

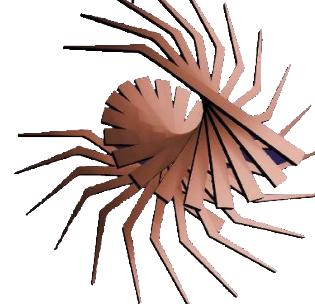
# Electronic Properties of Organic Semiconductors

Electronic Properties 1

Energy Bands  
Charge Transport and Mobility

Chapter 4.1 - 4.2

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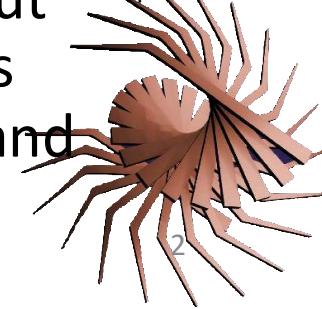


# Objectives: Electronic Properties

*“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.*

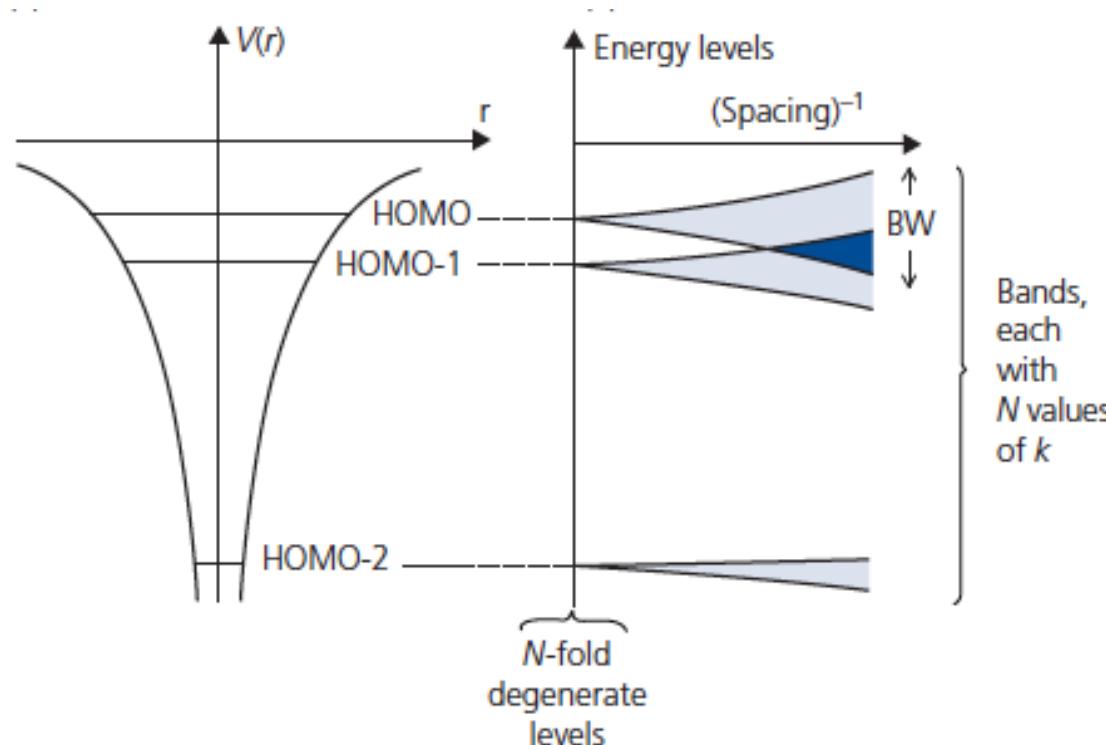
- Organic electronic devices can only be understood in the context of the conductive properties of materials
- In this discussion we introduce
  - Origins of electronic band structure
  - Concept of polarons (large and small)
  - Charge transfer
  - Conductivity, effective mass and mobility
  - Injection
  - 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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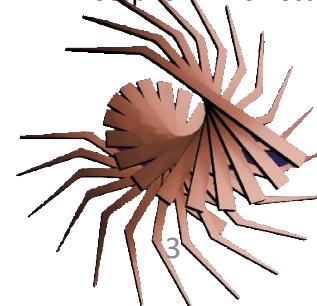


# Transport Bands in Organics

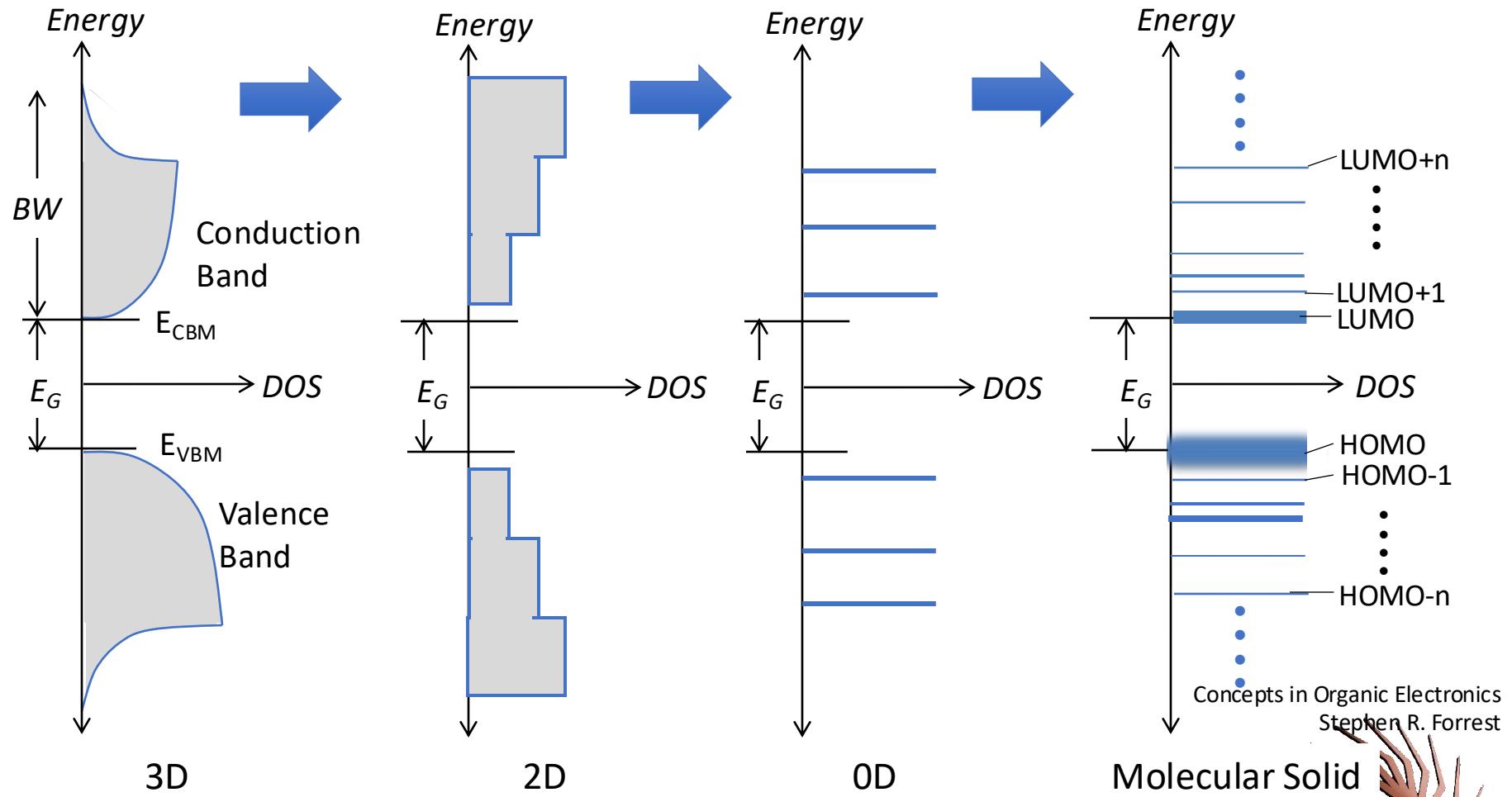
- **Tight binding** approximation is useful due to importance of only nearest neighbor interactions
- Recall case of dimers and larger aggregates on exciton spectrum. Close proximity of neighbors results in:
  - Coulomb repulsion
  - Pauli exclusion➤ Splitting leads to broadening of discrete energies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



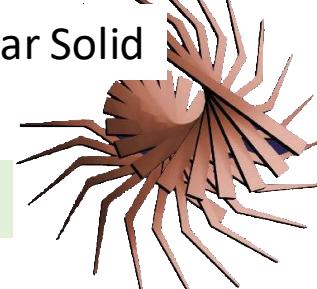
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# The Density of States from 3D to 0D to Molecular Solids

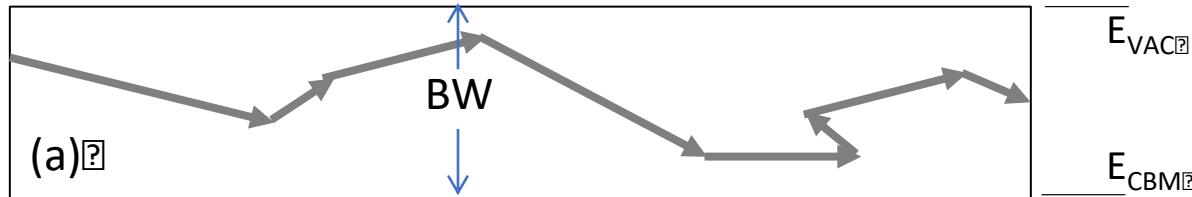


Molecular materials appear similar to 0D (quantum dot) solids



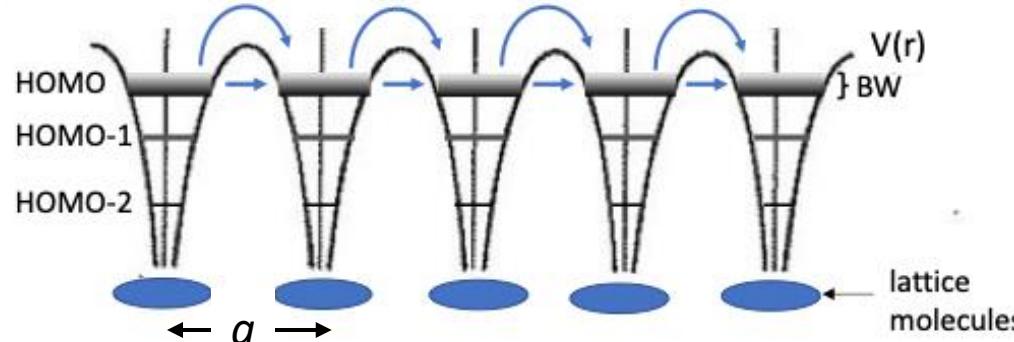
# Modes of Conduction

## Band transport



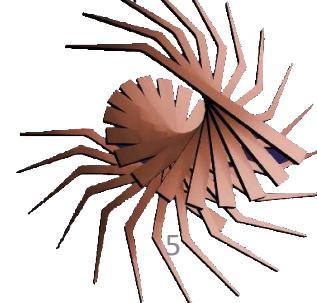
- Coherent
- Charge mean free path  $\lambda >> a$
- $BW > k_B T, \hbar\omega_0$

## Thermally assisted hopping and tunneling transport



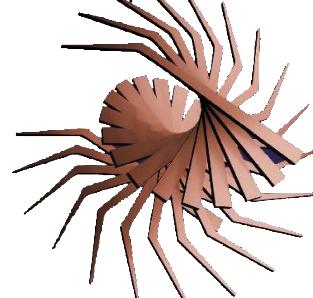
- Incoherent (each step independent of previous)
- Charge mean free path  $\lambda \sim a$
- Tunneling between states of equal energy is band-like
- $BW < k_B T, \hbar\omega_0$

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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:  $\mu$  (not the dipole moment!)
- Definition: “Constant” of proportionality between velocity and electric field:

$$\mathbf{v}(\mathbf{k}) = \vec{\mu}_k \mathbf{F}$$

- 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: 
$$\mu = \frac{q\tau}{m^*}$$

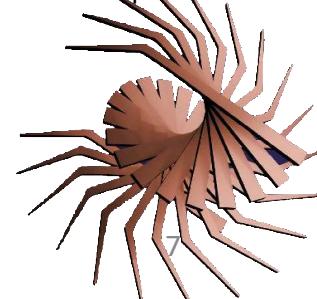
( $\tau$  = mean free scattering time of the charge in the crystal:

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

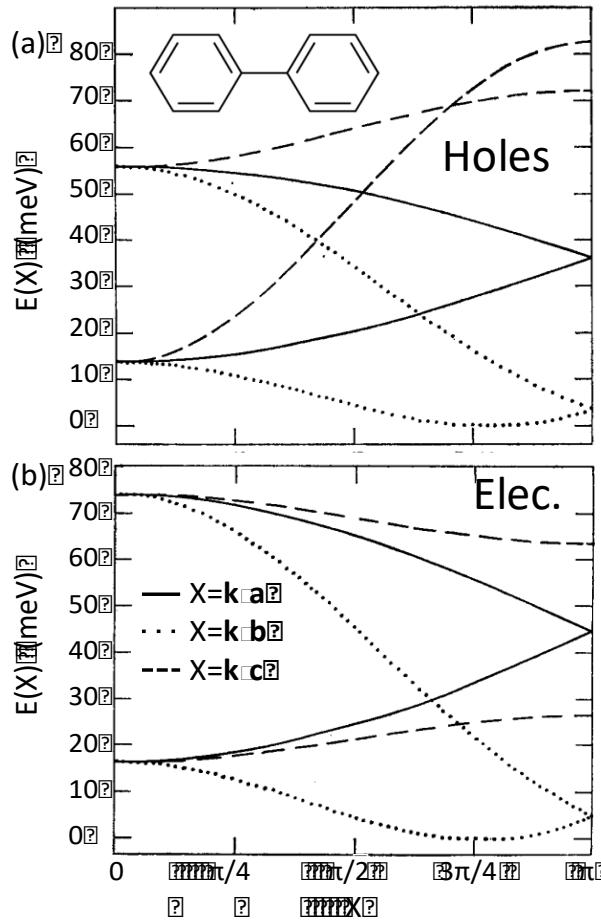
- Ohms Law: 
$$\mathbf{j} = q(n\mathbf{v}_e + p\mathbf{v}_h) = \vec{\sigma} \mathbf{F}$$

- or

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



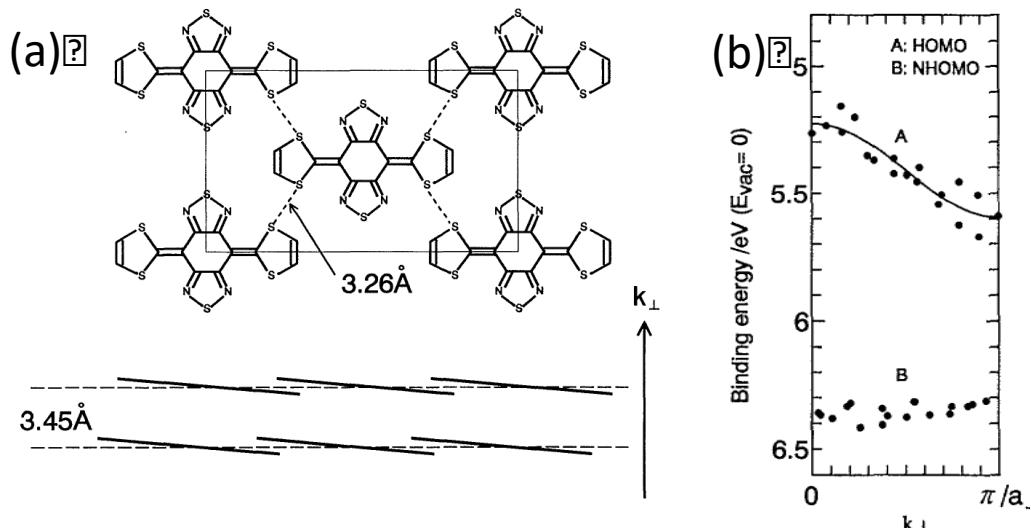
# Calculated and Measured Band Structures



## 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

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

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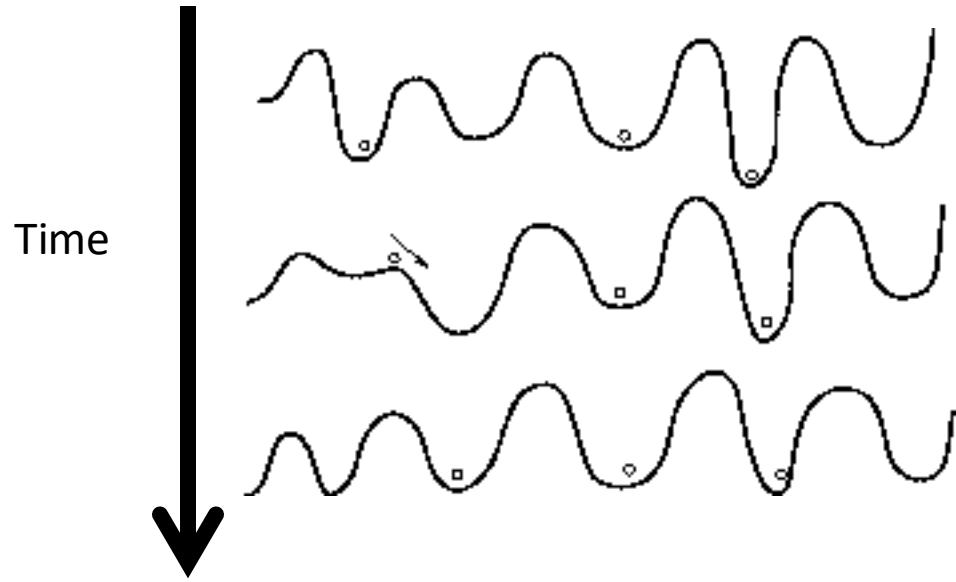
$$\tau > \hbar / k_B T$$

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

(NHOMO = next highest orbital)



# Hopping transport

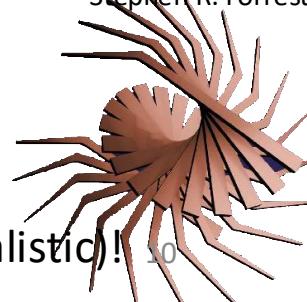


When there is strong electron-phonon (small polaron) coupling, we get another condition for band transport:

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

Optical phonon energy  
(typ.  $\sim 100$  meV)

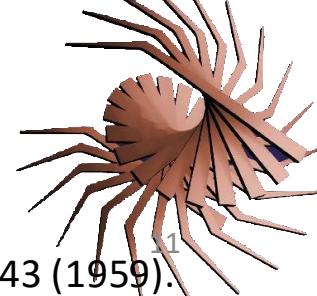
$\mu \sim 20 \text{ cm}^2/\text{V-s}$  at room temperature...very high (and probably unrealistic)! 

# 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  $\mu>5 \text{ cm}^2/\text{V-s}$ )

- 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**



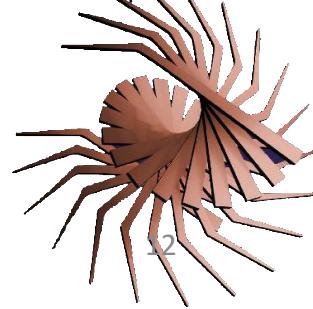
# Mobility and Charge Diffusion

- Near equilibrium, the Einstein relationship connects these quantities:

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

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

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# The theory of $\mu$

- **Goal:** To find  $\mu$ , include disorder expressed by the density of states:  $\rho(\varepsilon)$ .
- 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)

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

$\nu_0$ = hopping attempt freq.~opt. phonon freq.  
 $\gamma$ =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  $\varepsilon_j - \varepsilon_i < \Theta_m$  (Debye energy) of acoustic and optical phonons (~0.15 eV)  
low temperatures
- In F-field, add in  $-qr \cdot \mathbf{F}$  to exponential argument where F points from  $j$  to  $i$

# Model 2: Marcus Transfer

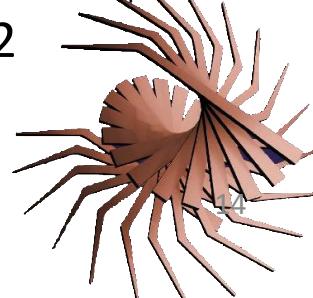
- Developed for understanding transfer of electron from donor to acceptor in solution (reaction kinetics)
  - Generalized form of mobility in the small polaron (non disordered) limit. Starting point is again from Holstein:

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

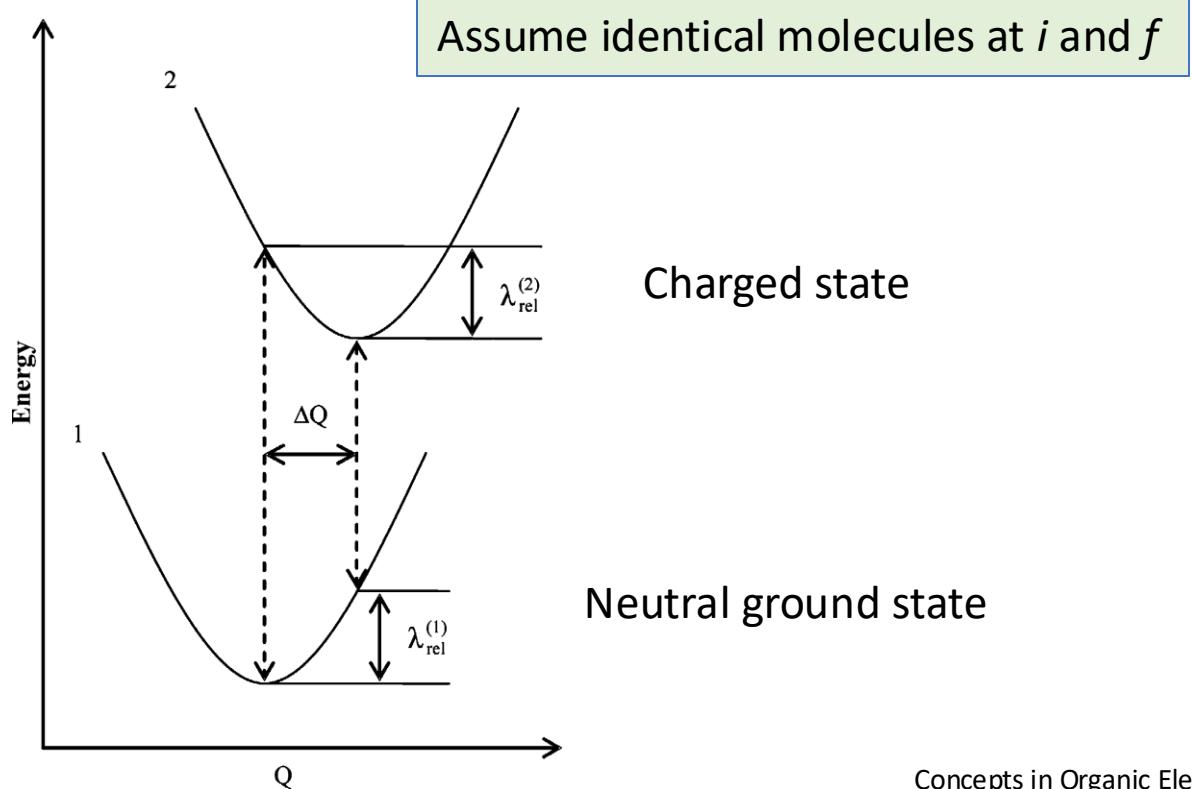
$$A = \frac{A_0 \exp(-2\gamma R)}{\hbar} \left( \frac{\pi}{\lambda_{reorg} k_B T} \right)^{1/2}$$

- *Valid for both upward and downward jumps:* Only based on difference in **free energy** between initial and final states,  $\Delta G$ .
- 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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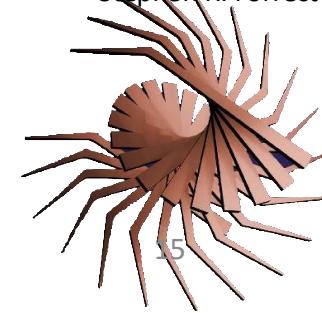
# Molecular energy changes when a charge is transferred



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

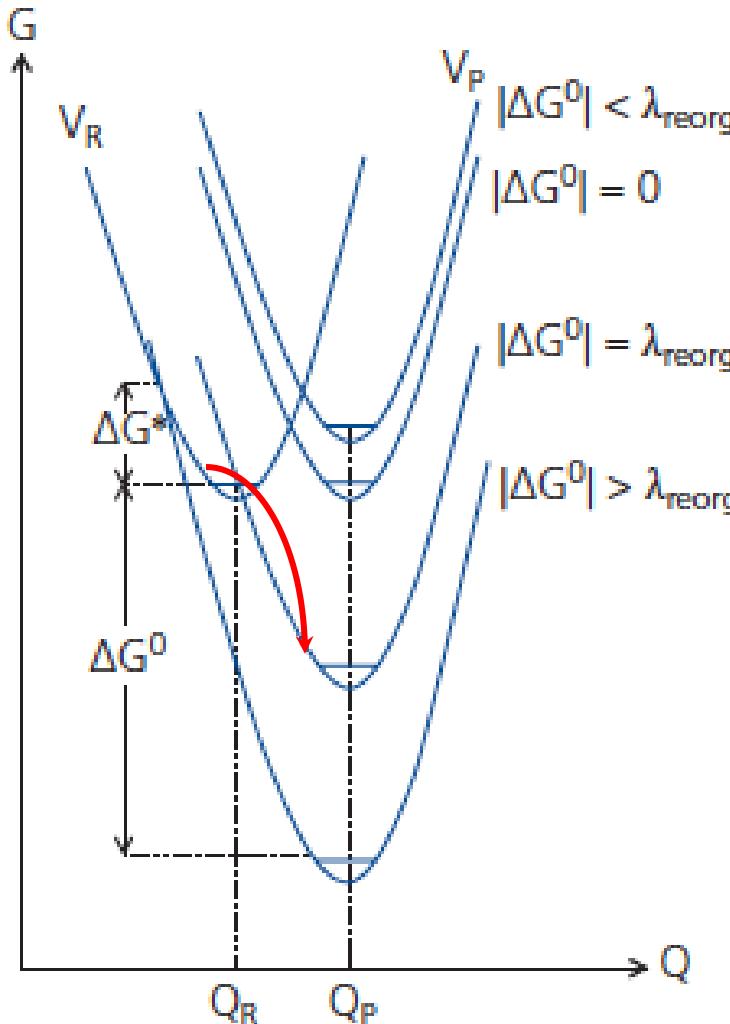
Or polarization energy  $\approx E_{pol}^{loc} = \lambda_{reorg} / 2$ .

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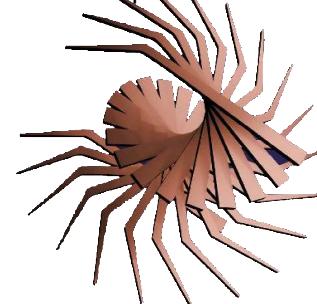
# Transfer regimes under Marcus

Transfer rate depends on  $\Delta G$  which can be less than or greater than 0.

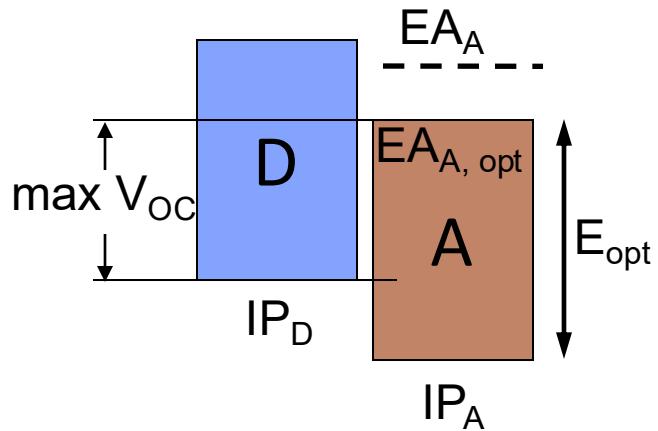


Red arrow shows inverted  
regime when the energy barrier  
vanishes, and then increases  
once again with increasing  $\Delta G$

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

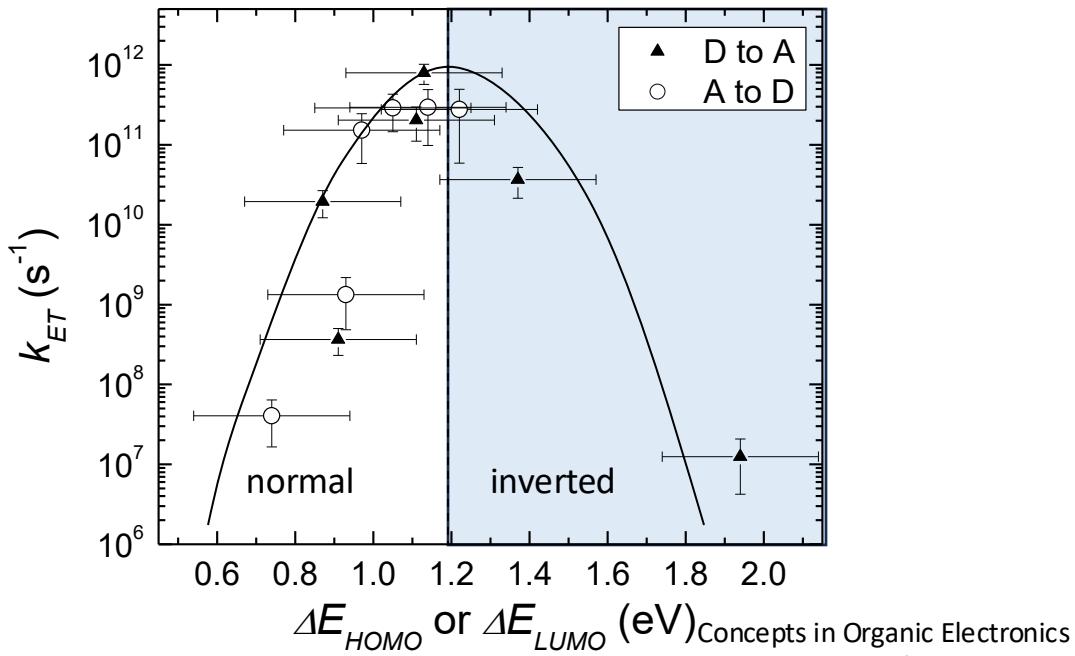


# Experimental observation of Marcus regimes in an organic heterojunction



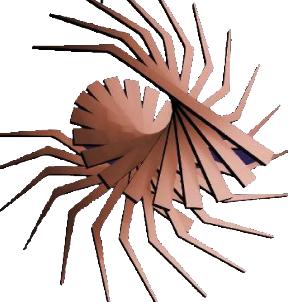
EA = electron affinity

IP = ionization potential



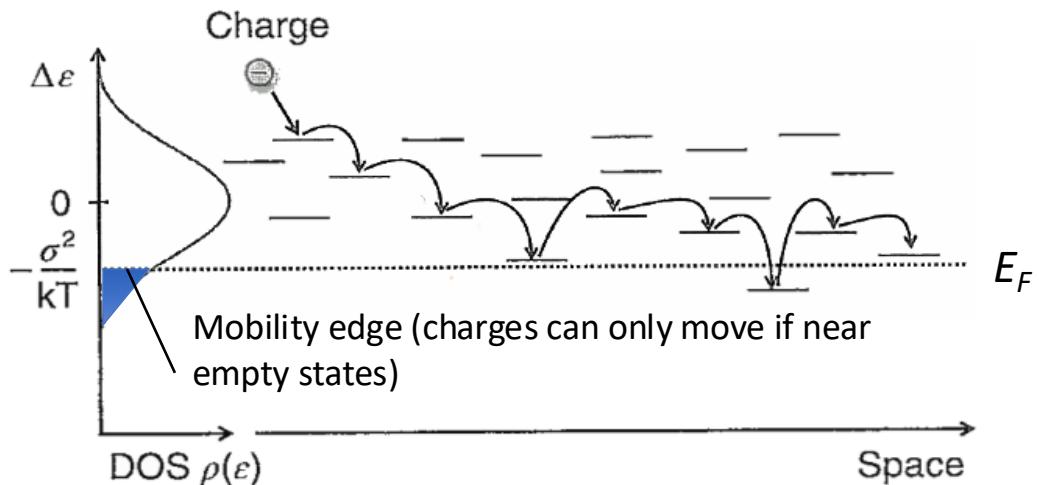
Electron transfer for  $D \rightarrow A$  or  $A \rightarrow D$

Rand, B. P., et al. *Phys. Rev. B*, **75**, 115327 (2007).

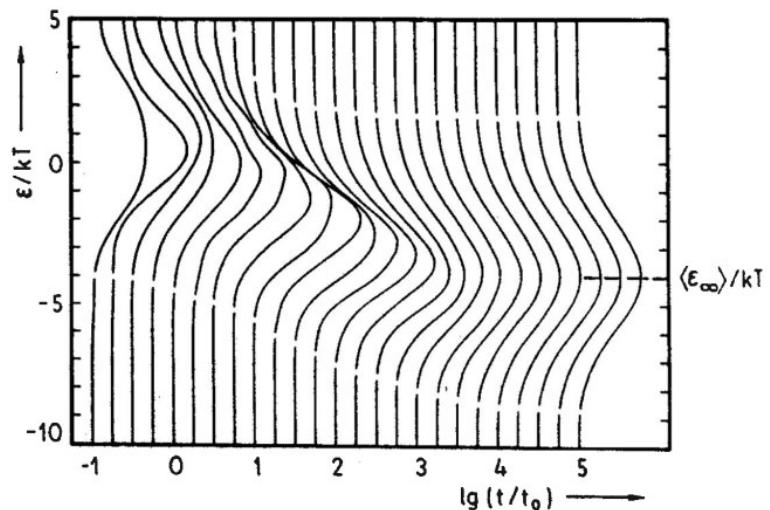


# Density of States and the Mobility Edge

Relaxation of a hot carrier



Charge relaxes to  $\epsilon_\infty$

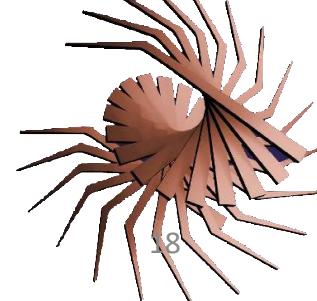


A commonly used model: Gaussian Disorder Model (GDM) introduced by Bässler

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

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

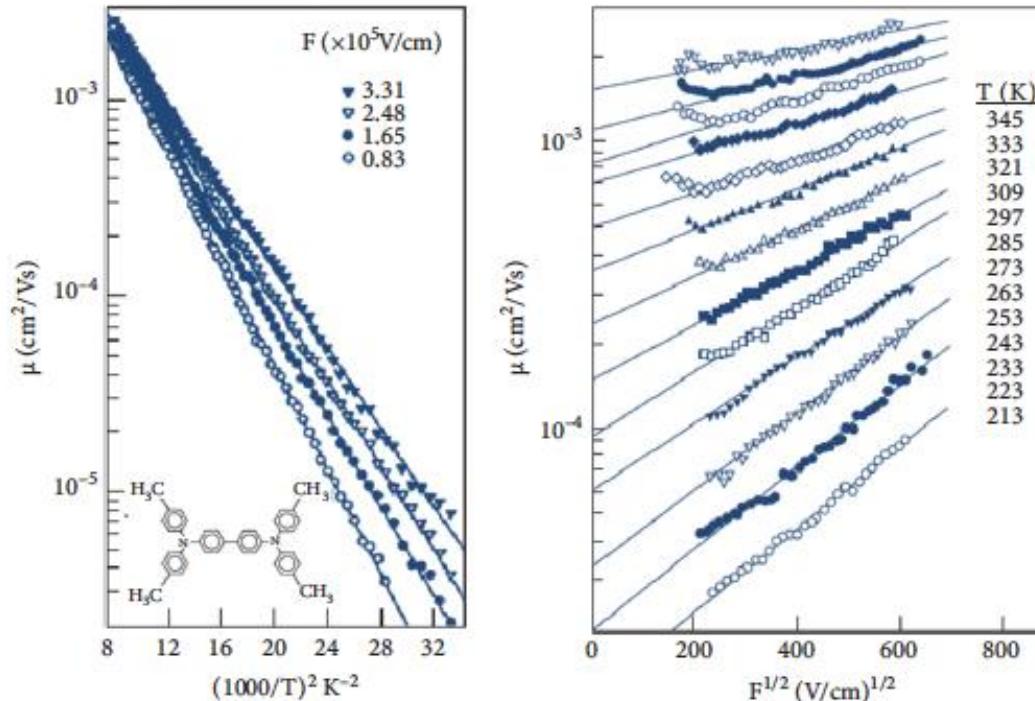
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# Empirical expressions for mobility

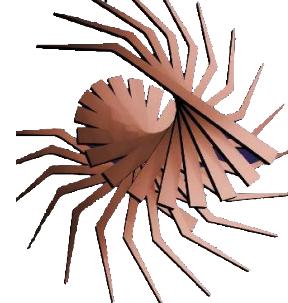
$$\mu = \mu_0 \exp\left(-\left(\frac{2\sigma_{GDM}}{3k_B T}\right)^2\right) \begin{cases} \exp\left[C\left(\left(\frac{\sigma_{GDM}}{k_B T}\right)^2 - \Sigma^2\right)\sqrt{F}\right] & \Sigma \geq 1.5 \\ \exp\left[C\left(\left(\frac{\sigma_{GDM}}{k_B T}\right)^2 - 2.25\right)\sqrt{F}\right] & \Sigma 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

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



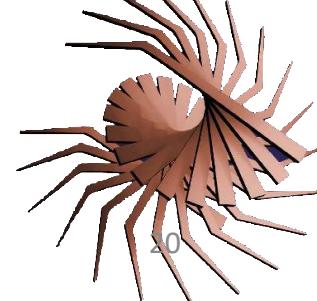
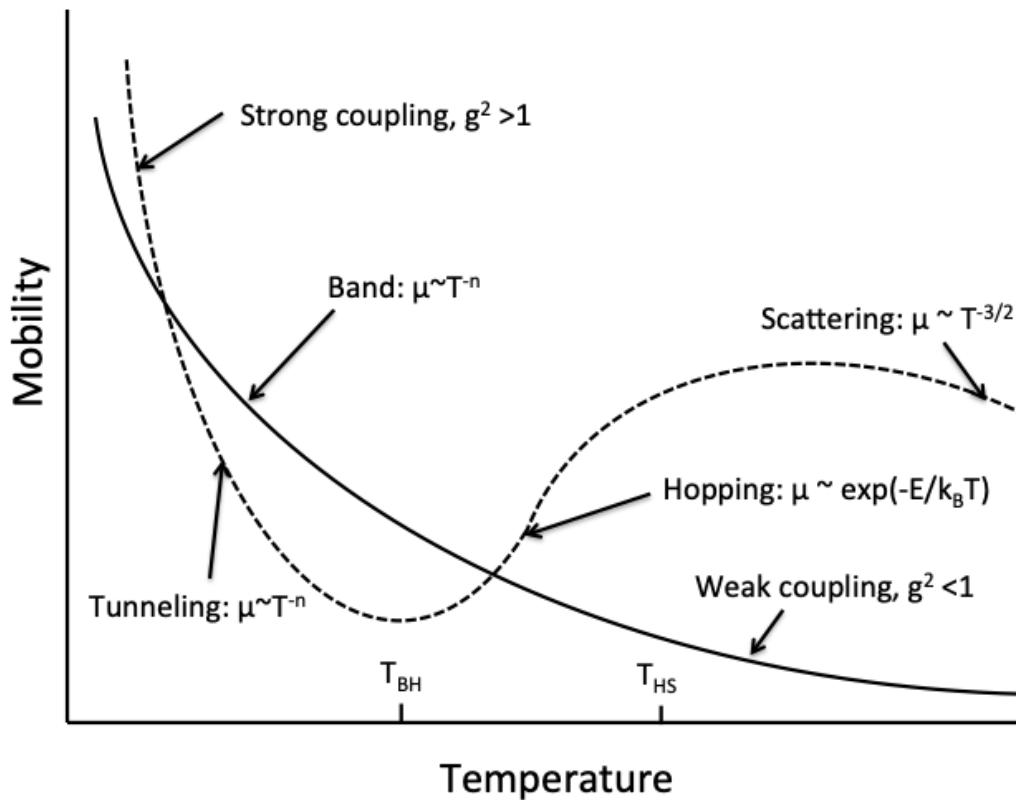
Heun, S. & Borsenberger, P. M. 1995. *Chem. Phys.*, 200, 245.

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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

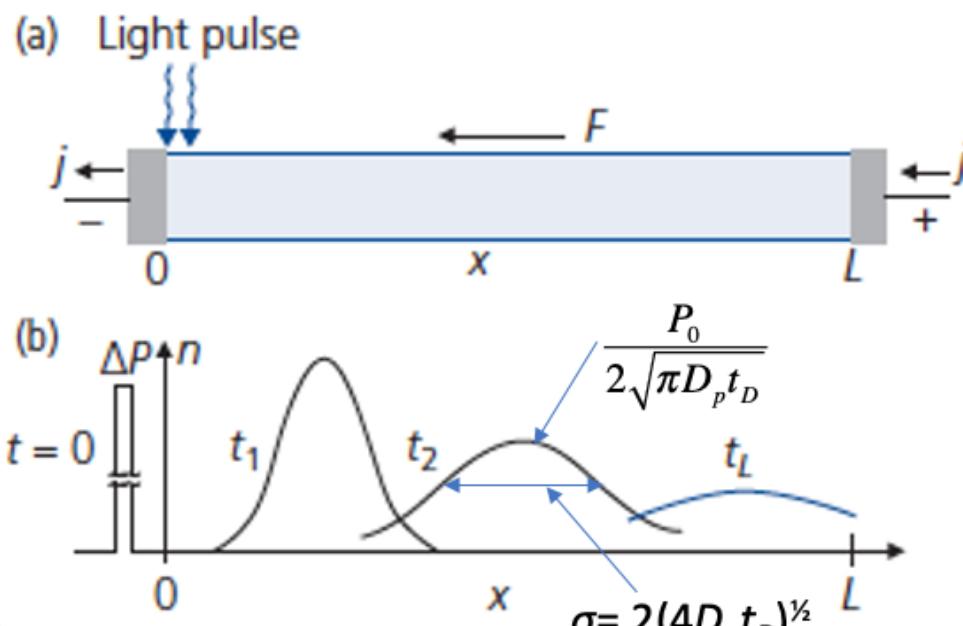


# An accurate method to extract the mobility and diffusion constant

## 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:

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

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

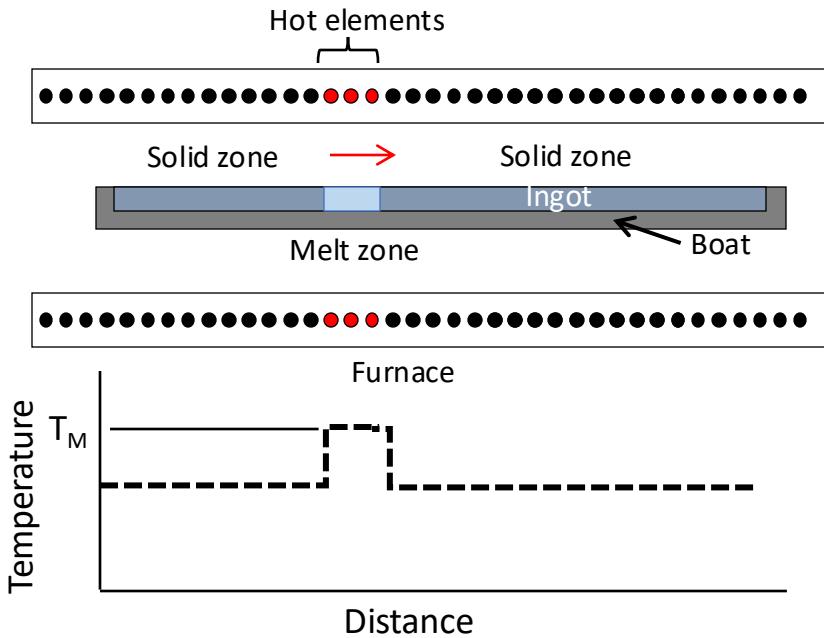
The width of the current pulse gives the diffusion constant of the charge,  $D_p$ .

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

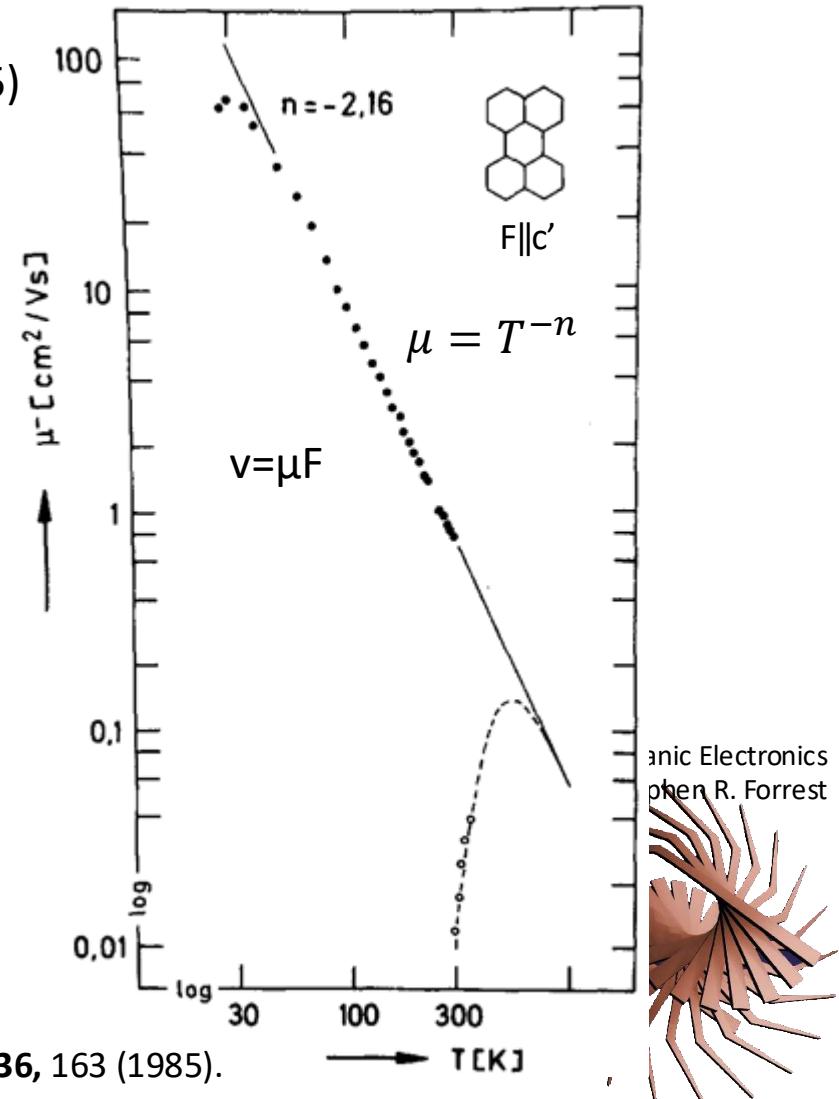


# Non-Dispersive Mobility in Ultrapure Perylene

High purity achieved via zone refining (see Ch. 5)

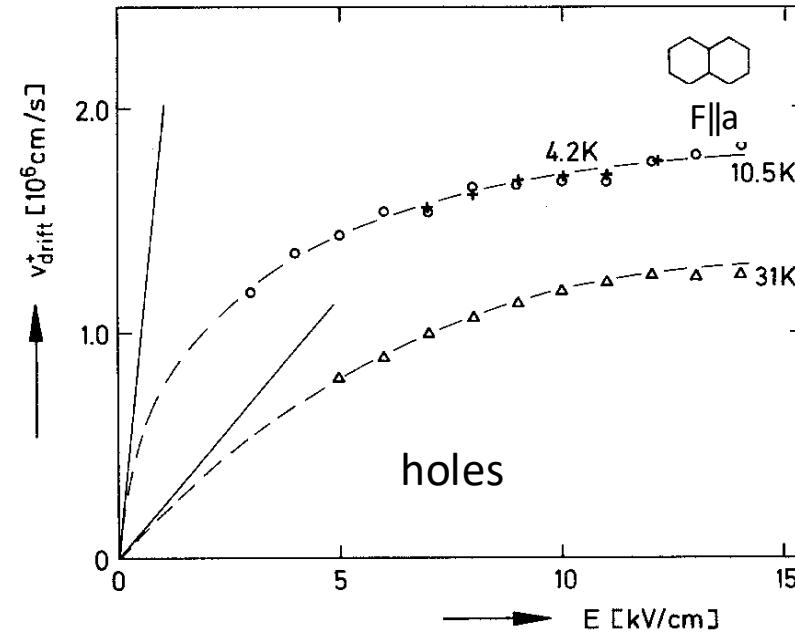
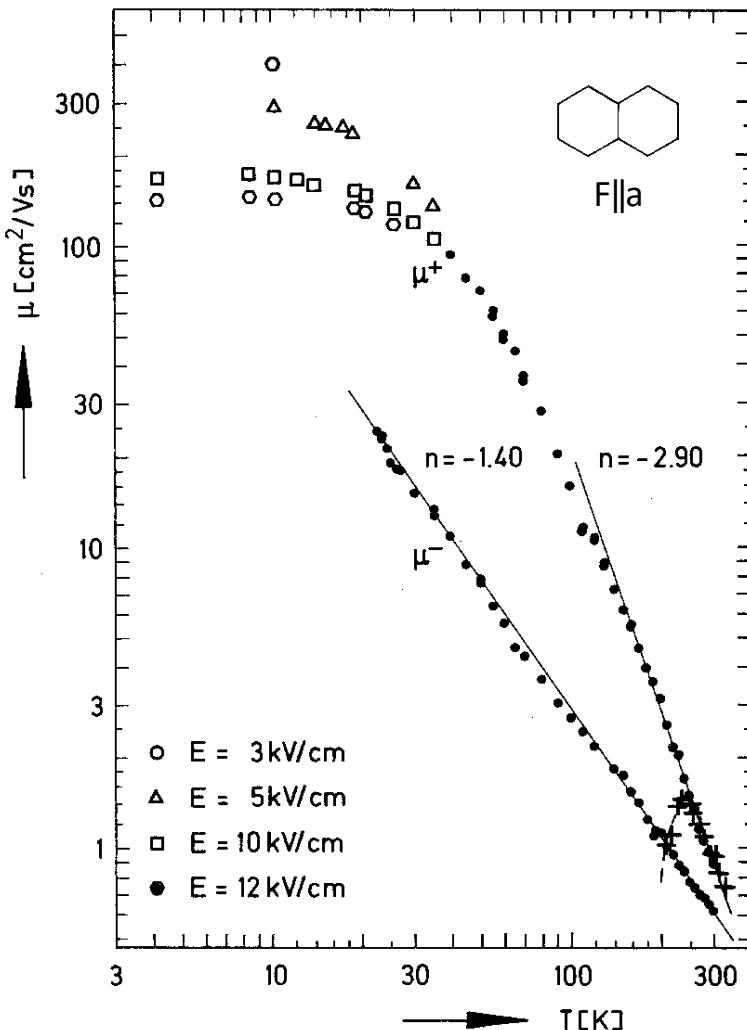


$n = 1.5$  band transport  
 $n = 2$  acoustic phonon scattering



# 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

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

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

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

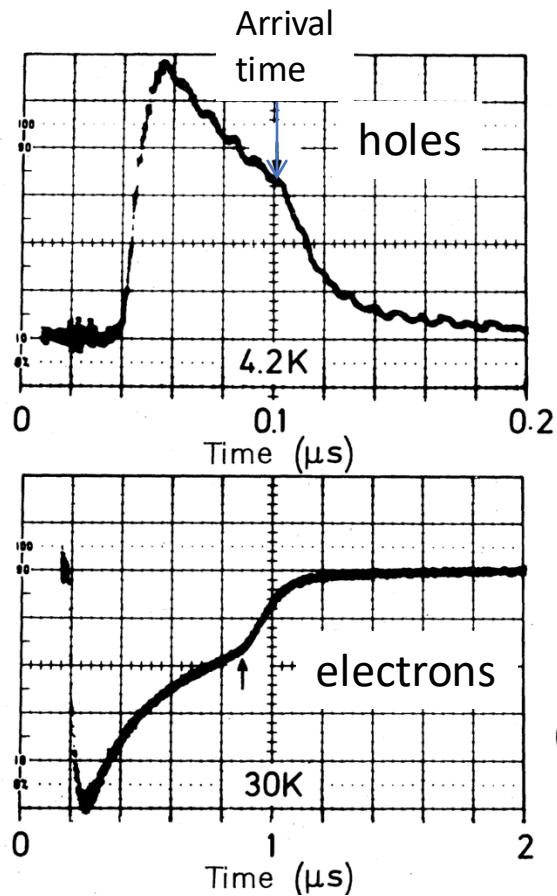
$$v = (3k_B T/m^*)^{1/2}$$

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

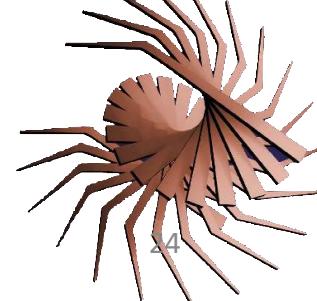
From the data on naphthalene:

$$m^* \sim 3-15m_0$$

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

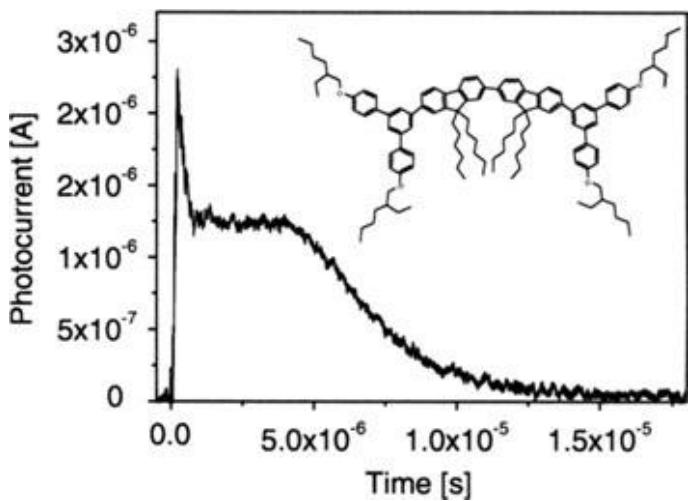
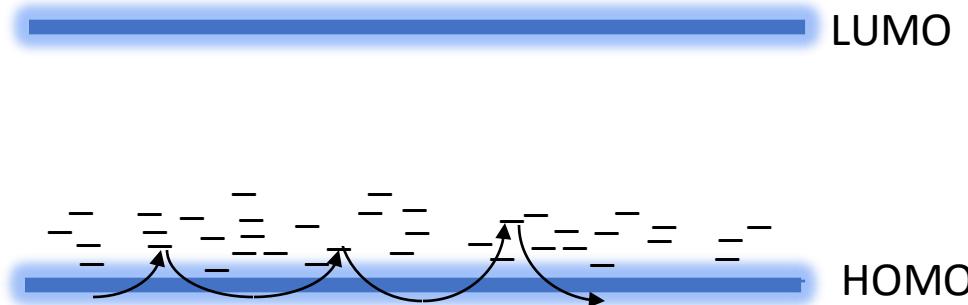


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# TOF Mobility with Traps

- 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 many different arrival times from trapping/de-trapping during transit.

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