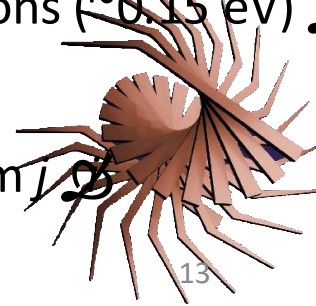
$$k_{ij} = \nu_0 \exp(-2\gamma_{ij}R_{ij}) \begin{cases} \exp\left(-\frac{\epsilon_j - \epsilon_i}{k_B T}\right) & \epsilon_j > \epsilon_i \\ 1 & \epsilon_j < \epsilon_i \end{cases}$$

ν_0 = hopping attempt freq. ~opt. phonon freq.
 γ =overlap factor, decay of wavefunction
 between i, j .
 R_{ij} =hopping distance

• Implications:

- “Uphill” transfers are thermally activated
- “Downhill” transfers encounter no barrier \Rightarrow occur with unity probability
- Valid when $\epsilon_j - \epsilon_i < \Theta_m$ (Debye energy) of acoustic and optical phonons (~0.15 eV) at low temperatures
- In F-field, add in $-q\mathbf{r} \cdot \mathbf{F}$ to exponential argument where F points from j to i

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Model 2: Marcus Transfer

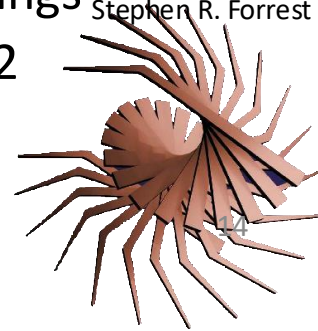
- Developed for understanding transfer of electron from donor to acceptor in solution (reaction kinetics)
- Generalized form of mobility in the small polaron (non disordered) limit. Starting point is again from Holstein:

$$k_{ET;R,P} = A \exp\left(-\frac{\Delta G^*}{k_B T}\right) = A \exp\left(-\frac{(\lambda_{reorg} + \Delta G^0)^2}{4\lambda_{reorg} k_B T}\right)$$

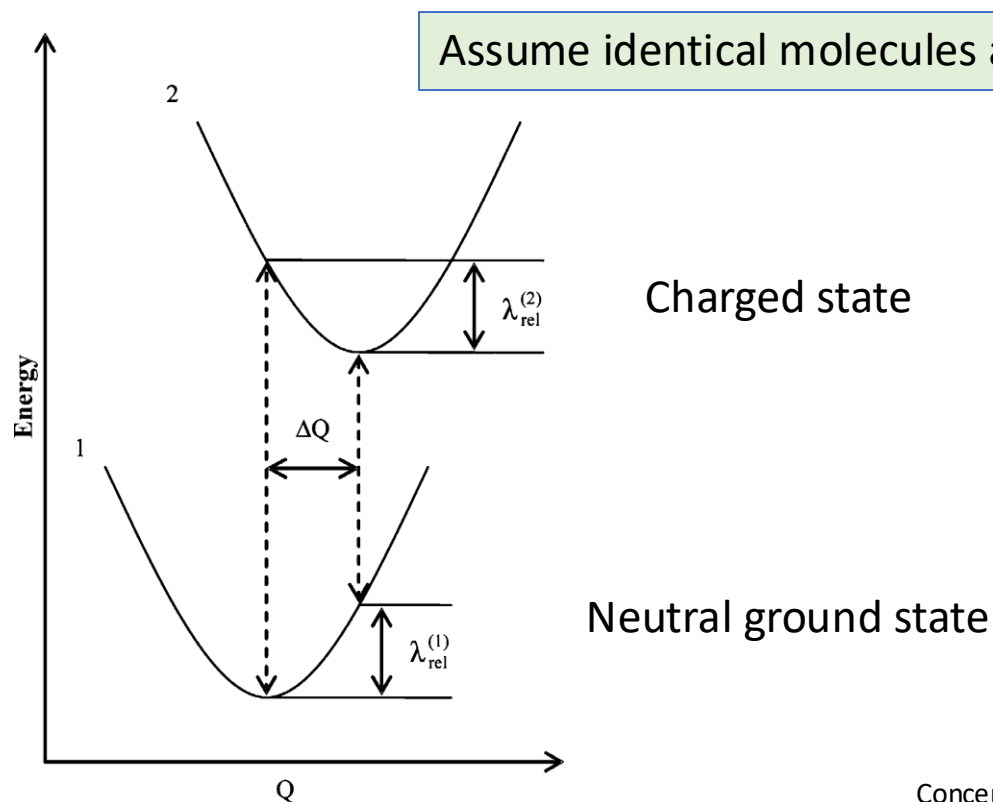
$$A = \frac{A_0 \exp(-2\gamma R)}{\hbar} \left(\frac{\pi}{\lambda_{reorg} k_B T} \right)^{1/2}$$

- *Valid for both upward and downward jumps:* Only based on difference in **free energy** between initial and final states, ΔG .
- Valid at high temperatures, and strong electron-phonon couplings
- Activation energy for the transfer reaction: $2E_{act} = E_{pol} = \lambda_{reorg}/2$

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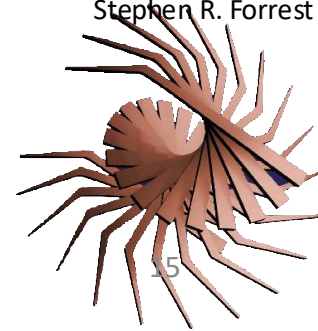
Molecular energy changes when a charge is transferred



Reorganization energy: $\lambda_{reorg} = \lambda_{rel}^{(1)} + \lambda_{rel}^{(2)}$

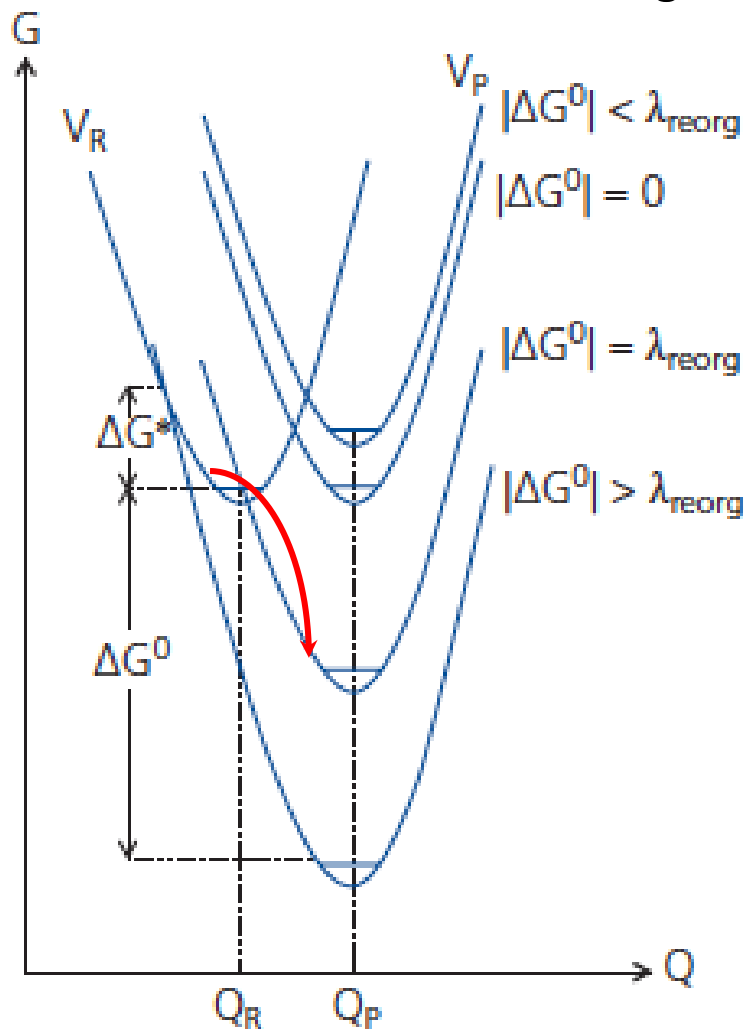
Or polarization energy $\approx E_{pol}^{loc} = \lambda_{reorg} / 2$.

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Transfer regimes under Marcus

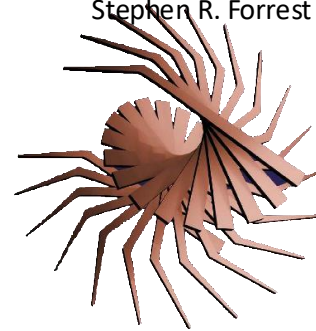
Transfer rate depends on ΔG which can be less than or greater than 0.



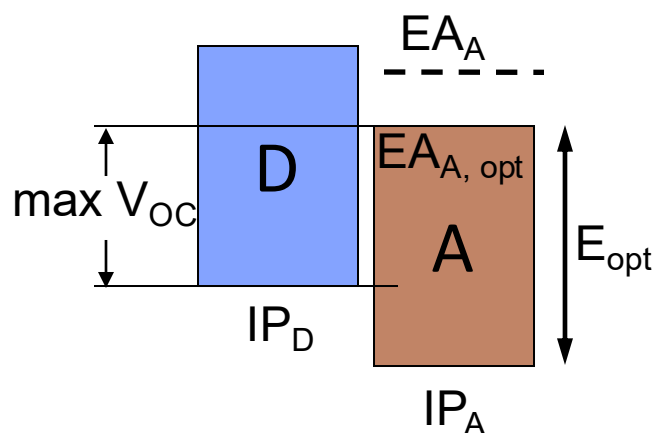
Red arrow shows inverted regime when the energy barrier vanishes, and then increases once again with increasing ΔG

$$k_{ET} = A \exp \left[-\frac{\Delta G^*}{k_B T} \right] = A \exp \left[-\frac{(\lambda_{reorg} + \Delta G^0)^2}{4 \lambda_{reorg} k_B T} \right]$$

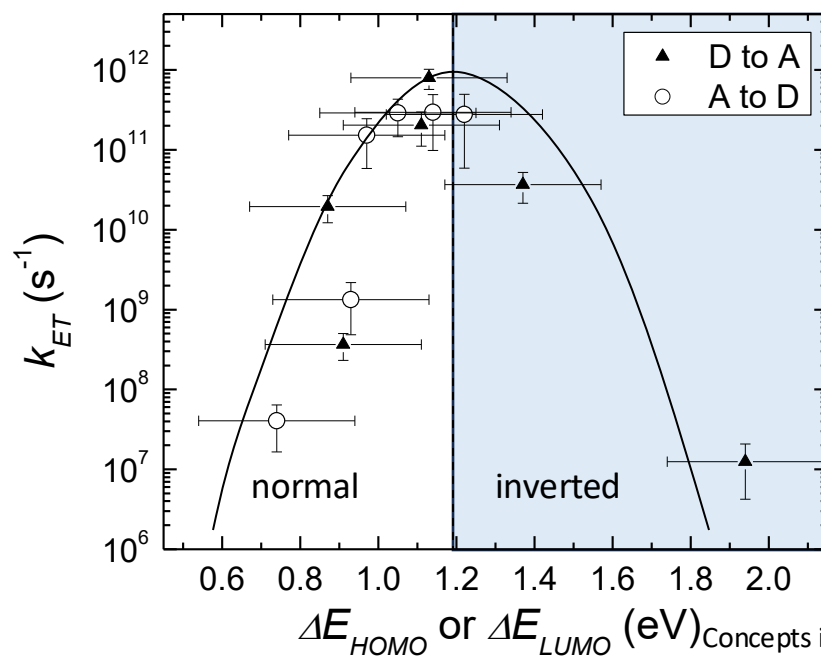
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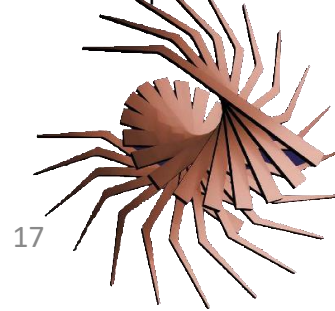
Experimental observation of Marcus regimes in an organic heterojunction



EA = electron affinity
IP = Ionization potential

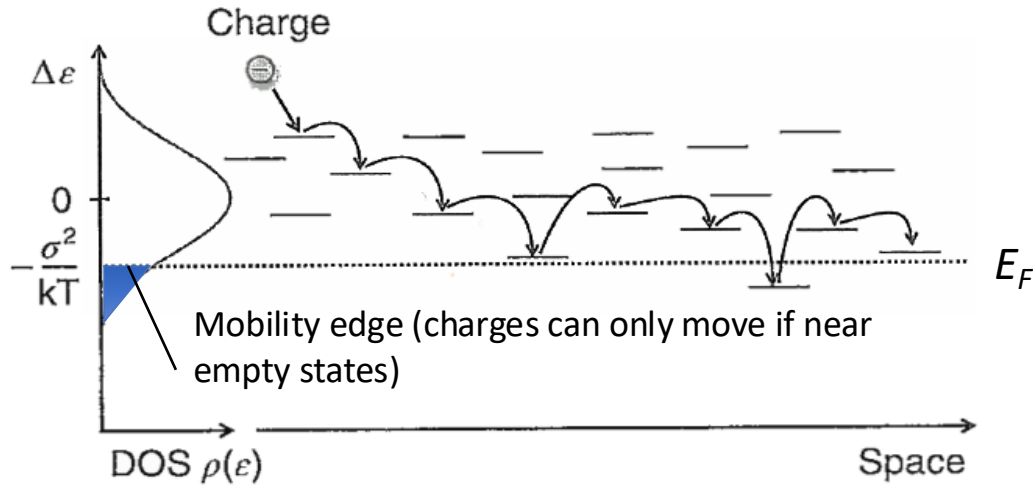


Electron transfer for $D \rightarrow A$ or $A \rightarrow D$

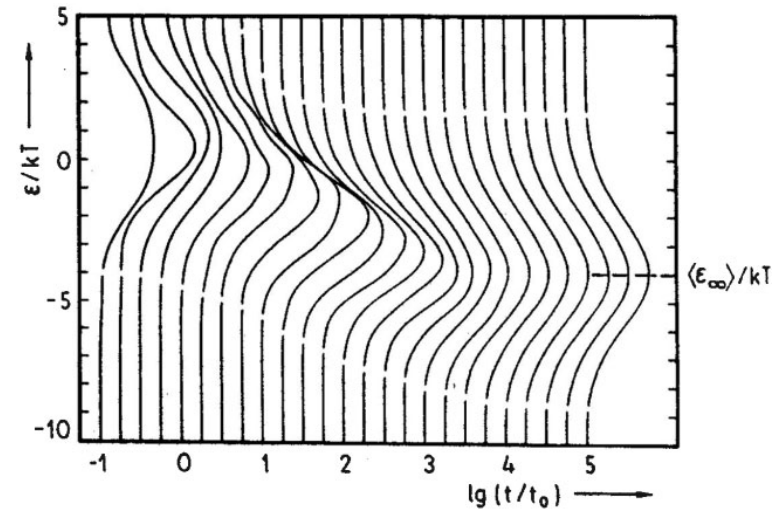


Density of States and the Mobility Edge

Relaxation of a hot carrier



Charge relaxes to ϵ_∞

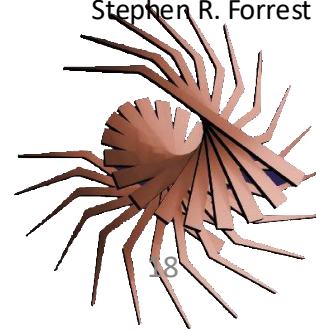


A commonly used model: Gaussian Disorder Model (GDM) introduced by Bäessler

$$\langle\epsilon_\infty\rangle = \frac{\int_{-\infty}^{\infty} \epsilon \rho(\epsilon) \exp(-\epsilon/k_B T) d\epsilon}{\int_{-\infty}^{\infty} \rho(\epsilon) \exp(-\epsilon/k_B T) d\epsilon} = -\frac{\sigma^2}{k_B T}$$

Mean equilibrium carrier energy—
Charges relax into the tail of the distribution
of half width, σ .

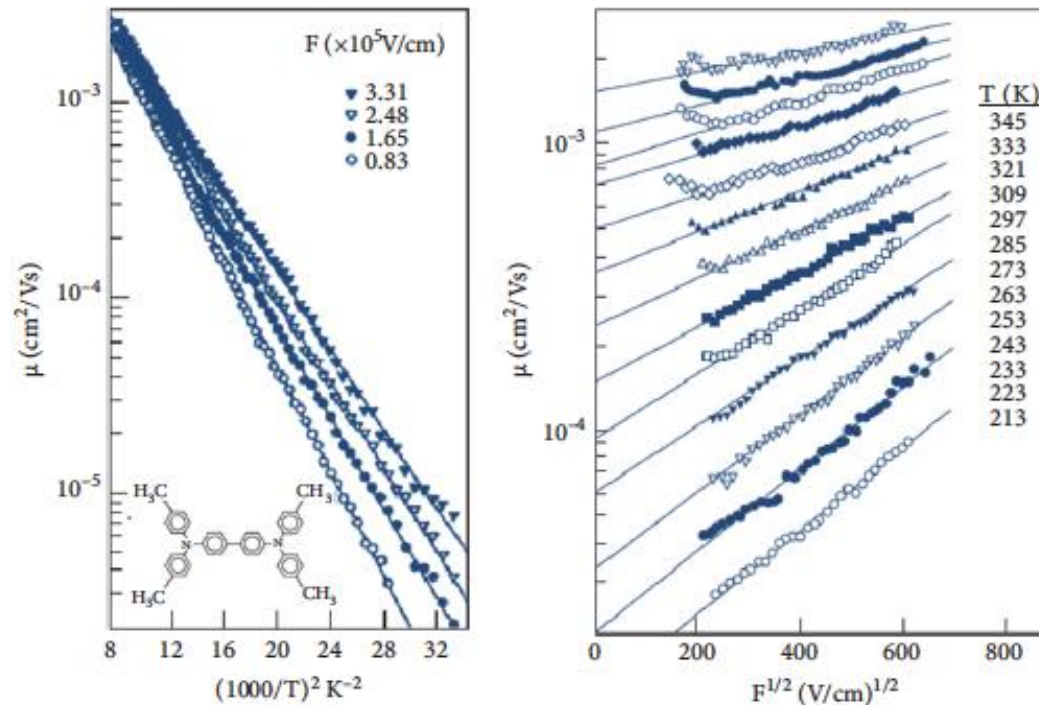
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Empirical expressions for mobility

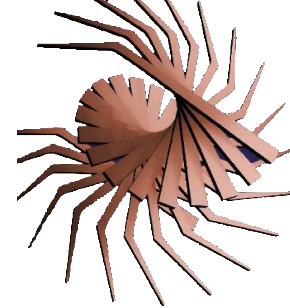
$$\mu = \mu_0 \exp\left(-\left(\frac{2\sigma_{GDM}}{3k_B T}\right)^2\right) \begin{cases} \exp\left[C\left(\left(\frac{\sigma_{GDM}}{k_B T}\right)^2 - \Sigma^2\right)\sqrt{F}\right] & \Sigma \geq 1.5 \\ \exp\left[C\left(\left(\frac{\sigma_{GDM}}{k_B T}\right)^2 - 2.25\right)\sqrt{F}\right] & \Sigma < 1.5 \end{cases}$$

These expressions work reasonably well over a range of temperatures and fields



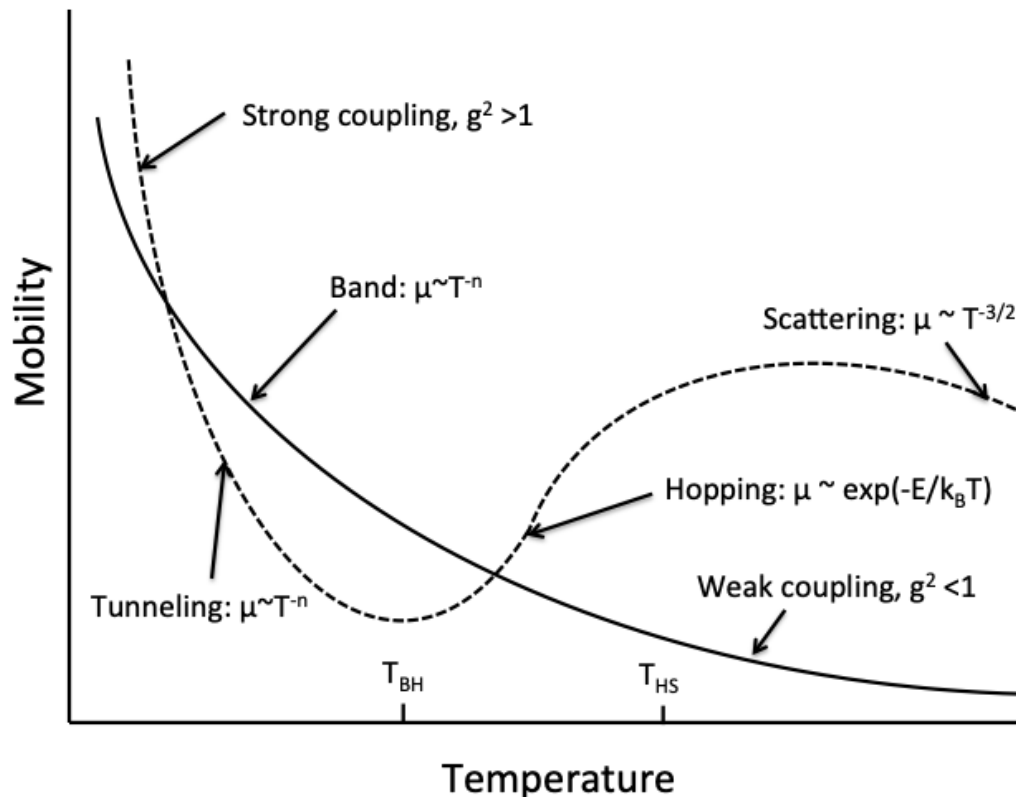
Heun, S. & Borsenberger, P. M. 1995. *Chem. Phys.*, 200, 245.

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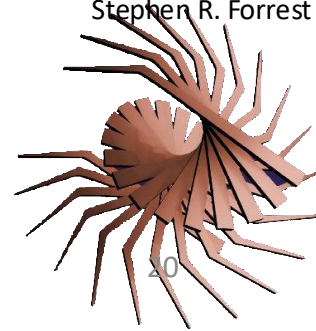


Small polaron theory predicts several transport regimes

- Dependent on coupling strength, g
- Static disorder not included here
- Band and tunneling both coherent and follow power law dependence



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An accurate method to extract the mobility and diffusion constant

Shockley-Haynes Method (time of flight)

- Bias sample at quasi-equilibrium to avoid injection (Ohmic at $V_a \rightarrow 0$).
- Light pulse generates excitons that separate into charges at $t = 0$
- Measure arrival time (t_D) of the photogenerated current pulse.

$$t_D = \frac{L^2}{\mu V_a}$$

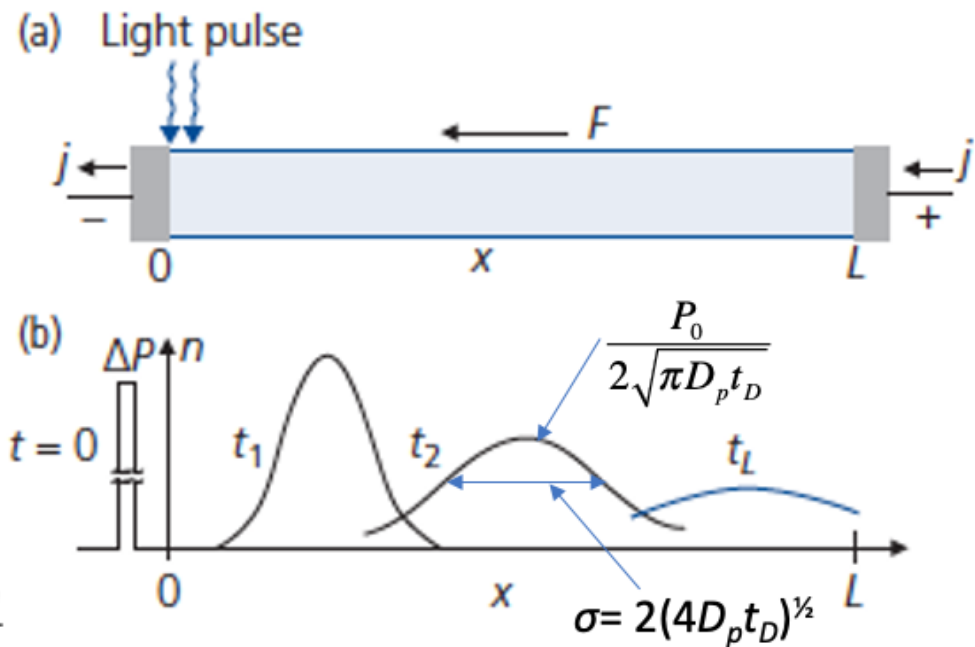
Start with diffusion equation: $\frac{\partial p}{\partial t} = D_p \frac{\partial^2 p}{\partial x^2}$

With solutions: $p(x,t) = \left[\frac{P_0}{2\sqrt{\pi D_p t}} \right] \exp(-x^2 / 4D_p t)$ (A single $\mu \Rightarrow$ Gaussian spreading)

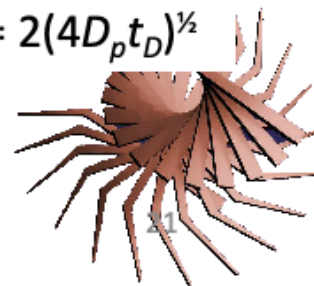
The peak decreases with t_D , and it spreads with half width at $1/e$ from max.: $\sigma = 2(4D_p t_D)^{1/2}$

The width of the current pulse gives the diffusion constant of the charge, D_p .

D_p should be consistent with the Einstein relation $\Rightarrow \mu$

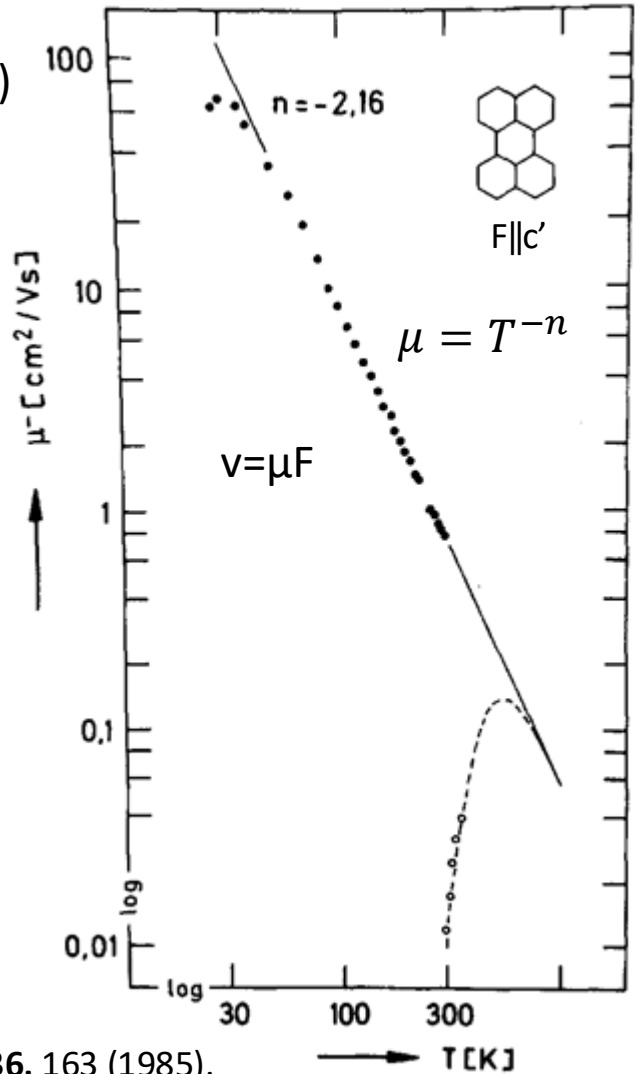
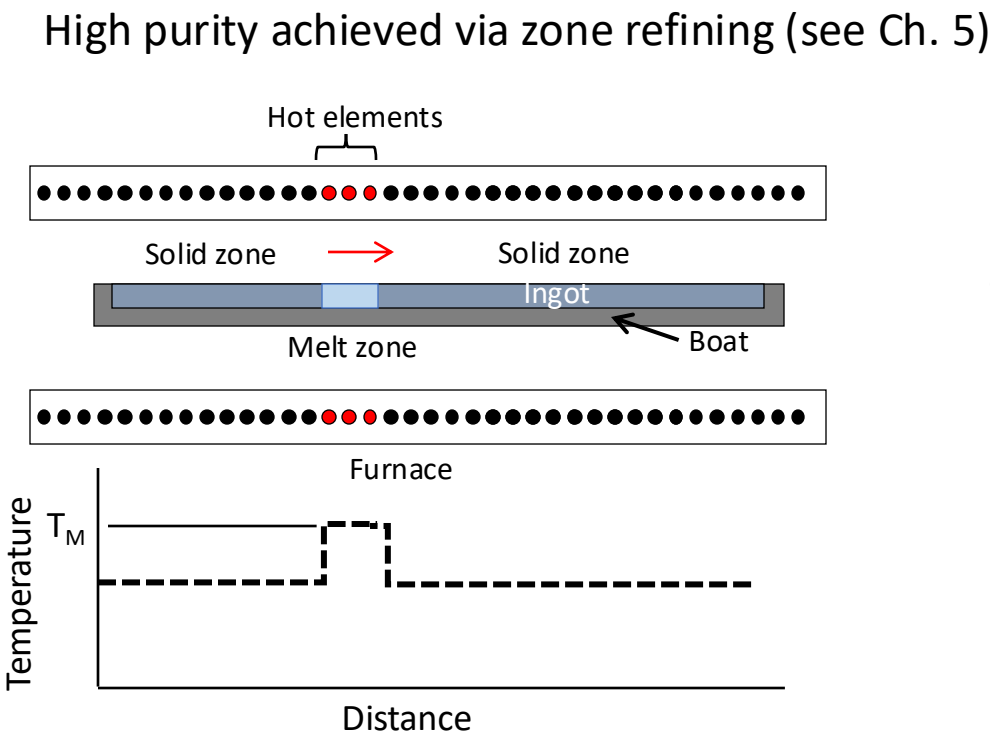


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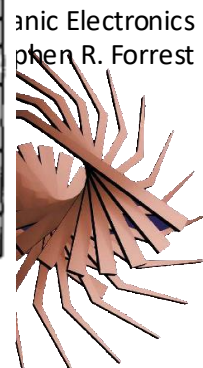


Non-Dispersive Mobility in Ultrapure Perylene

$n = 1.5$ band transport
 $n = 2$ acoustic phonon scattering

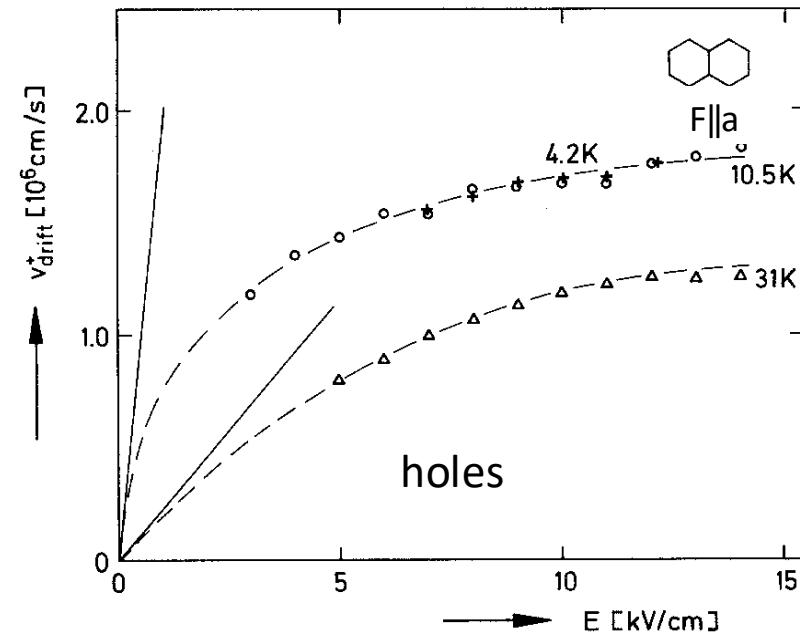
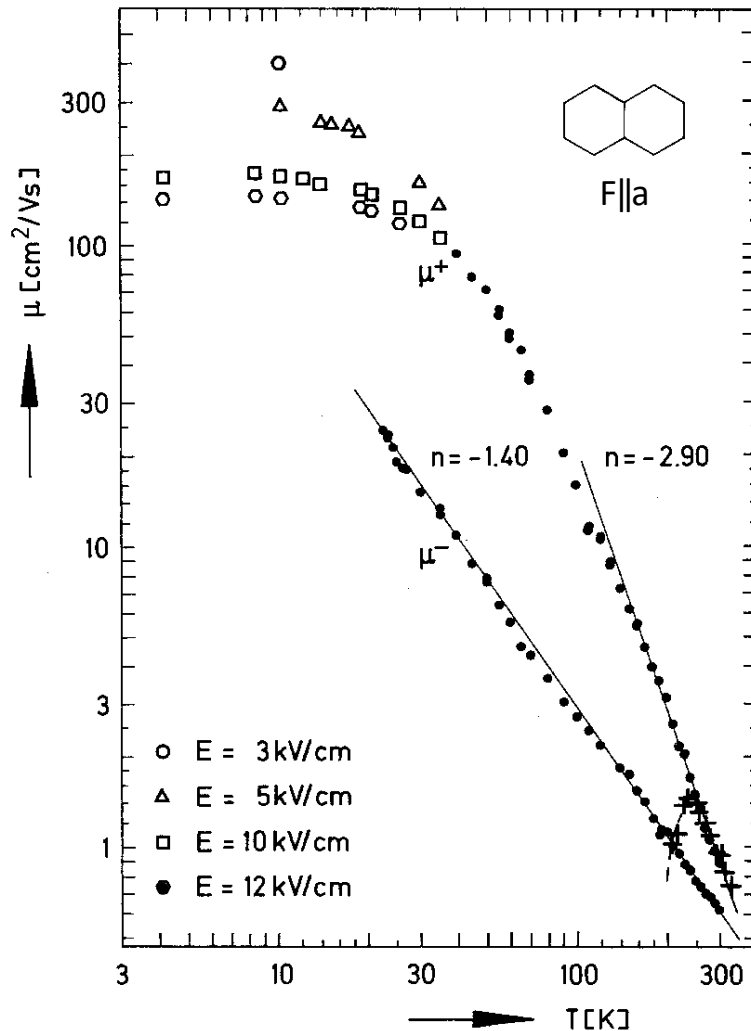


W. Warta, R. Stehle & N.Karl, *Appl. Phys. A*, **36**, 163 (1985).



Band Transport in Ultrapure Naphthalene

- Ultra-purified naphthalene



- Mobility vs. majority carrier type
e.g. If the mobility of holes > electrons,
does NOT imply the material is *p*-type
- The “type” of a material depends on the polarity of the **majority** carrier

Time of Flight Experiment

Ultrapurified Naphthalene Crystals

- Current pulse

$$v > 10^6 \text{ cm/s!}$$

$$\lambda = v\tau \text{ (mean free path)}$$

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

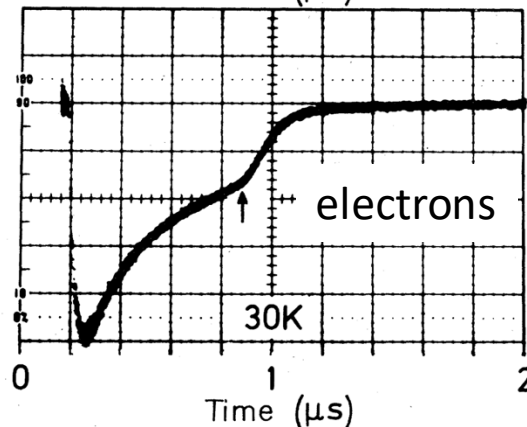
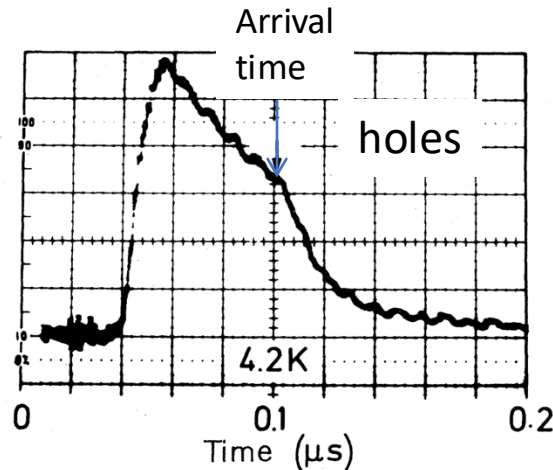
$$v = (3k_B T / m^*)^{1/2}$$

$$\Rightarrow \lambda = (\mu/q)(3m^*k_B T)^{1/2}$$

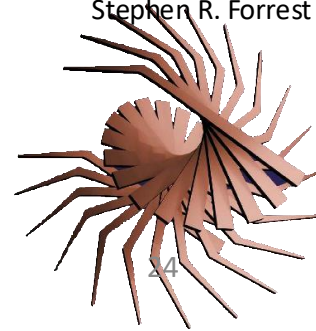
From the data on naphthalene:

$$m^* \sim 3\text{-}15m_0$$

$\lambda \sim 8a$: definitely in the band transport regime

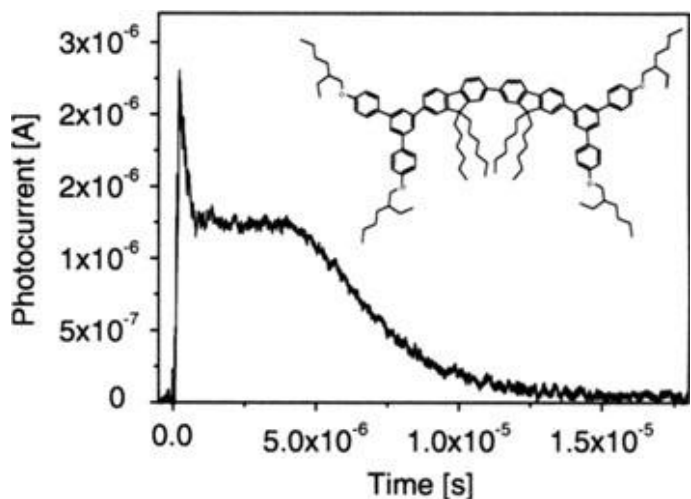
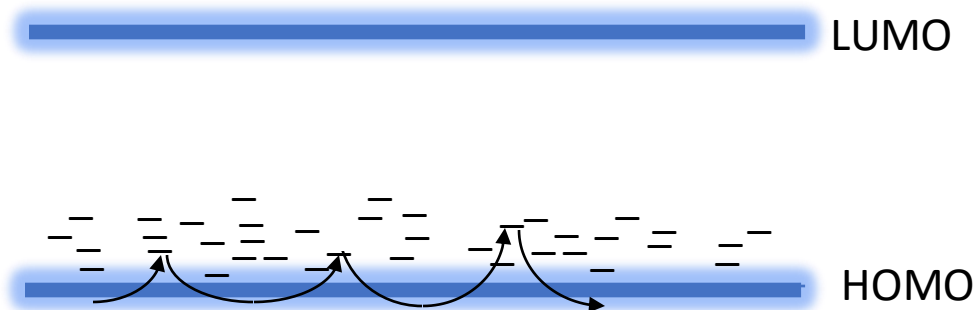


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TOF Mobility with Traps

- In the presence of defect states, charges continually trap and de-trap during transit
 - The mobility is not a good number—there are several mobilities, one for each carrier
 - Results in **dispersive transport**



- Initial spike: Charge motion prior to energetic relaxation in the DOS if the RC time constant is short (i.e. reactance small)
- Plateau and broad tail indicate dispersive transport Concepts in Organic Electronics, 2008, R. Forrest many different arrival times from trapping/de-trapping during transit.

