Week 5

Optical Properties 3
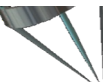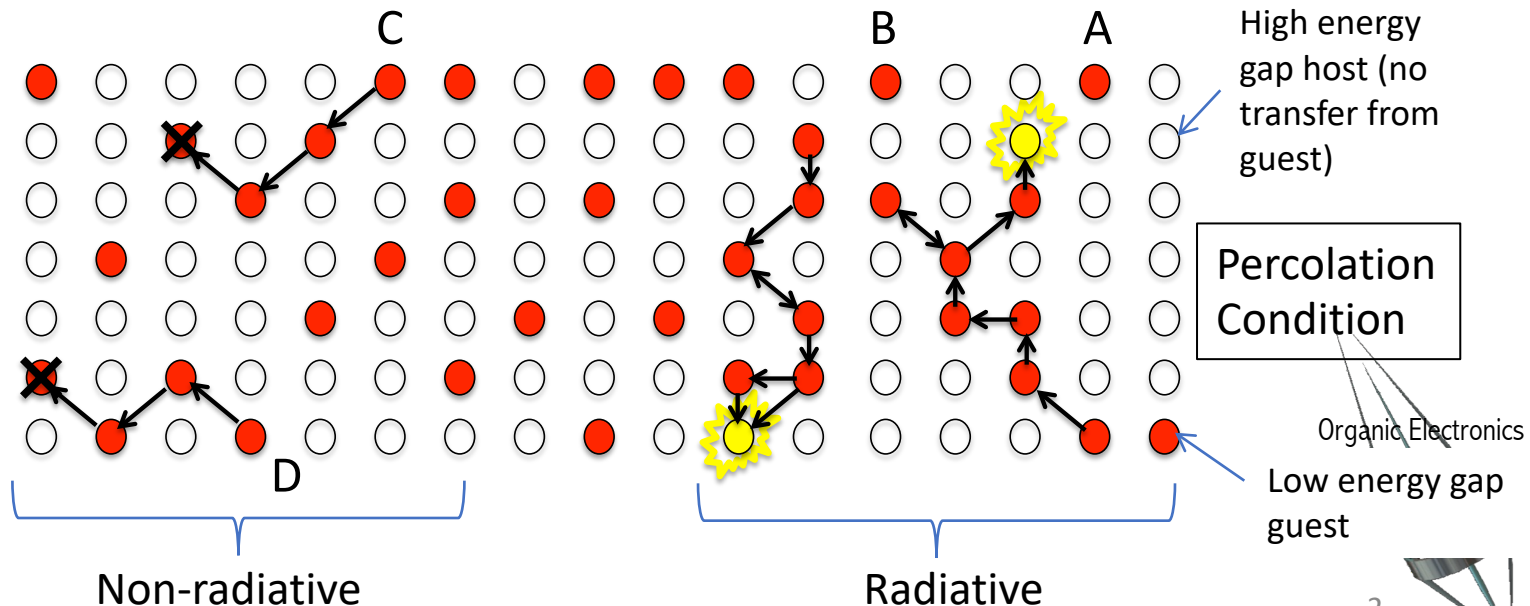
Exciton Diffusion

Chapter 3.9-3.10

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Exciton Diffusion

- **The macroscopic transfer of energy resulting from a series of exciton transfers between molecules**
  - Process is random
  - Duration of process determined by lifetime τ_D of the exciton
  - Mean distance travelled known as diffusion length, L_D
  - Diffusion constant: $$L_D^2 = D\tau_D$$

Donor-Acceptor Transfer

Non-radiative

Radiative

High energy gap host (no transfer from guest)

Percolation Condition

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Low energy gap guest

Capture of excitons by acceptors

Diffusion over large distances occurs by a series of random transfer steps from donor to acceptor

➔ Relationship between capture rate, k_c, and the diffusion constant is obtained using the diffusion equation

➔ Assume probability for capture is unity when the exciton arrives within a distance R_c from the acceptor. (R_c = exciton *capture radius*.)
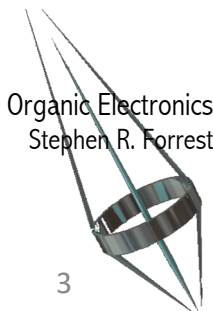
$$k_c \approx 4\pi D R_c$$

Chandrasekhar, S. 1943. *Rev. Modern Phys.,* 15**,** 1.

If diffusion occurs by individual FRET steps, then the relationship between L_D and the Förster radius is:

$$L_{D,FRET} = \frac{1}{\sqrt{6}} \frac{R_0^3}{a^2}$$

- Assumes molecules on a 3D cubic lattice, lattice constant a.
- Analogous relationship holds for Dexter transfer

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Diffusion Equation

$$D\nabla^2 n(\mathbf{r},\lambda,t) - \frac{n(\mathbf{r},\lambda,t)}{\tau_D} + G(\mathbf{r},\lambda,t) = \frac{\partial n(\mathbf{r},\lambda,t)}{\partial t}$$

Diffusion from point of origin   Generation due to incident light, etc.

Loss due to recombination

n = exciton density
τ_D = exciton natural lifetime
G = Generation rate

All variables functions of position, wavelength and time

Fick's Law: In steady state, the flux is given by: $J = -D\nabla n$

That is, flux is driven by a gradient in the concentration of n.

But energy conservation (no losses or sources) gives: $\nabla J = -\dfrac{\partial n}{\partial t}$

Which leads to Fick's 2nd Law and the diffusion equation: $D\nabla^2 n = \dfrac{\partial n}{\partial t}$

Measured Diffusion Lengths

Table 3.6: Measured diffusion lengths (L_D) for singlet (S) and triplet (T) excitons of crystalline (C.) and amorphous (A.) films measured by spectrally resolved photoluminescence quenching.

Material[a,b]	Exciton	Morphology[c]	Quenching/Blocking Layer[b]	L_D (nm)	D (10^{-4}cm^2/s)
NPD	S	A.	C_{60}/BCP	5.1 ($\pm$1.0)	0.7 ($\pm$0.2)
CBP	S	A.	C_{60} (or NTCDA)/ Free	16.8 ($\pm$0.8)	40 ($\pm$12)
SubPc	S	A.	C_{60}/Bare	8.0 ($\pm$0.3)	$\geq$6.4
PTCDA	S	C. - 55nm (flat)	C_{60} (or NPD)/ NTCDA	10.4 ($\pm$1.0)	3.4 ($\pm$0.9)
DIP	S	C. - >150nm (up)	C_{60}/ Free	16.5 ($\pm$0.4)	15 ($\pm$4)
DIP	S	C. - 30nm (flat)	C_{60}/ Free	21.8 ($\pm$0.6)	26 ($\pm$7)
C_{60}	S	A.	NPD/BPhen	34 ($\pm$3)	20 ($\pm$4)
C_{70}	S	A.	NPD/BPhen	10 ($\pm$2)	
PtOEP	T - Mon.	C. - >150nm (up)	C_{60}/BCP	18.0 ($\pm$0.6)	0.041 ($\pm$0.003)
PtOEP	T – Dim.	C. - >150nm (up)	C_{60}/BCP	13.1 ($\pm$0.5)	0.00061 ($\pm$0.0001)

[a] All data are from (Lunt et al., 2009) except for C_{60} and C_{70} from (Bergemann et al., 2015). The larger error bars for L_D for C_{60} and C_{70} is due to their comparatively weak luminescence.
[b] Materials used: NPD= N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'biphenyl-4,4''diamine; CBP=4'-bis(9-carbazolyl)-2,2'-biphenyl; PTCDA=3,4,9,10-perylenetetracarboxylic dianhydride; NTCDA=3,4,7,8 naphthalenetetracarboxylic dianhydride; SubPc= boron subphthalyocyanine chloride; DIP= diindenoperylene; PtOEP=Pt octaethylporphorin; BCP=bathocuproine; BPhen=bathophenanthroline; Free=no layer.
[c] Up/flat refers to whether the molecular plane is perpendicular/parallel to the substrate.
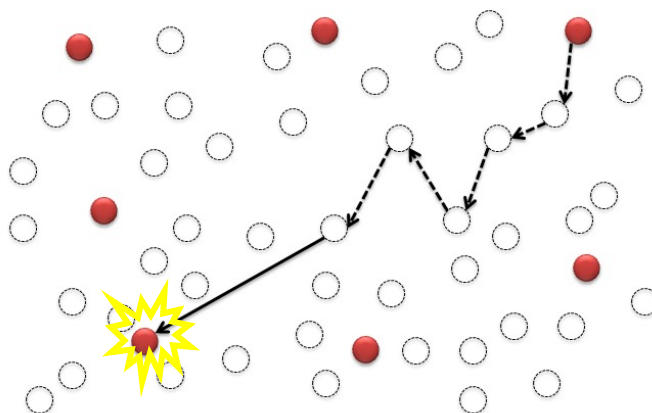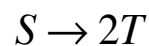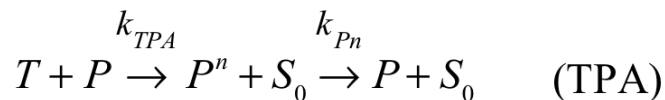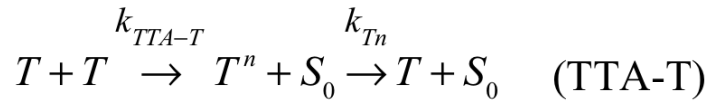
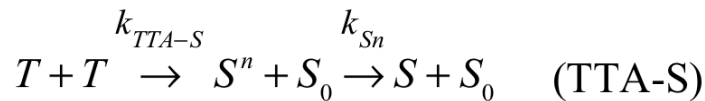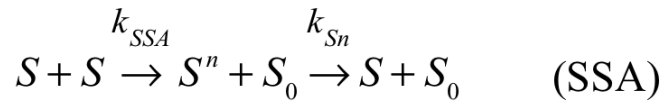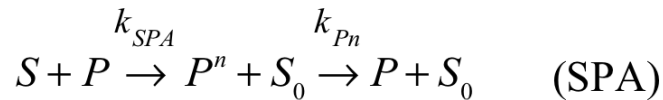Organic Electronics
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Annihilation!

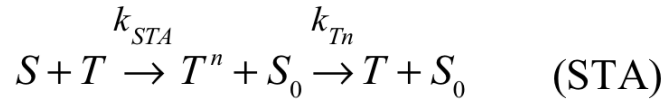When excitons collide at a single molecular site, they can combine to form a single exciton and a ground state molecule: Exciton-exciton annihilation

Spin multiplicity can determine annihilation efficiency (Dexter vs FRET). Annihilation leads to losses, and phenomena like delayed fluorescence.
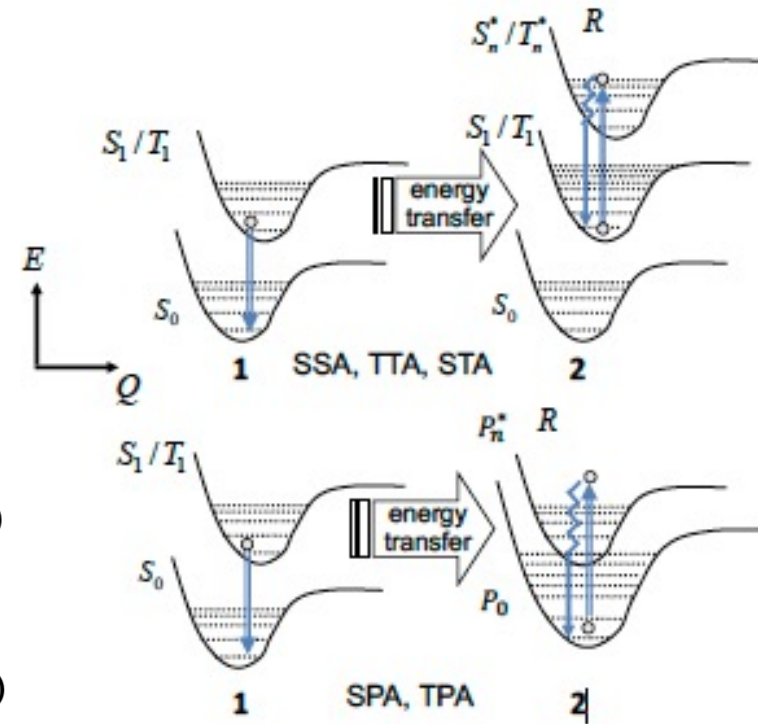
When excitons collide with charges, the charge can be excited, losing the exciton: Exciton-polaron annihilation

Bad things happen to good excitons

$$S + T \xrightarrow{k_{STA}} T^n + S_0 \xrightarrow{k_{Tn}} T + S_0 \qquad \text{(STA)}$$

$$S + P \xrightarrow{k_{SPA}} P^n + S_0 \xrightarrow{k_{Pn}} P + S_0 \qquad \text{(SPA)}$$

$$S + S \xrightarrow{k_{SSA}} S^n + S_0 \xrightarrow{k_{Sn}} S + S_0 \qquad \text{(SSA)}$$

Delayed fluorescence
Triplet fusion

$$T + T \xrightarrow{k_{TTA-S}} S^n + S_0 \xrightarrow{k_{Sn}} S + S_0 \qquad \text{(TTA-S)}$$

$$T + T \xrightarrow{k_{TTA-T}} T^n + S_0 \xrightarrow{k_{Tn}} T + S_0 \qquad \text{(TTA-T)}$$

$$T + P \xrightarrow{k_{TPA}} P^n + S_0 \xrightarrow{k_{Pn}} P + S_0 \qquad \text{(TPA)}$$

Singlet fission when
$$E_S \geq 2E_T$$

$$S \rightarrow 2T$$

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What we learned

- The concepts leading to our understanding of individual molecular spectra
  - ➢ Born-Oppenheimer, Franck-Condon, Pauli Exclusion
  - ➢ Molecular orbitals
- Understanding molecular spectra
  - ➢ Excitons
  - ➢ Fermi's Golden Rule
  - ➢ Selection rules
  - ➢ Spin: Fluorescence, phosphorescence, delayed fluorescence
- Building up to a solid
  - ➢ Dimers, excimers, exciplexes
  - ➢ Polarization effects in solution and the solid state
- Exciton diffusion and annihilation

The next step: Charge transport in solids

Electronic Properties of Organic Semiconductors

Electronic Properties 1

Energy Bands
Electron Transport and Mobility

Chapter 4.1, 4.2, 4.3.1, 4.3.2.1, 4.3.2.2
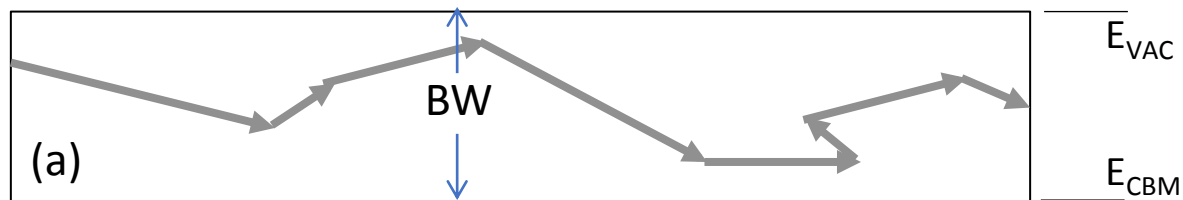
Objectives: Electronic Properties

"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
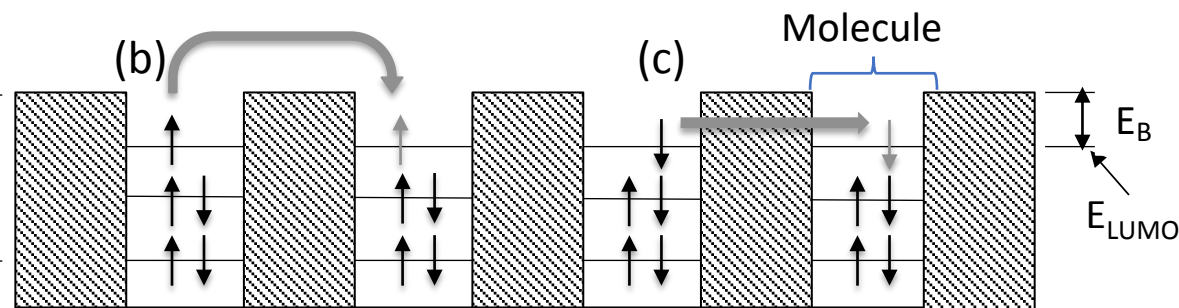
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Modes of Conduction
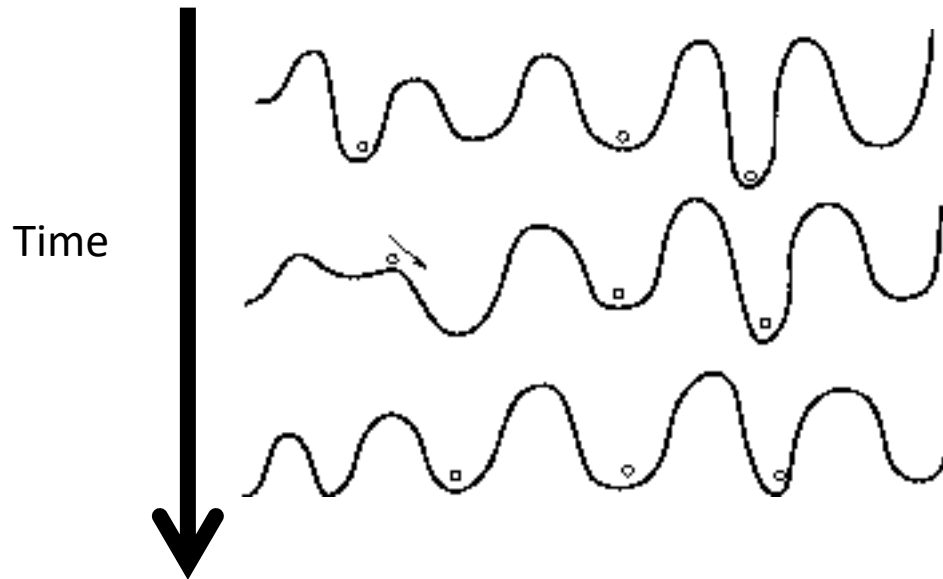
Band transport

(a)

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

Hopping and tunneling transport

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

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Hopping

Time

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

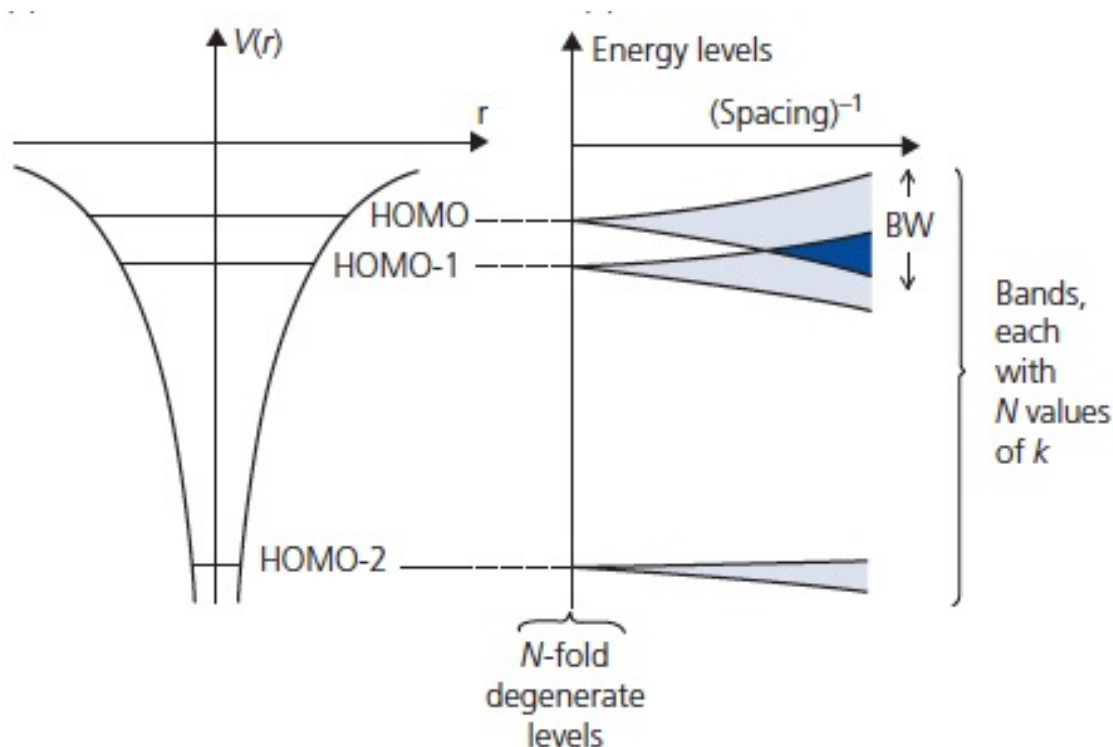$$\mu > \frac{qa^2}{\hbar}\left(\frac{\hbar\omega_0}{k_B T}\right)$$

Optical phonon energy
(typ. ~ 100 meV)

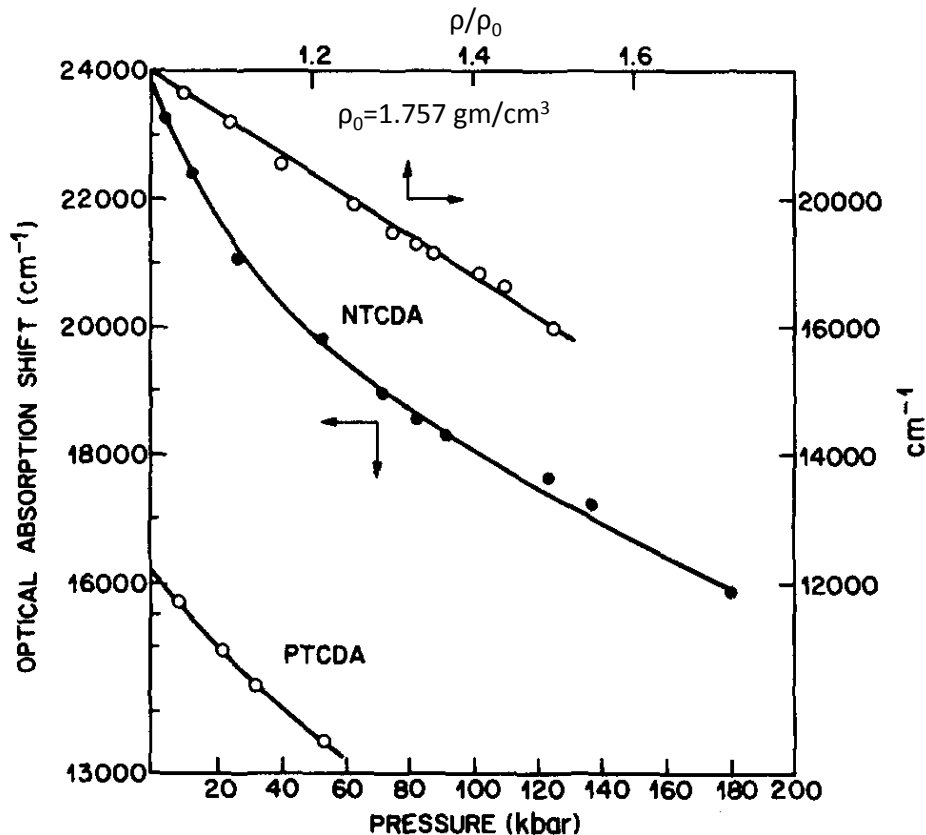μ ~ 20 cm^2/V-s at room temperature...very high (and probably unrealistic)!

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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Can we count on such a simple theory?

- Weak binding makes this approach plausible

- Nearest neighbor interactions (e.g. due to vdW forces) makes the solutions tractable.
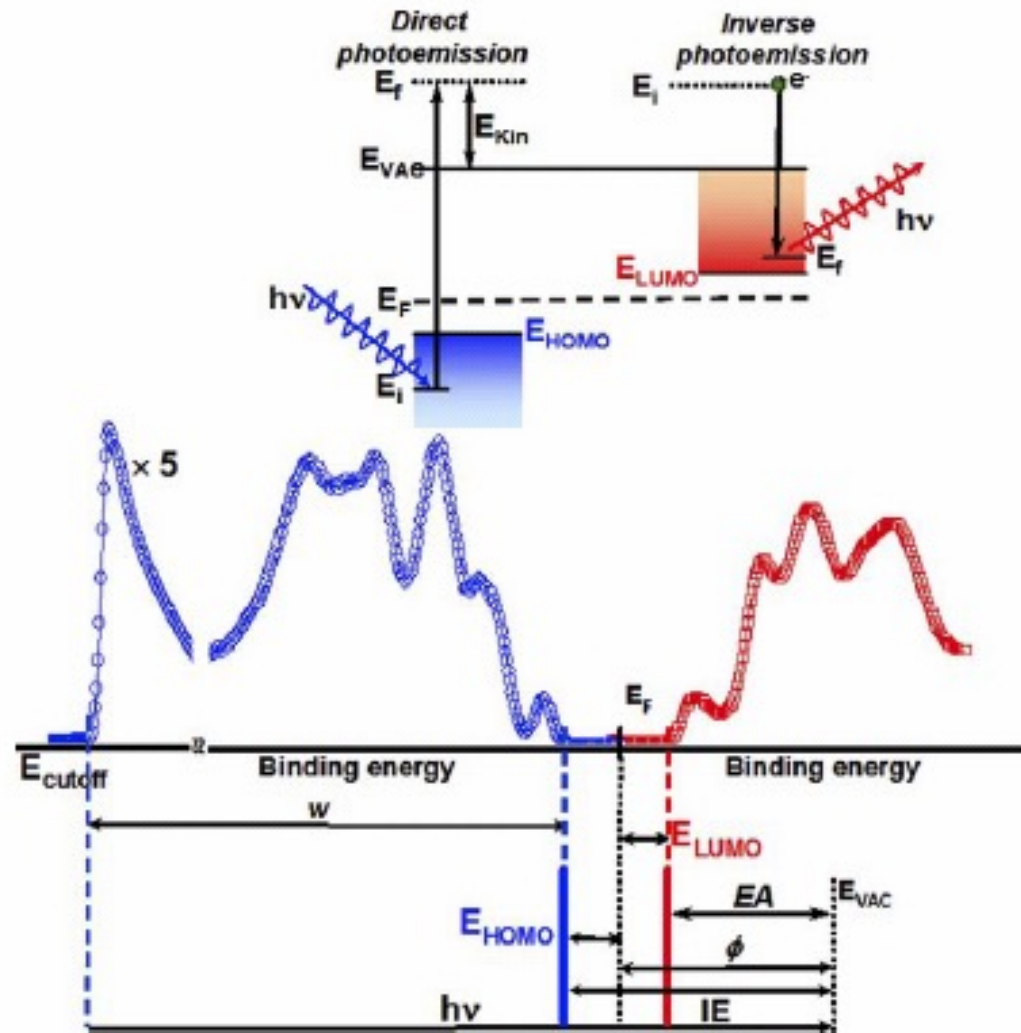
- What does it predict?

Molecules under hydrostatic pressure have a decreasing energy gap.

Jayaraman, et al. 1985. *J. Chem. Phys.,* 82**,** 1682.

Measuring Band Structure
(and other energies of interest)

- Ultraviolet photoelectron spectroscopy (UPS)

- Photoelectric effect used to measure energy of a single electron from the HOMO to the vacuum level.
- Gives k of photoemitted electron
- Varying angle (ARUPS) of sample gives dispersion E($\mathbf{k}$) for $k_\perp$

Interpretation of PES Spectra

$$\varphi_m = h\upsilon - W$$

He I = 21.2 eV

Seki, Trans. on Electron Devices, 44, (1997), 1295

$$\epsilon_{HOMO} = \epsilon^F_{HOMO} + \Phi_m + \Delta$$

SOMO=singly occupied MO

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Calculated and Measured Band Structures

(a)

(b)

Holes

Elec.

E(X) (meV)

E(X) (meV)

— X=**k**•**a**
···· X=**k**•**b**
--- X=**k**•**c**

0   π/4   π/2   3π/4   π

X

(a)

3.26Å

3.45Å
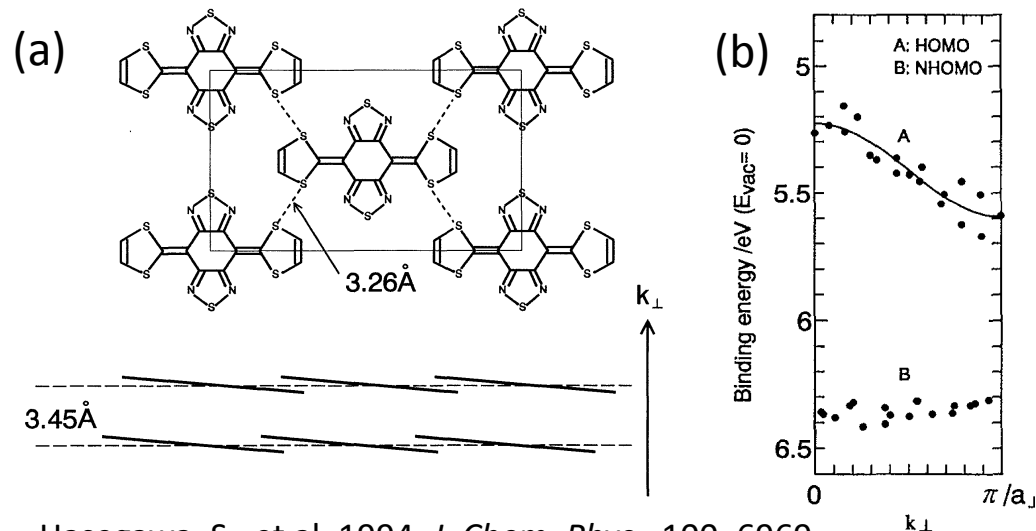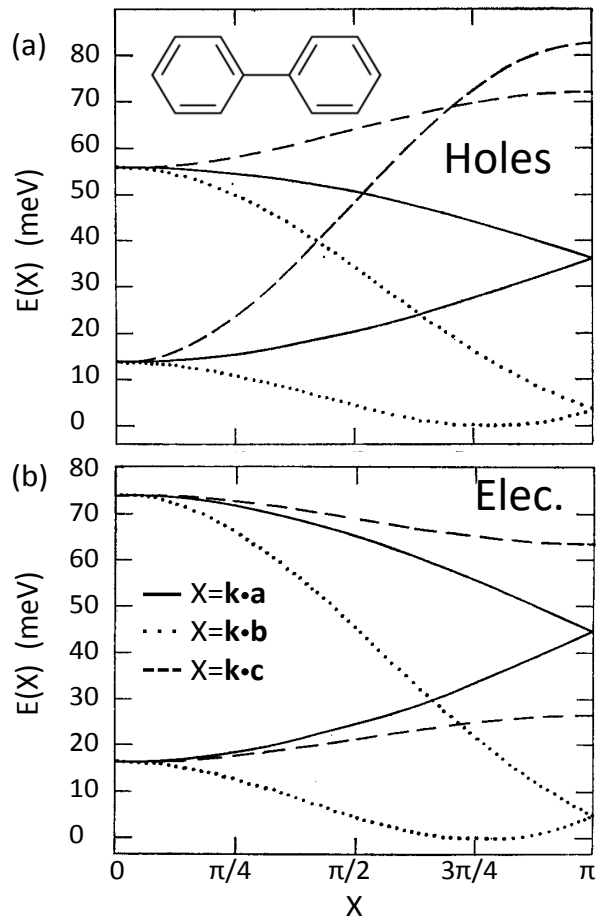
$k_\perp$

(b)

A: HOMO
B: NHOMO

A

B

Binding energy /eV ($E_{vac}= 0$)

0    $\pi/a_\perp$

$k_\perp$

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

Measured structure for BTQBT:

- Technique: ARUPS
- Minimum contact distance: 3.26 Å
- HOMO BW = 400 meV
- m* = 3.1 m_0
- Recall: $\mu_h = \dfrac{q\tau}{m_h^*}$
- But thermally broadened bands have $\tau > \hbar / k_B T$
- μ ~ 6.5 cm^2/V-s (c.f. Hall measurement of 4 cm^2/V-s)

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. 1963. *J. Chem. Phys.,* 39**,** 1683.

(NHOMO = next highest orbital)

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Charge Mobility Describes Transport in Solids

- Charge mobility: μ (not the dipole moment!)

- Definition: Constant of proportionality between velocity and electric field:

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

  ➤ 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: $\quad \mu = \dfrac{q\tau}{m^*}$

  (τ = mean free scattering time of the charge in the crystal:
  For thermally broadened bands: $\tau > \hbar / k_B T$)

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

  ➤ or $\quad \vec{\vec{\sigma}} = q\left(n\vec{\vec{\mu}}_e + p\vec{\vec{\mu}}_p\right)$
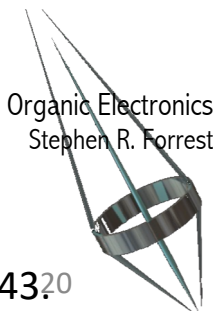
Mobility and Charge Diffusion

- <u>Near equilibrium</u>, 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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Band vs. Hopping Transport

- The charge diffusion length is: $L_q = \sqrt{D\tau} = \left[\dfrac{\mu\tau k_B T}{q} \right]^{\frac{1}{2}}$

- Band transport occurs when $L_q \gg a$.

- From uncertainty: $BW \cdot \tau > \hbar$

- Condition for band conduction $\Rightarrow \mu > \dfrac{qa^2}{\hbar}\left(\dfrac{BW}{k_B T} \right)$

  - (Ex. Room temperature, let BW=25 meV, a=5Å. Then μ>5 cm^2/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 ~1/r = **large polaron**

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Holstein, T. 1959. Studies of Polaron Motion. Part II. The "Small" Polaron. *Ann. Phys.,* 8**, 343.** 20

Hopping Formalism

- Total Hamiltonian:

$$H_T = H_e^0 + H_{ph}^0 + H_e^{tr} + H_{e-ph}^{loc} + H_{e-ph}^{non} + H_e^{stat}$$

Unperturbed molecule — Electron transfer: *BW ~ J* — Dynamic disorder — Static disorder

- Important terms:

$$H_e^{tr} = \sum_{m \neq n}^{N} J_{nm} a_n^+ a_m \qquad a^+(a) = \text{electron creation (annihilation) operator}$$

$$J_{nm} = \left\langle \psi_n (\mathbf{r} - \mathbf{R}_n) \middle| H_e^{tr} \middle| \psi_m (\mathbf{r} - \mathbf{R}_m) \right\rangle \quad \text{Overlap between molecules } m, n$$
- As in tight binding, leads to BW

$$\mathcal{N}_i = a_i^+ a_i \quad \text{Number operator}$$

e-phonon coupling constant

$$H_{e-ph}^{loc} = \frac{1}{\sqrt{N}} \sum_{\mathbf{q},j} \sum_{m}^{N} \hbar \omega_{\mathbf{q},j} \left(g_m(\mathbf{q},j) b_{\mathbf{q},j} + g_m^*(\mathbf{q},j) b_{-\mathbf{q},j}^+ \right) a_m^+ a_m$$

$\mathbf{q}$ = phonon wavevector
j = phonon branch

On-diagonal dynamic disorder: couples excess electron to molecular vibronic levels
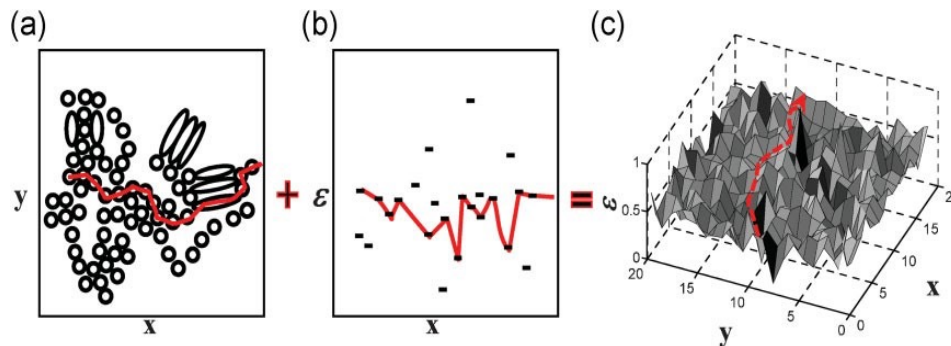
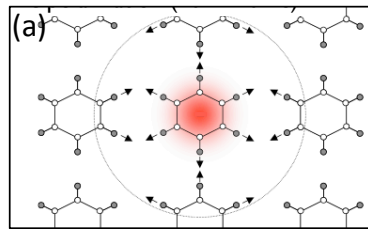And so on….

The case for static disorder

- Most organic semiconductors are permanently disordered

  - Polymers generally not formed into crystals
  - Small molecules used in devices are often amorphous or nanocrystalline
  - Even "perfect" crystals have impurities, stacking faults, dislocations

- A complete picture thus must include static disorder term:

$$H_e^{stat} = \sum_n \delta\varepsilon_n a_n^+ a_n + \sum_{\substack{m,n \\ m \neq n}} \delta J_{nm} a_n^+ a_m$$

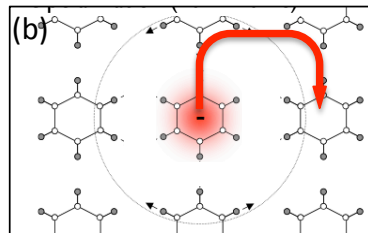- Static disorder leads to hopping in both energy and space.

Visualizing Lattice Distortions

(a) Electronic polarization: ~10^{-16}s — dipole, dipole, Lattice polarization: ~10^{-13}-10^{-12}s

Unperturbed molecule
$$H_e^0 + H_{ph}^0$$
$$\varepsilon_n^0; \ \hbar\omega_{\mathbf{q},j}$$

(b) Electronic polarization: ~10^{-16}s — dipole, dipole, Lattice polarization: ~10^{-13}-10^{-12}s

Electron transfer
$$H_e^{tr}$$
$$J_{nm}$$

(c) Electronic polarization: ~10^{-16}s — dipole, dipole, Lattice polarization: ~10^{-13}-10^{-12}s
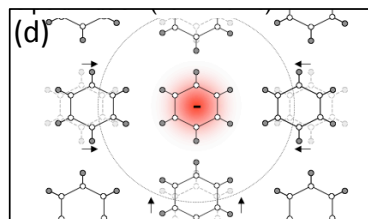
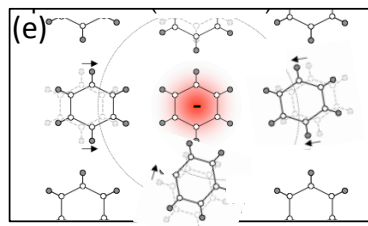*Intra*molecular phonons
$$H_{e-ph}^{loc}$$
$$g_m(\mathbf{q},j)$$

(d)

*Inter*molecular phonons
$$H_{e-ph}^{non}$$
$$g_{nm}(\mathbf{q},j)$$

(e)

Static disorder
$$H_e^{stat}$$
$$\delta\varepsilon_n; \ \delta J_{nm}$$

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

Strong coupling, $g^2 > 1$

Band: $\mu \sim T^{-n}$

Scattering: $\mu \sim T^{-3/2}$

Hopping: $\mu \sim \exp(-E/k_B T)$

Weak coupling, $g^2 < 1$

Tunneling: $\mu \sim T^{-n}$

T_{BH}

T_{HS}

Mobility

Temperature

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Going from formal theory to a practical quantity (mobility: μ)

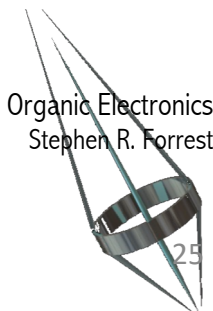- Diffusion constant is calculated from hops from site p: $p \to p \pm 1$

- Then in 3D: $D = \dfrac{1}{3} k_{ET} (p \to p \pm 1) \dfrac{a^2}{2}$ (6 sites to choose from on a cube)

- It follows from Einstein: $\mu = \dfrac{q}{3k_B T} k_{ET} (p \to p \pm 1) \dfrac{a^2}{2}$

- From small polaron theory we obtain k_{ET} (remember Fermi's Golden Rule!)

- And with Holstein's help, in the high temperature limit ($k_B T > \hbar\omega_0$):

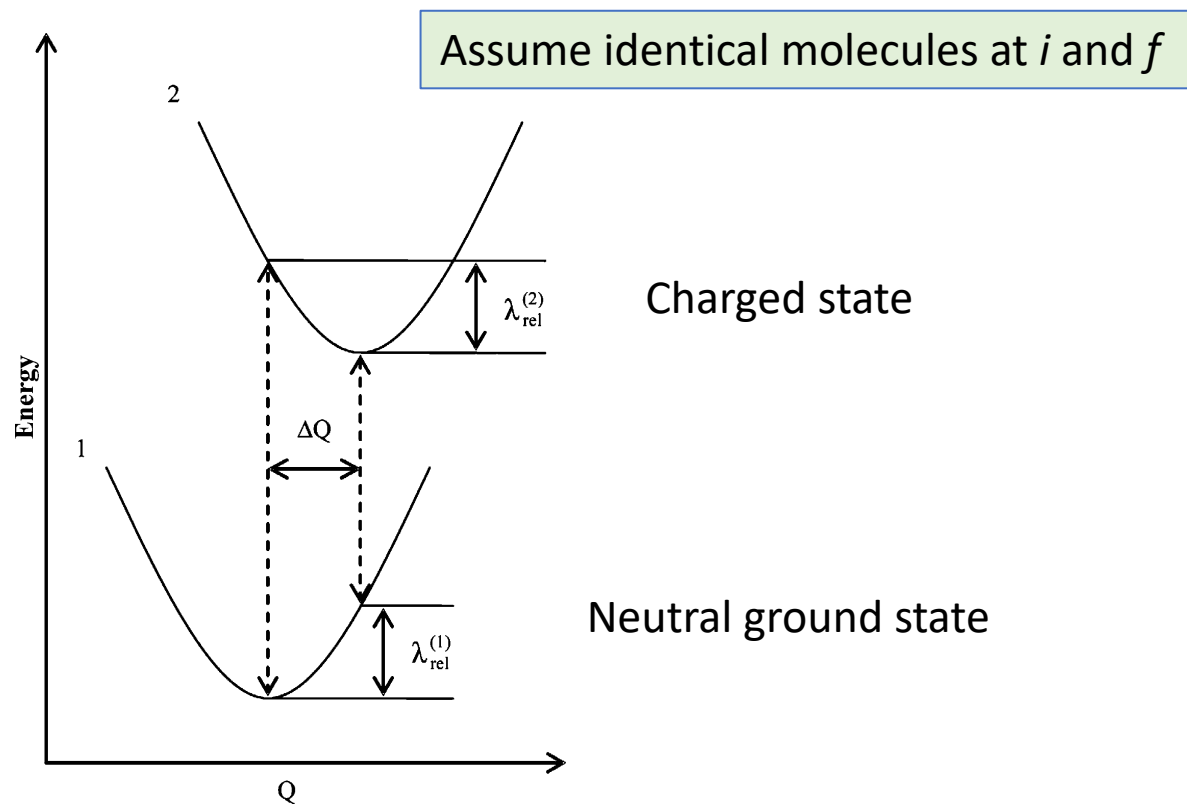$$\mu_{hop} = \frac{qJ^2 a^2}{6k_B T \hbar} \left[\frac{\pi}{2E_{pol} k_B T} \right]^{1/2} \exp\left(-\frac{E_{pol}}{2k_B T} \right)$$

✓ The hopping mobility is thermally activated

✓ It scales with the square of the bandwidth, J^2.

✓ As E_{pol} increases, μ_{hop} decreases

✓ As $T \to$ large; then $\mu_{hop} \sim T^{-3/2}$: scattering!

- As $T \to$ small; then μ_{hop} replaced by μ_{tun}

Molecular energy changes when a charge is transferred

Assume identical molecules at i and f

2

$\lambda_{rel}^{(2)}$

Charged state

Energy

ΔQ

1

Neutral ground state

$\lambda_{rel}^{(1)}$

Q

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

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

The theory of μ

- **Goal:** To find μ, but now with disorder expressed through $\rho(\varepsilon)$.

- 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)

$$k_{ij} = \upsilon_0 \exp\left(-2\gamma_{ij}R_{ij}\right) \begin{cases} \exp\left(-\dfrac{\varepsilon_j - \varepsilon_i}{k_B T}\right) & \varepsilon_j > \varepsilon_i \\ 1 & \varepsilon_j < \varepsilon_i \end{cases}$$

υ_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
  - Valid when ε_j - ε_i < Θ_m (Debye energy) of acoustic and optical phonons (~0.15 eV) $\Rightarrow$ low temperatures
  - In F-field, add in $-q\mathbf{r}\cdot\mathbf{F}$ to exponential argument where F points from $j \Rightarrow i$

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Miller, A. & Abrahams, E. 1960. *Phys. Rev.,* 120**,** 745.

Model 2: Marcus Transfer

- Developed for understanding transfer of electron from donor to acceptor in solution

  - Generalized form of mobility in the small polaron (non disordered) model. Starting point will again be from Holstein:
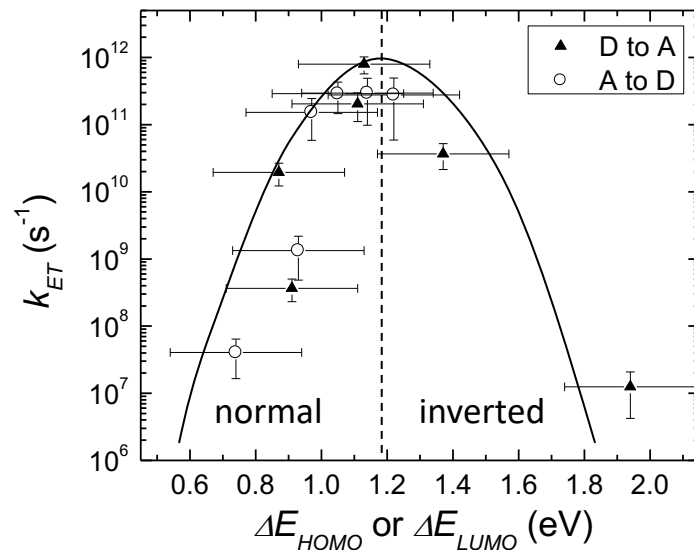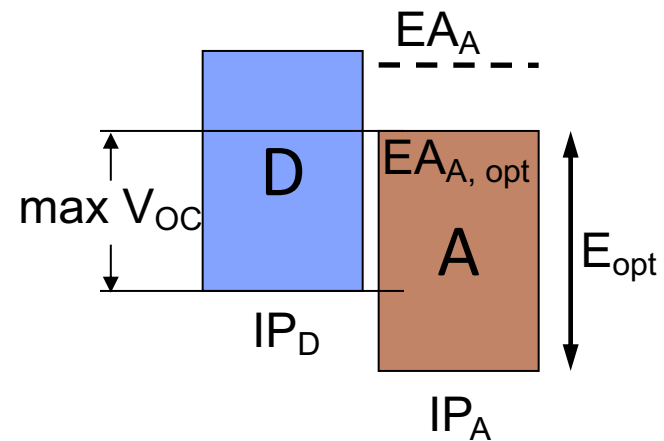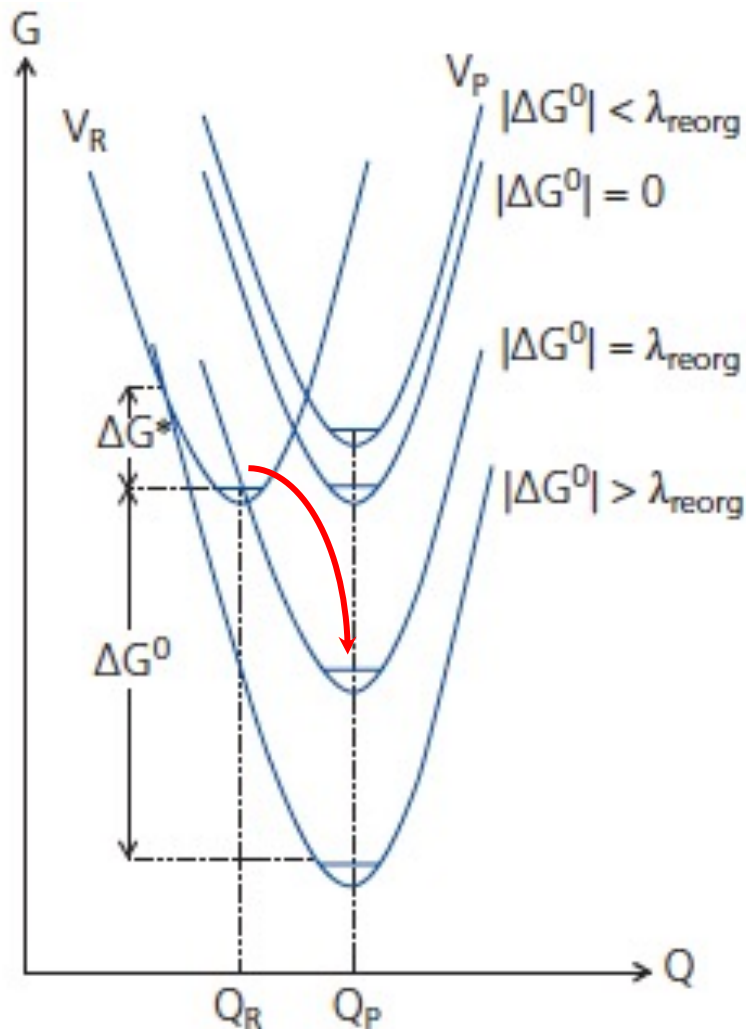
$$k_{ET} = \frac{6k_B T \mu}{qa^2} \; \text{x} \; \frac{J^2}{\hbar} \left[\frac{\pi}{2E_{pol}k_B T} \right]^{1/2} \exp\left(-\frac{E_{pol}}{2k_B T} \right)$$

- 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: $2E_{act} = E_{pol} = \lambda_{reorg}/2$
- From Miller-Abrahams:

$$J = J_0 \exp\left(-\gamma_{ij} R_{ij} \right)$$

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Marcus, R. A. 1993. *Rev. Modern Phys.,* 65, 599.

Transfer regimes under Marcus

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

V_P

$|\Delta G^0| < \lambda_{reorg}$

$|\Delta G^0| = 0$

$|\Delta G^0| = \lambda_{reorg}$

$|\Delta G^0| > \lambda_{reorg}$

ΔG^*

ΔG^0

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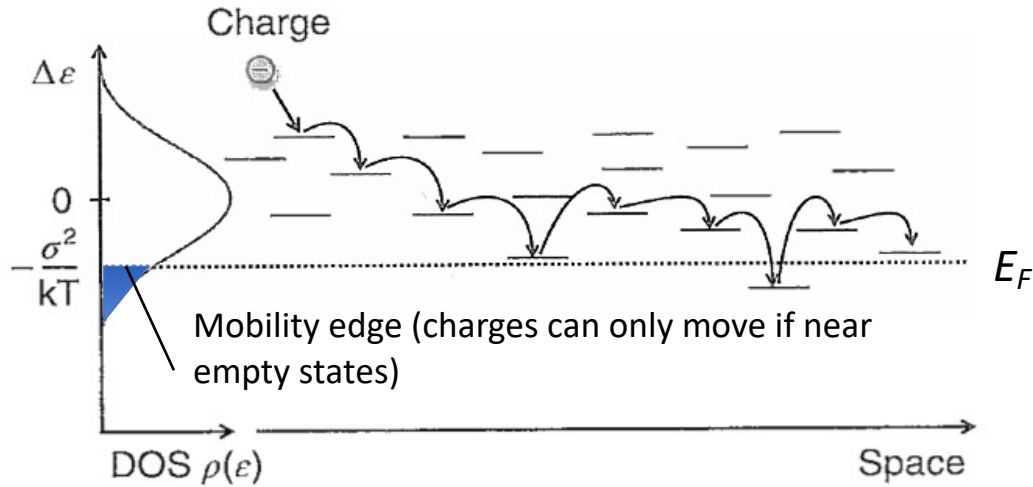

Electron transfer for $D \rightarrow A$ or $A \rightarrow D$

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Rand, B. P., et al. 2007. *Phys. Rev. B,* 75, 115327. 29

Density of States and the Mobility Edge

Relaxation of a hot carrier

Mobility edge (charges can only move if near empty states)

Charge relaxes to ε_∞

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

DOS: $\rho(\varepsilon) = \dfrac{N_V}{\sqrt{2\pi\sigma^2}} \exp\left[-\dfrac{(\varepsilon - \varepsilon_0)^2}{2\sigma^2} \right]$ (consequence of the central limit theorem)

$$\langle \varepsilon_\infty \rangle = \frac{\displaystyle\int_{-\infty}^{\infty} \varepsilon \rho(\varepsilon)\exp(-\varepsilon/k_B T)\,d\varepsilon}{\displaystyle\int_{-\infty}^{\infty} \rho(\varepsilon)\exp(-\varepsilon/k_B T)\,d\varepsilon} = -\frac{\sigma^2}{k_B T}$$

Mean equilibrium carrier energy—
Charges relax into the tail of the distribution

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Mobility (at last!)

- We now have everything we need:
  - Site occupation: $f_i(\varepsilon)$ from Fermi statistics
  - Transfer rate: k_{ij}
  - Site DOS: $\rho(\varepsilon)$

- As seen previously, mobility depends on k: $\quad \mu = \dfrac{q}{3k_B T} k_{ET}(p \rightarrow p \pm 1)\dfrac{a^2}{2}$

- But this is not possible to solve exactly.

- Based on Marcus theory (most applicable), including electric field effects we get (ouch!):

$$\mu \approx \mu_0 \exp\left\{ -\frac{E_{act}}{k_B T} - \frac{1}{8q^2}\left(\frac{\sigma}{k_B T}\right)^2 + \frac{1}{2\sqrt{2}q^2}\left[\left(\frac{\sigma}{k_B T}\right)^{3/2} - \left(\frac{\sigma}{k_B T}\right)^{1/2}\right]\sqrt{\frac{qaF}{\sigma}} \right\}$$

Poole-Frenkel type dependence

- At F=0, mobility activation ~ $1/T^2$ at low T, $1/T$ at high T
- Recall polaronic dependence follows ~$1/T$
- Monte-Carlo simulations show similar form

Fishchuk, I., et al. 2003. *Phys. Rev.,* 67, 224303.

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