7th edition

ORGANIC ELECTRONICS

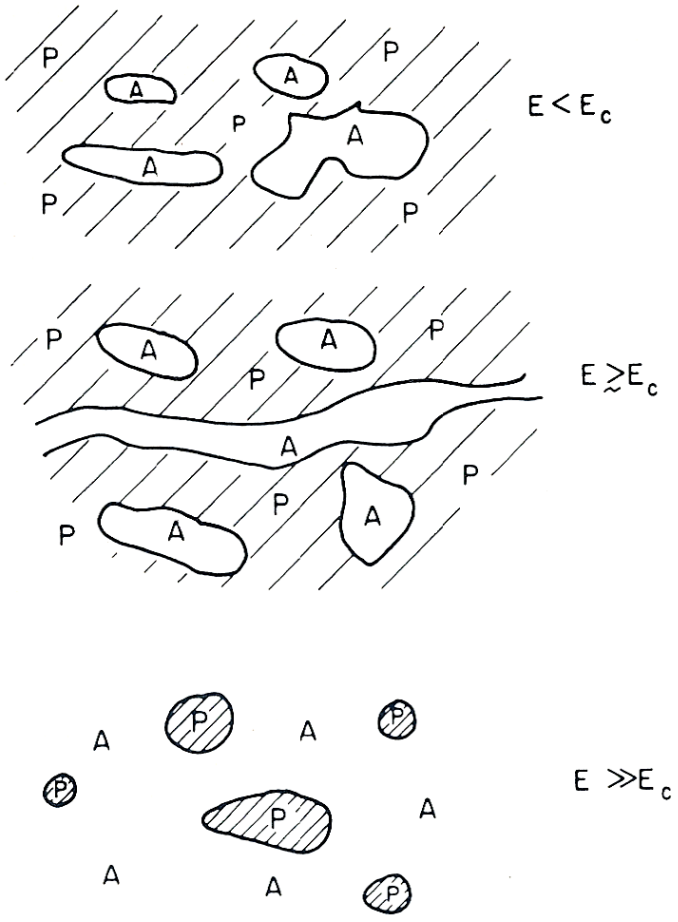
Principles, devices and applications

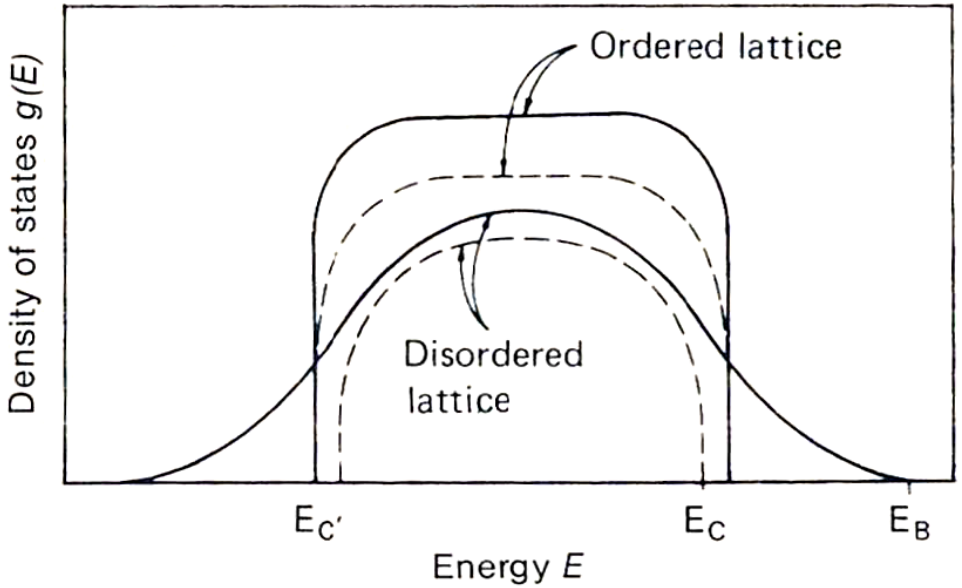
Charge Transport

D. Natali

Milano, 23-27 Novembre 2015

From Order to Disorder



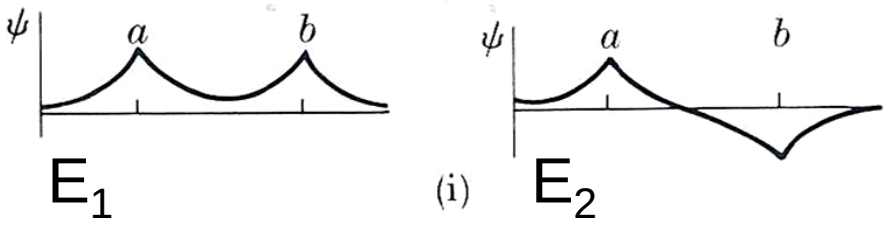


From delocalized to localized states

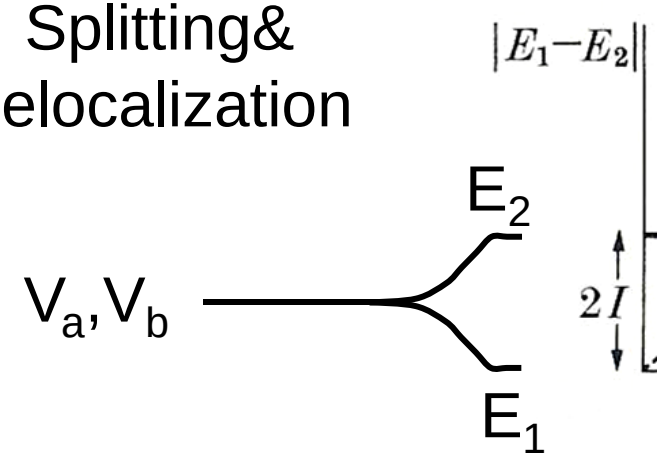
Madelung, Introduction to Solid-State Theory, Springer

The Two-Site approximation

a,V_a b,V_b

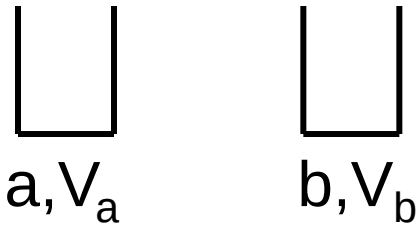


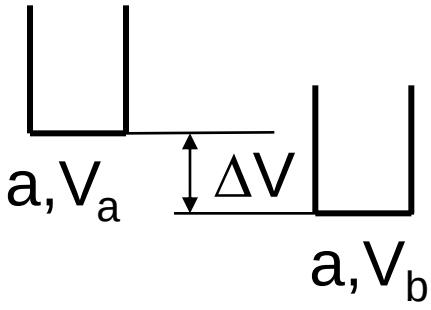
Splitting& delocalization

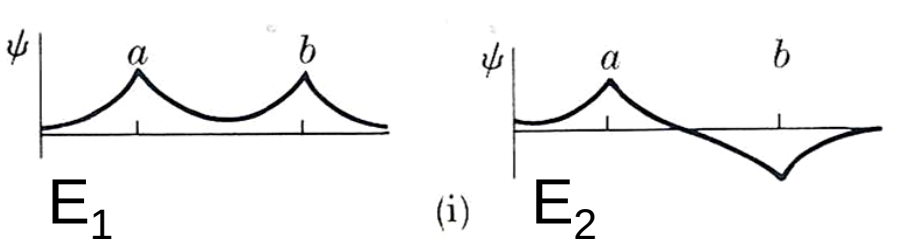


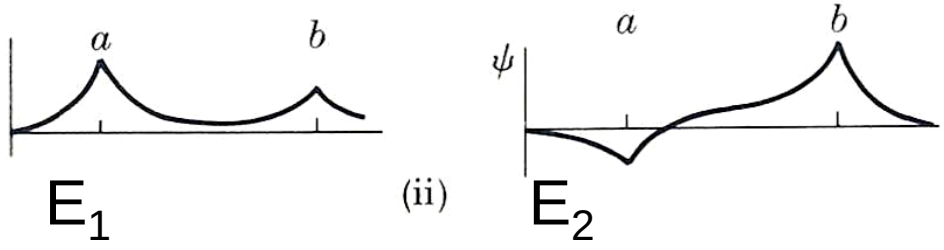
Mott Electronic processes in non-crystalline materials, Clarendon Press 1979

The Two-Site approximation

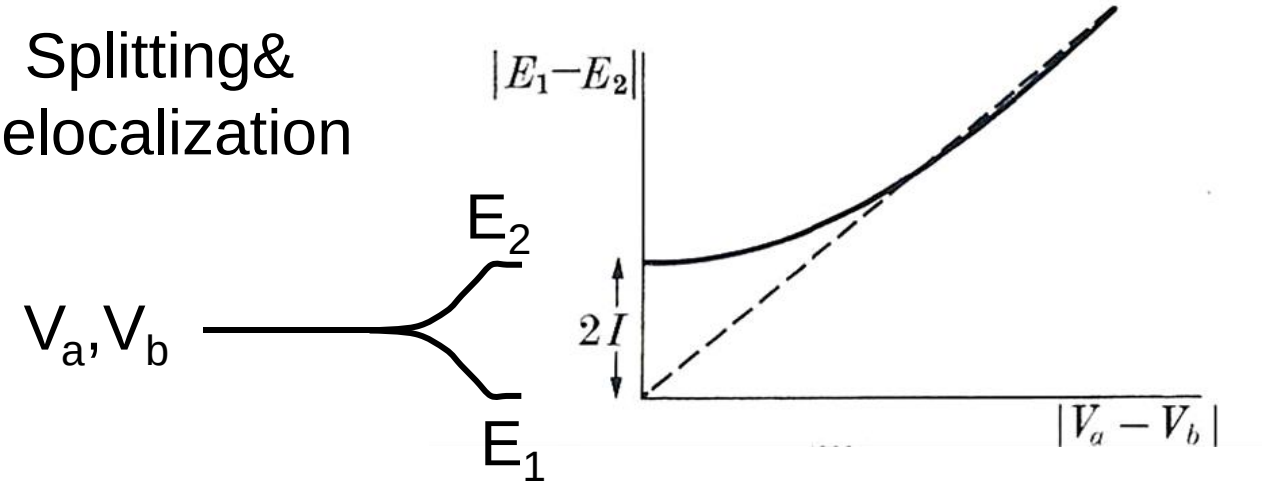




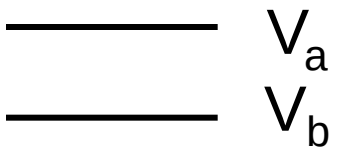




Splitting& delocalization

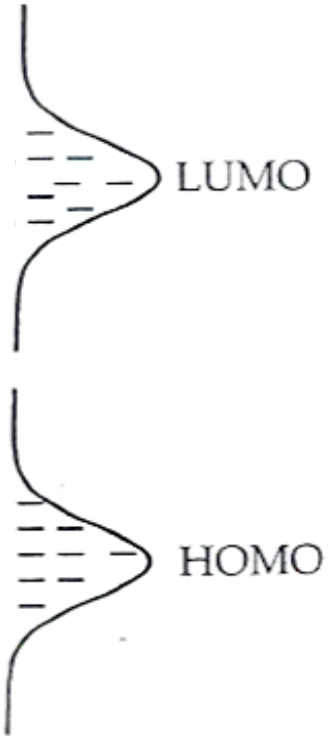


Localization



Mott Electronic processes in non-crystalline materials, Clarendon Press 1979

Density of States

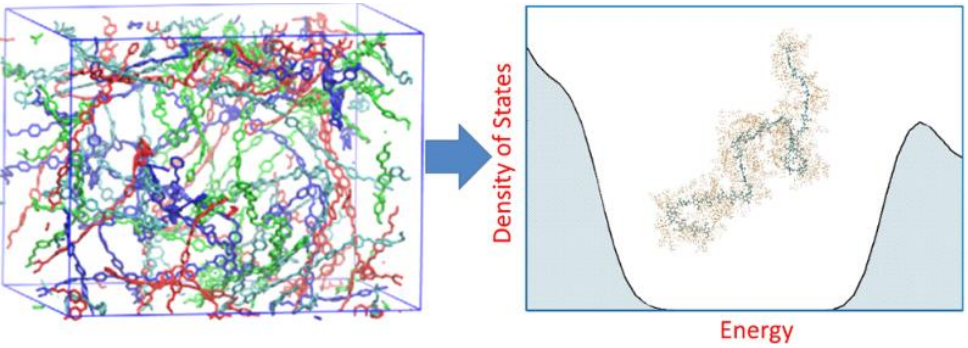


Due to ***energetic disorder***

DOS is **gaussian**

(or an exponential tail, or Gauss+exp or others….)

having σ of about 60-100 meV**.**



Atomistic models: the challenge is large size of the system and the nontrivial force fields

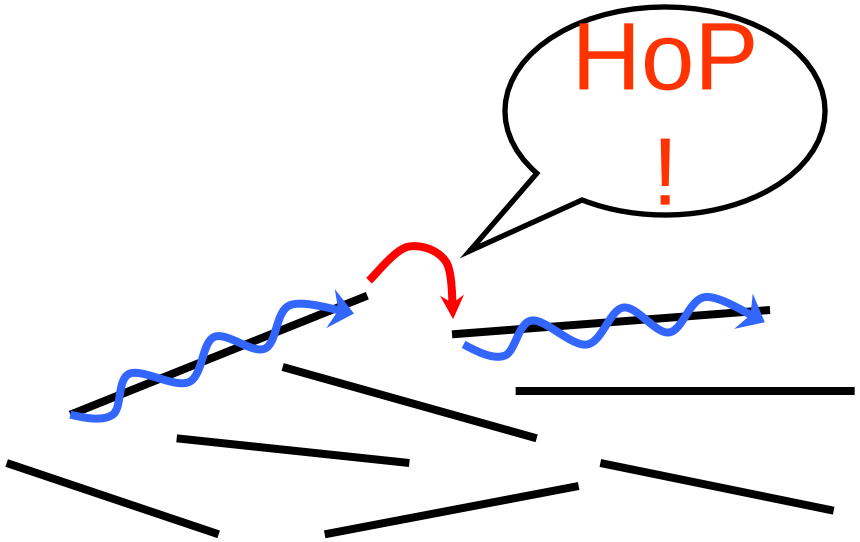
Troisi et al.
10.1021/ja404385y | J. Am. Chem. Soc. 2013, 135, 11247-11256

Bassler, Phys. Stat. Sol. B 175(1993) 15

Hopping

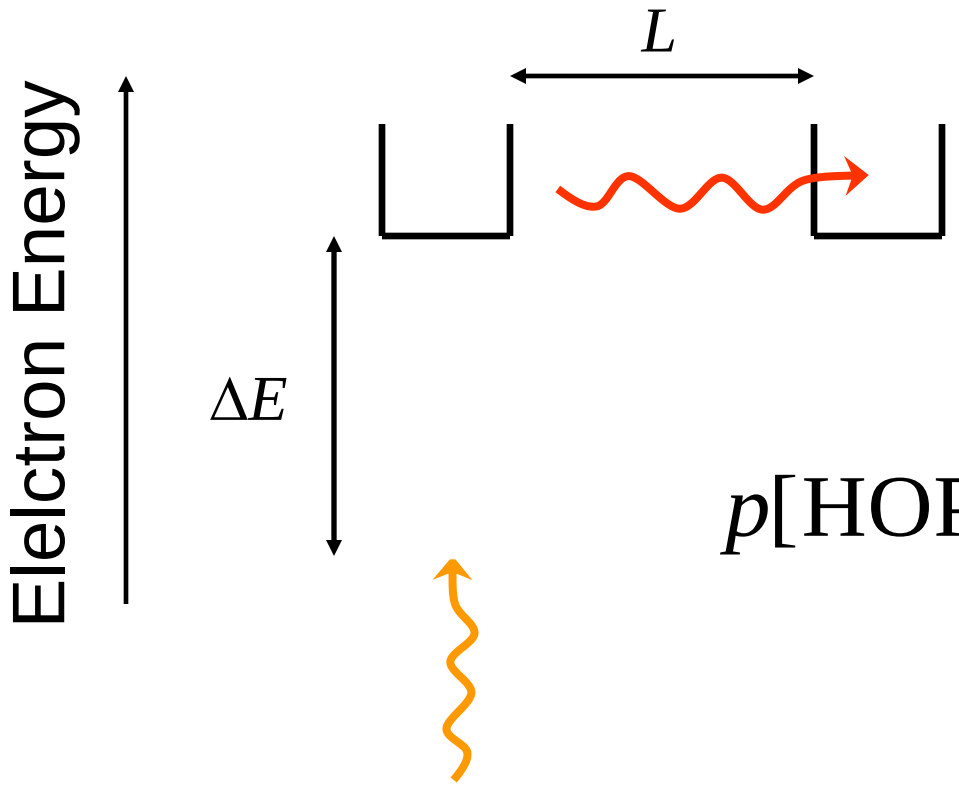
Charge carriers are **localized**

Transport occurs by ***hopping*** between localized states



Hopping

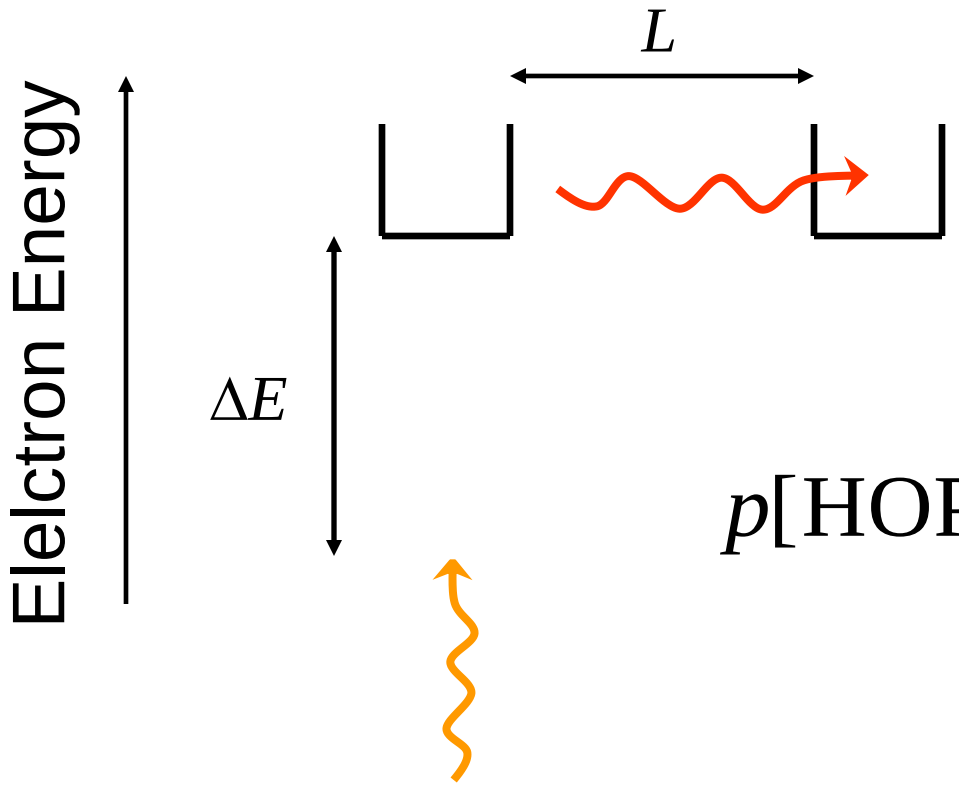
thermally activated tunnelling



$$p[\mathrm{HOP}] \propto \exp^{-\frac{\Delta E}{\mathrm{k}T}} \exp^{-\alpha L}$$

Hopping

thermally activated tunnelling



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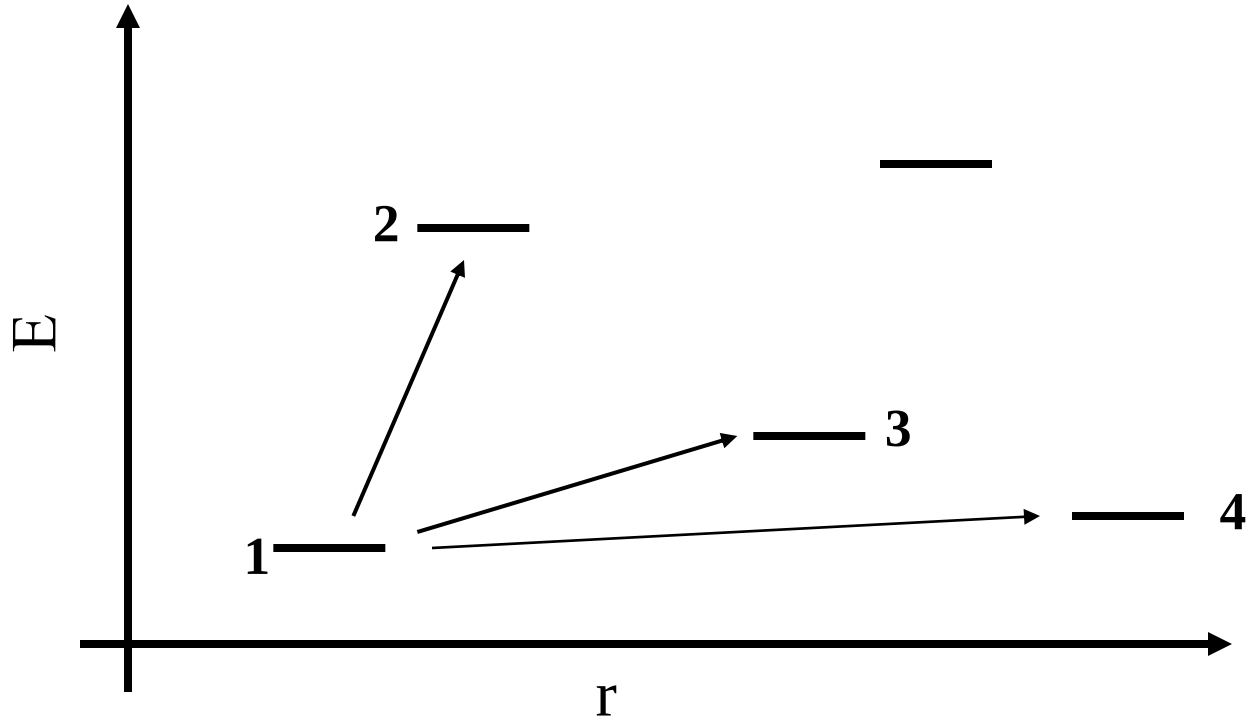
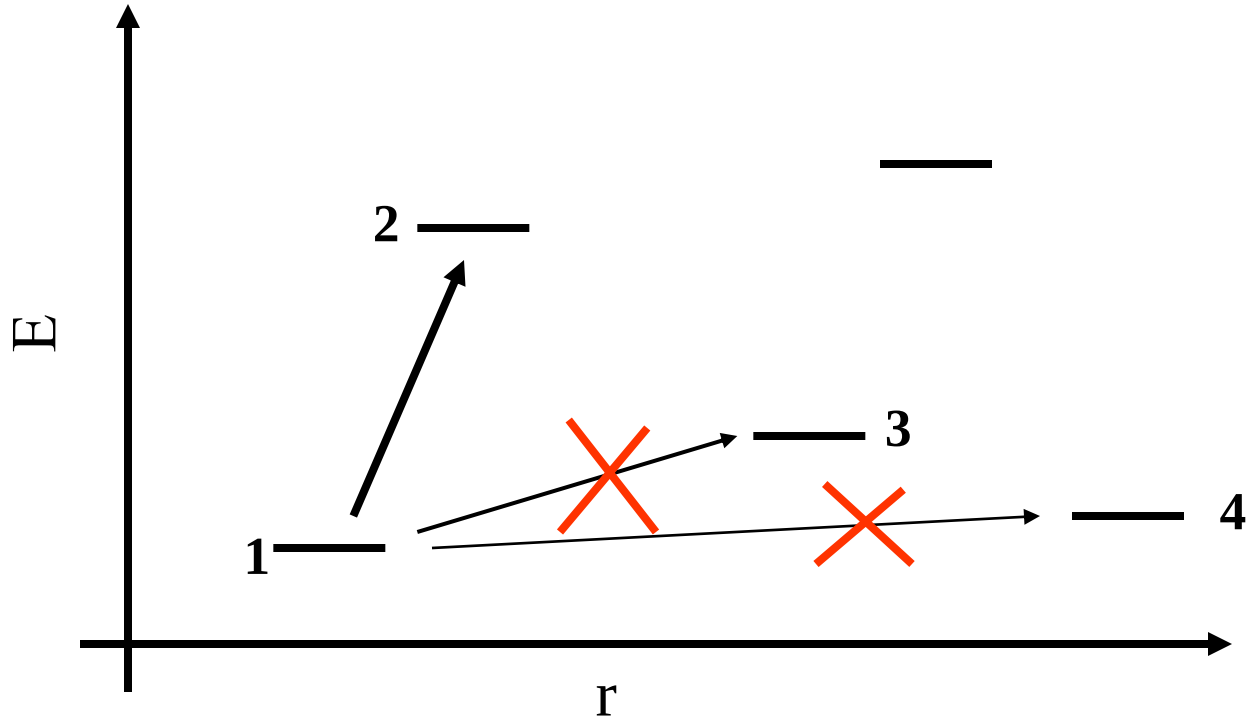
Hopping: effect of temperature (1)



$p[\mathrm{HOP}] \propto \exp^{-\frac{\Delta E}{kT}} \exp^{-\alpha L}$

Hopping: effect of temperature (2)

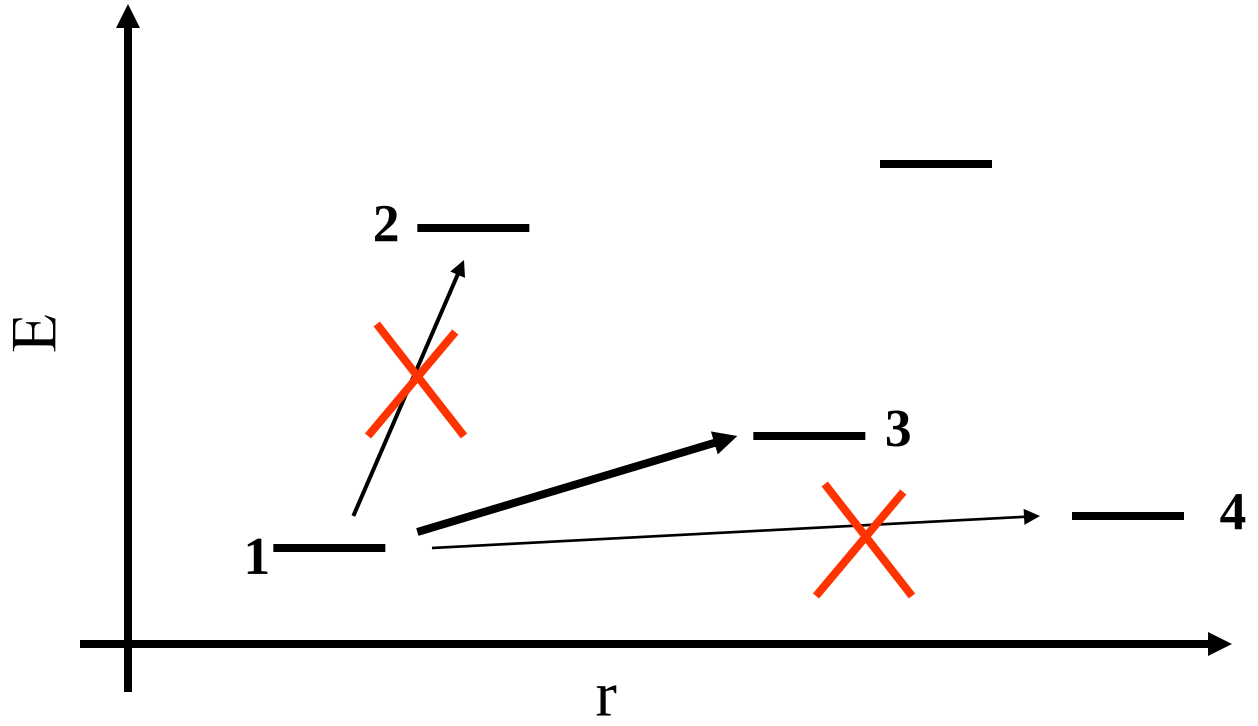


High T: $p[\mathrm{HOP}] \propto \exp^{-\frac{\Delta E}{kT}} \exp^{-\alpha L}$

$\exp^{-\frac{\Delta E}{kT}} \approx 1$

Nearest neighbor fixed range hopping

Hopping: effect of temperature (3)



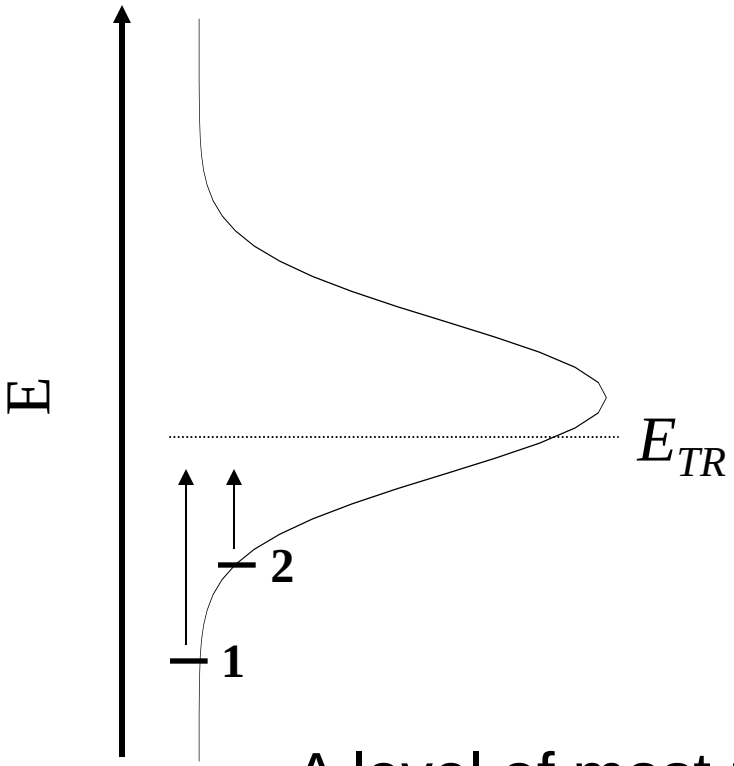
intermediate T: $p[\mathrm{HOP}] \propto \exp^{-\frac{\Delta E}{kT}} \exp^{-\alpha L}$

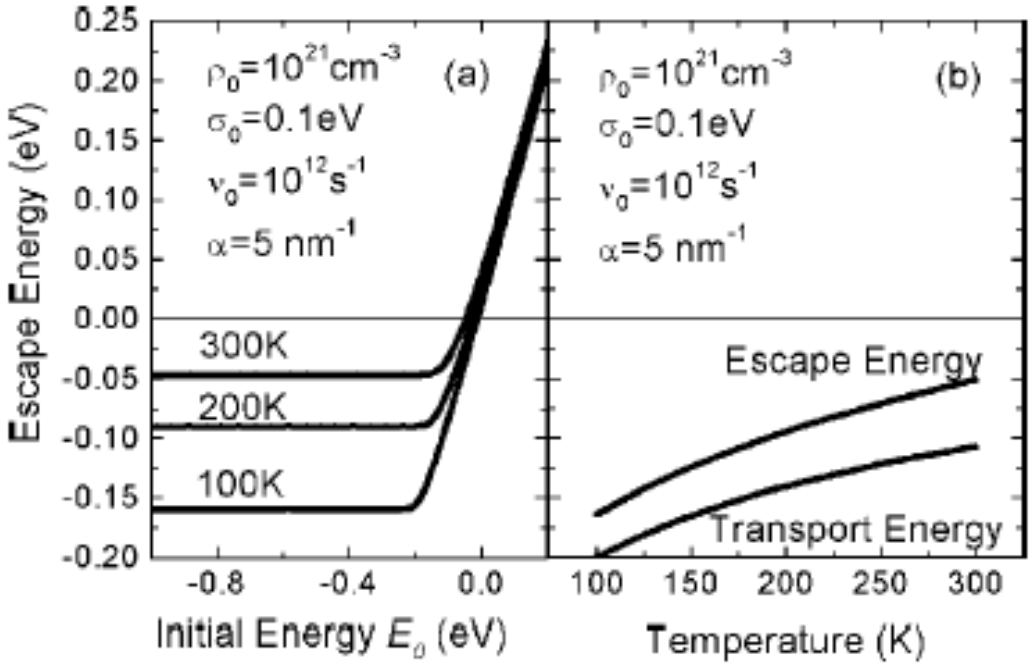
Variable range hopping: an optimum hopping distance

Madelung, Introduction to Solid State Theory, Springer Verlag 1978

Hopping & Gaussian DOS: transport energy(1)

$p[\mathrm{HOP}] \propto \exp^{-\frac{\Delta E}{kT}} \exp^{-\alpha L}$

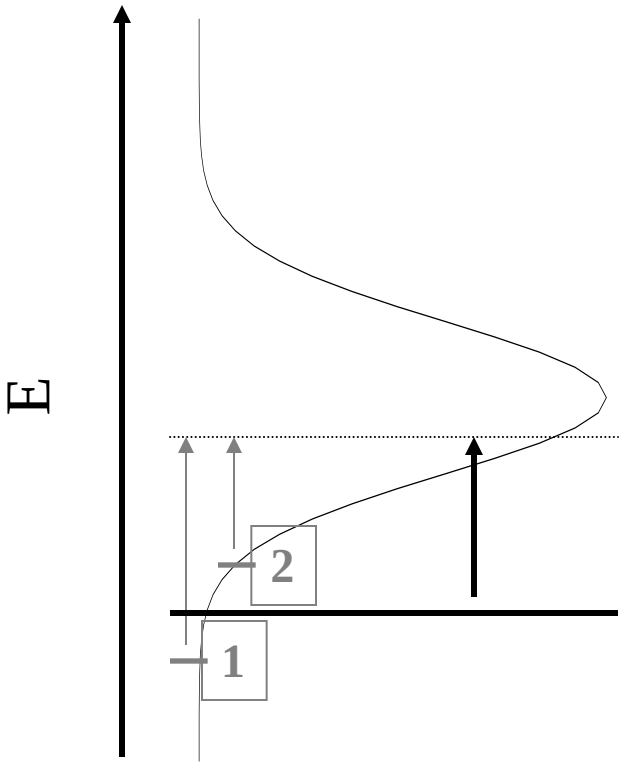




A level of most probable excitation EXISTS
And does not depend upon the site starting energy
(for tail states…)

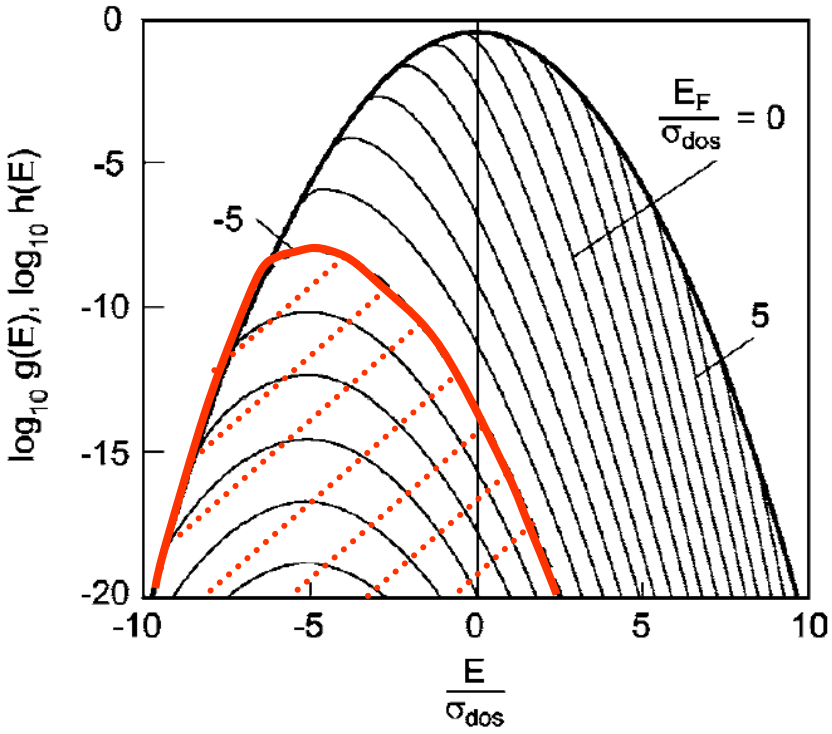
Schmechel, PHYS.REV. B **66**, 235206 ~2002

Hopping & Gaussian DOS: effect of T @ low density



$$E_{TR} = -\frac{5}{9}\frac{\sigma^2}{kT}$$

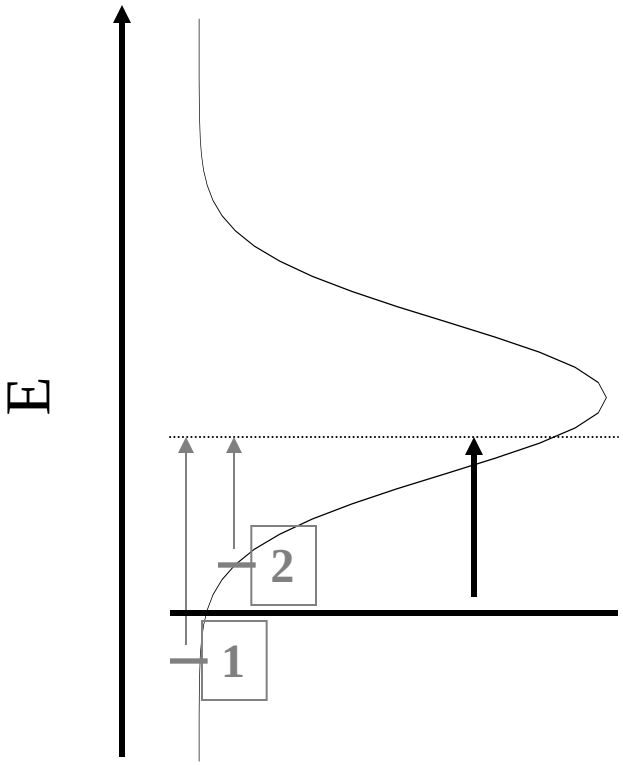
$$\overline{E} = -\frac{\sigma^2}{kT}$$



Excitation from $\overline{E}$ to $E_{TR} \propto \exp\left(-\frac{E_{TR}-\overline{E}}{kT}\right) \propto \exp\left(-\frac{2}{3}\frac{\sigma^2}{kT^2}\right)$

$p[\mathrm{HOP}] \propto \exp^{-\frac{\Delta E}{kT}} \exp^{-\alpha L}$

Hopping & Gaussian DOS: effect of T @ low density



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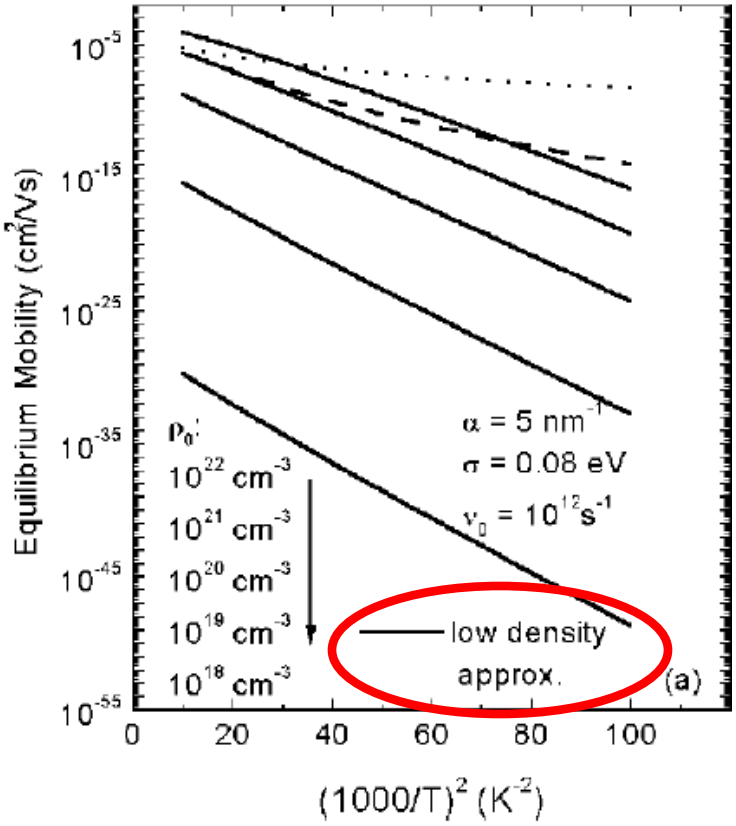
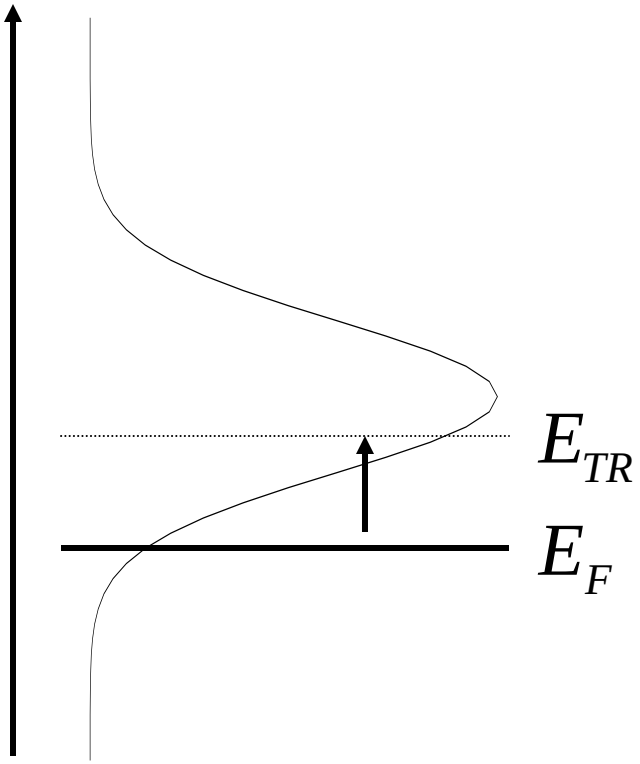
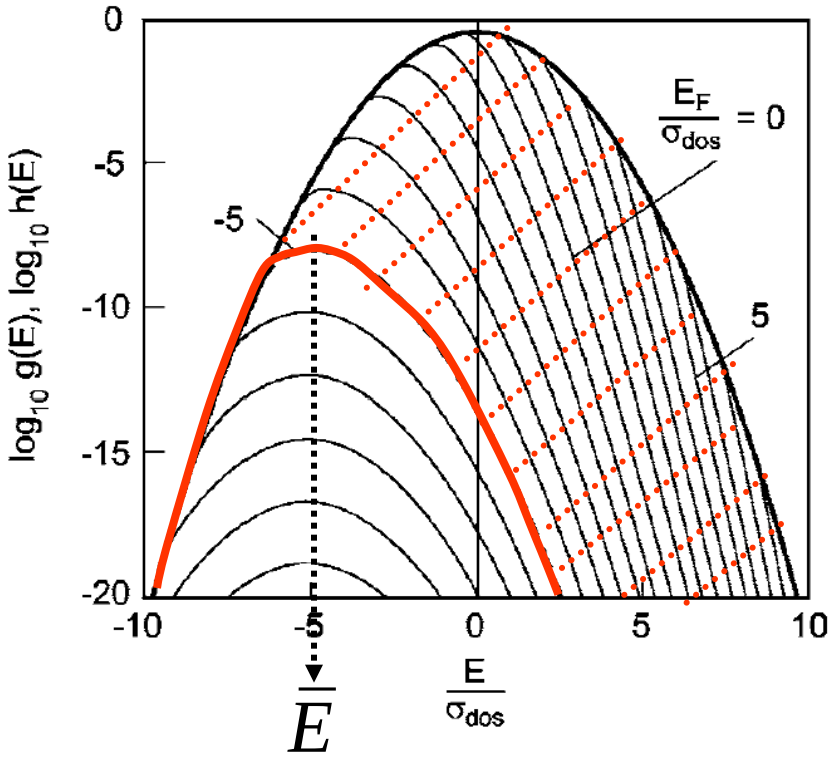


Excitation from $\overline{E}$ to E_{TR} $\quad \mu \propto \exp\left(-\frac{E_{TR}-\overline{E}}{kT}\right) \propto \exp\left(-\frac{2}{3}\frac{\sigma^2}{kT^2}\right)$

Hopping & Gaussian DOS: effect of T @ high density



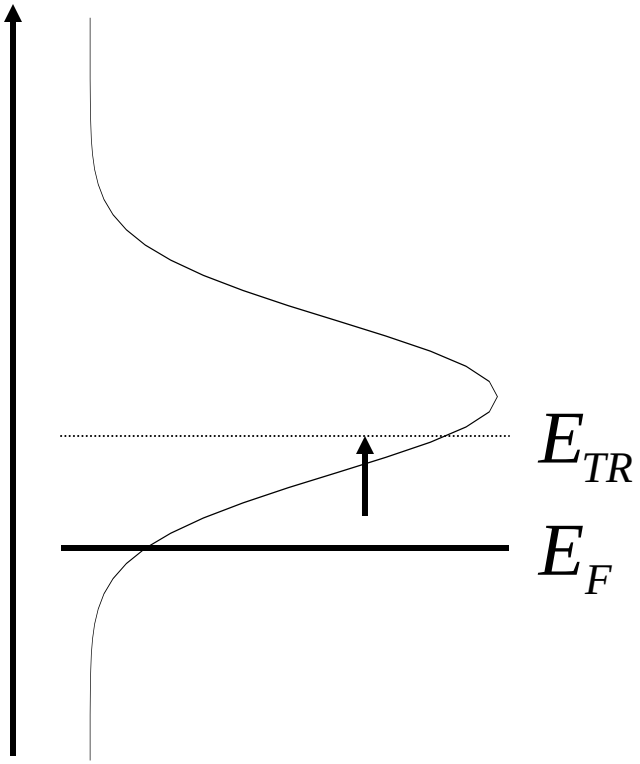


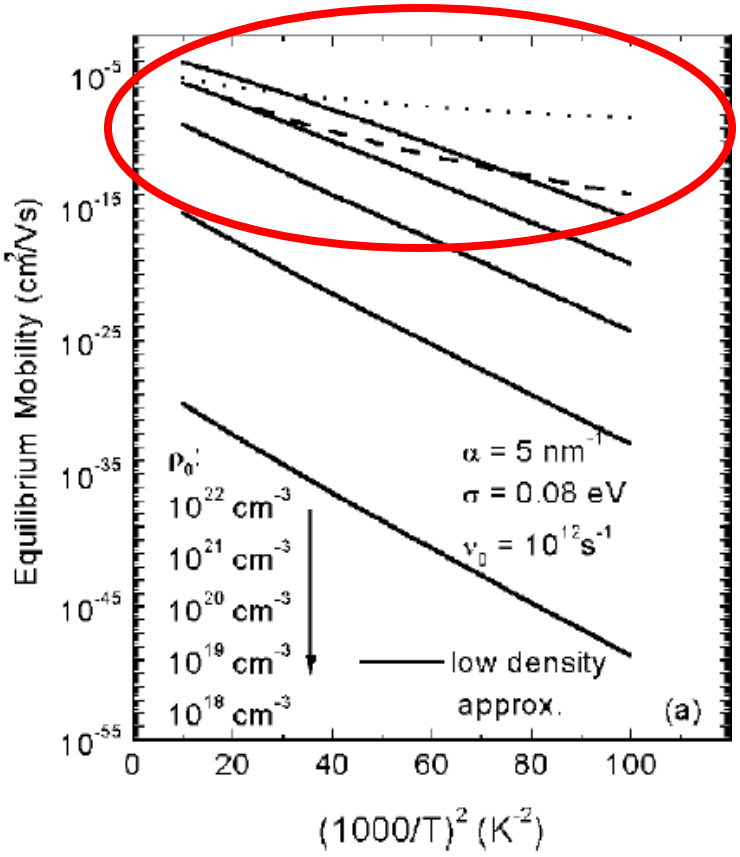
Excitation from E_F to E_{TR} $\quad \mu \propto \exp\left(-\frac{E_{TR} - E_F}{kT}\right)$

Coehoorn et al., PHYS. REV. B **72**, 155206 2005

$p[\mathrm{HOP}] \propto \exp^{-\frac{\Delta E}{kT}} \exp^{-\alpha L}$

Hopping & Gaussian DOS: effect of T @ high density





Excitation from E_F to E_{TR} $\propto \exp\left(-\frac{E_{TR}-E_F}{kT}\right) \cong \exp\left[-\left(-\frac{5}{9}\frac{\sigma^2}{kT^2}-\frac{E_F}{kT}\right)\right]$

Coehoorn et al., PHYS. REV. B **72**, 155206 2005

Mobility expression

$$\mu(T, n, F) = \mu_0 \exp^{-2\alpha a} \exp^{-0.42\hat{\sigma}} \times g_1(F, \mathrm{T}) \times g_2(F, T)$$

Density enhancement

At higher density,
the E_F to E_{TR} distance diminishes

Coehoorn Phys rev B 78 85207 2008

Mobility expression

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Coehoorn Phys rev B 78 85207 2008

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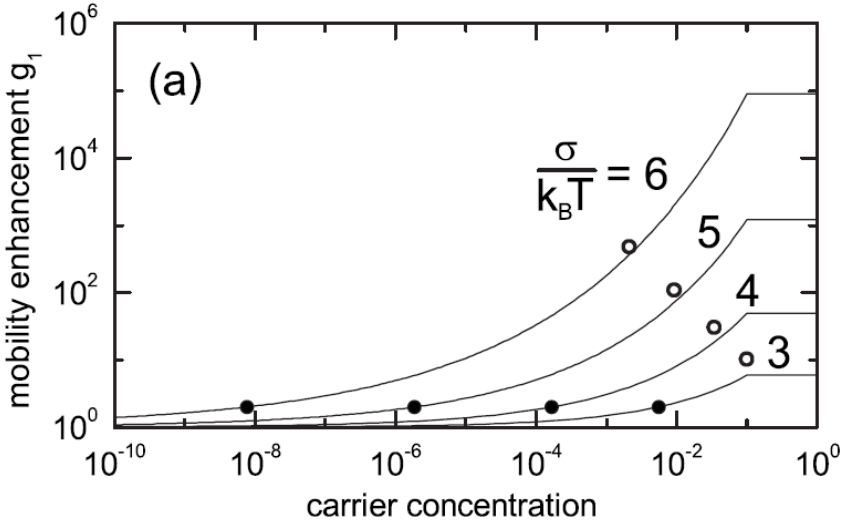
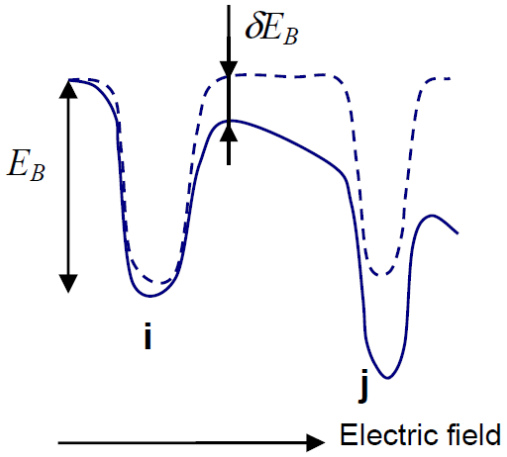
$$g_1(T,c) = \exp\left[\frac{1}{2}(\hat{\sigma}^2 - \hat{\sigma})(2c)^{\delta}\right]$$

$$\hat{\sigma} = \sigma/(k_B T) \quad c = n/N_t \quad \delta = 2\frac{\ln(\hat{\sigma}^2 - \hat{\sigma}) - \ln(\ln 4)}{\hat{\sigma}^2}$$



E-field enhancement

The applied field modifies energetic barriers



Coehoorn Phys rev B 78 85207 2008

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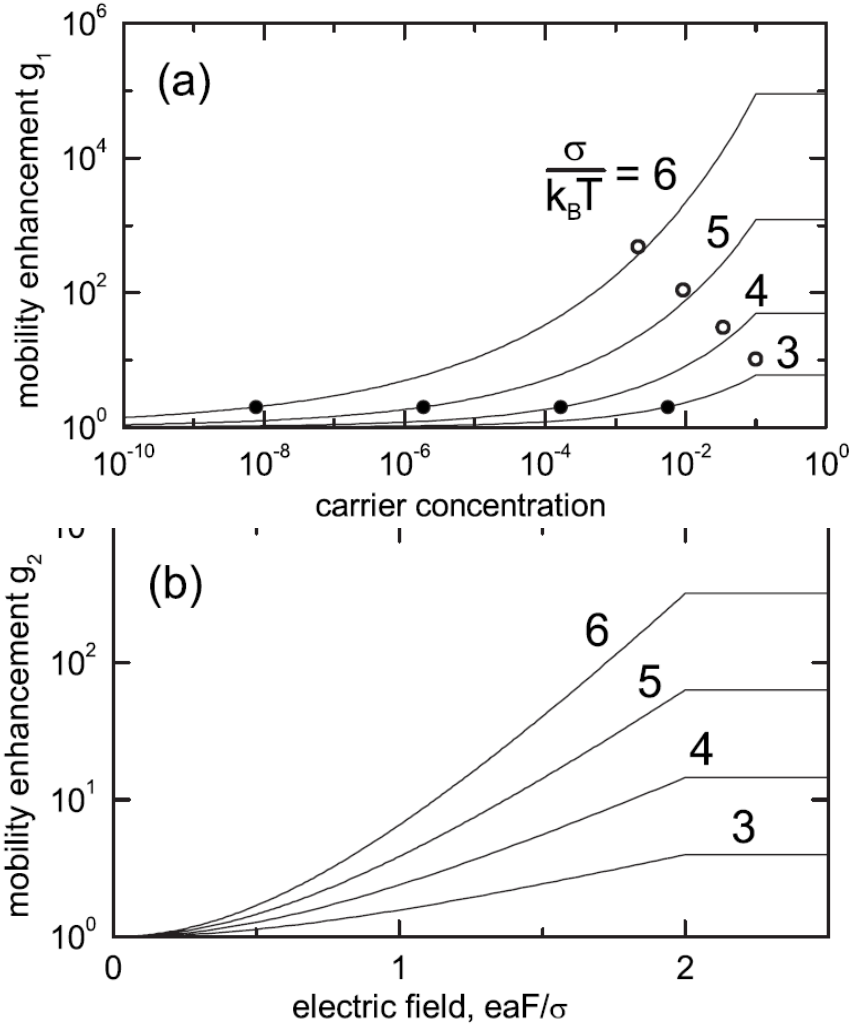
E-field enhancement

$$g_2(T,F) = \exp\left[0.44(\hat{\sigma}^{3/2} - 2.2)\left(\sqrt{1 + 0.8\hat{F}^2} - 1\right)\right]$$



Coehoorn Phys rev B 78 85207 2008

Mobility expression

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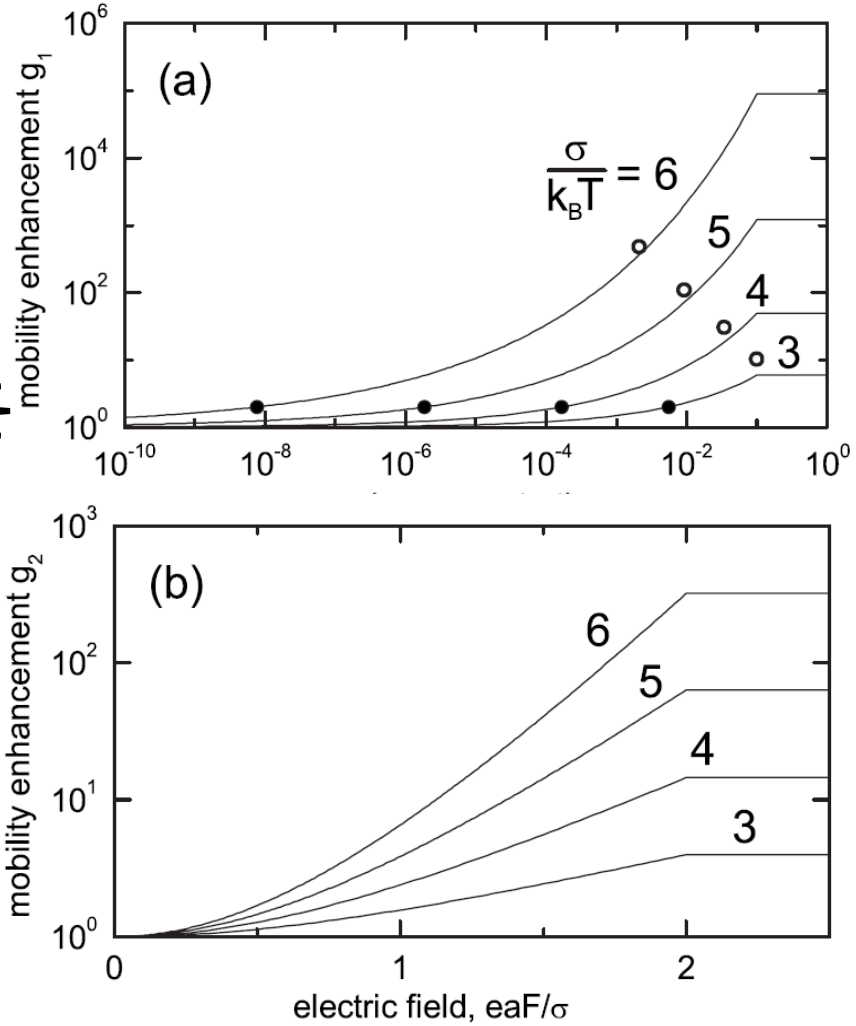
$$g_1(T,c) = \exp\left[\frac{1}{2}(\hat{\sigma}^2 - \hat{\sigma})(2c)^{\delta}\right]$$

Higher at larger disorder

E-field enhancement

$$g_2(T,F) = \exp\{0.44(\hat{\sigma}^{3/2} - 2.2)\}\left[\sqrt{1 + 0.8\left(\frac{eaF}{\sigma}\right)^2} - 1\right]$$

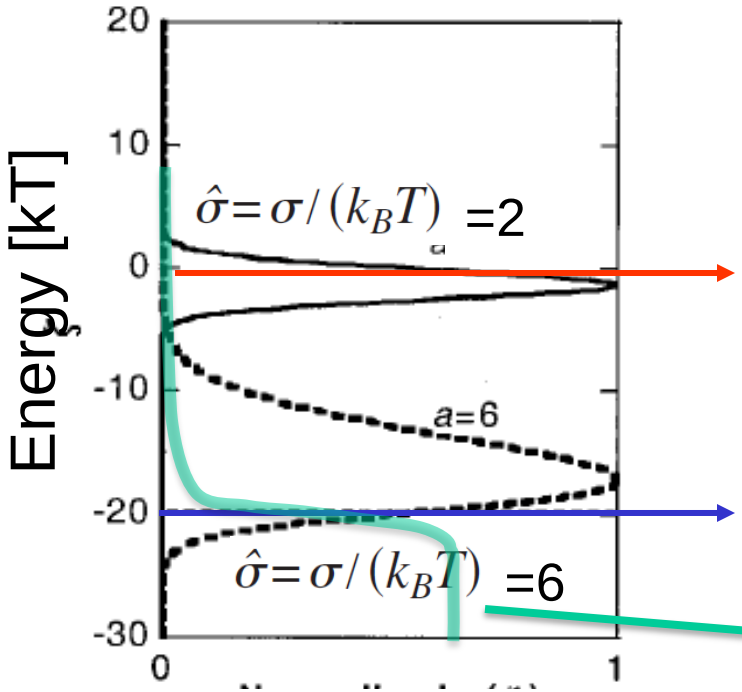
Higher at larger disorder



Coehoorn Phys rev B 78 85207 2008

Einstein relation

$$D = \frac{kT}{e}\mu \times g_3(T,n)$$



DOS center

Chemical potential

Fermi-Dirac

A disordered s.c. is practically always degenerate!

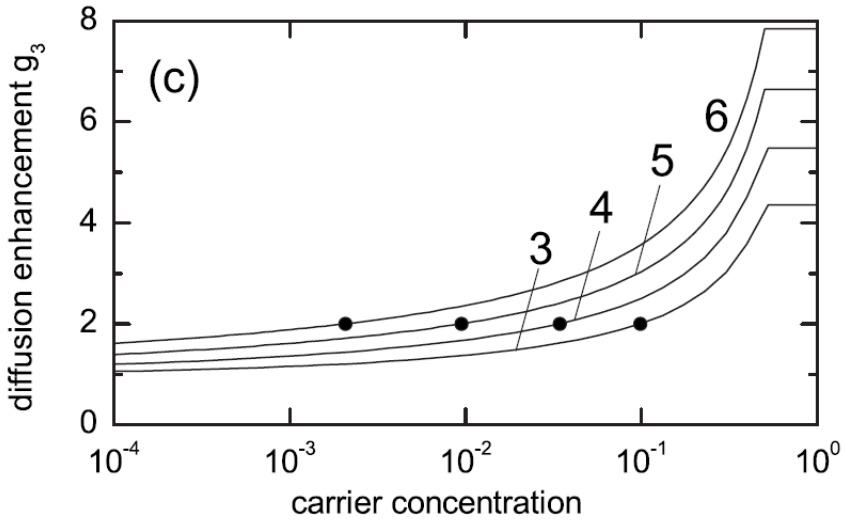
Tessler Appl. Phys. Lett., Vol. 80, No. 11, 18 March 2002

Einstein relation

$$D = \frac{kT}{e}\mu \times g_3(T,n)$$

Diffusion enhancement

$$g_3(T,n) = \frac{1}{k_B T}\frac{p}{\left.\frac{dp(E_F)}{dE_F}\right|_p},$$

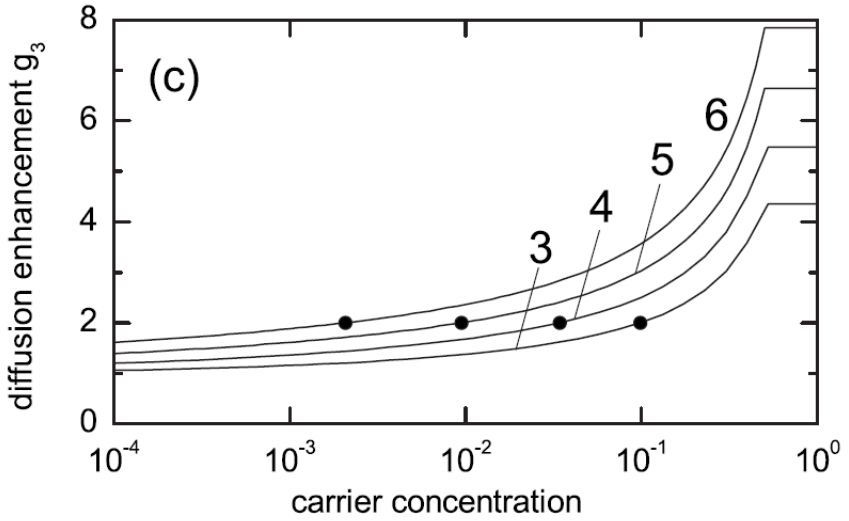


Diffusion vs. Mobility enhancement relation

$$D = \frac{kT}{e}\,\mu \times g_3(T,n)$$

Diffusion enhancement

$$g_3(T,n) = \frac{1}{k_B T}\,\frac{p}{\left.\dfrac{dp(E_F)}{dE_F}\right|_p},$$



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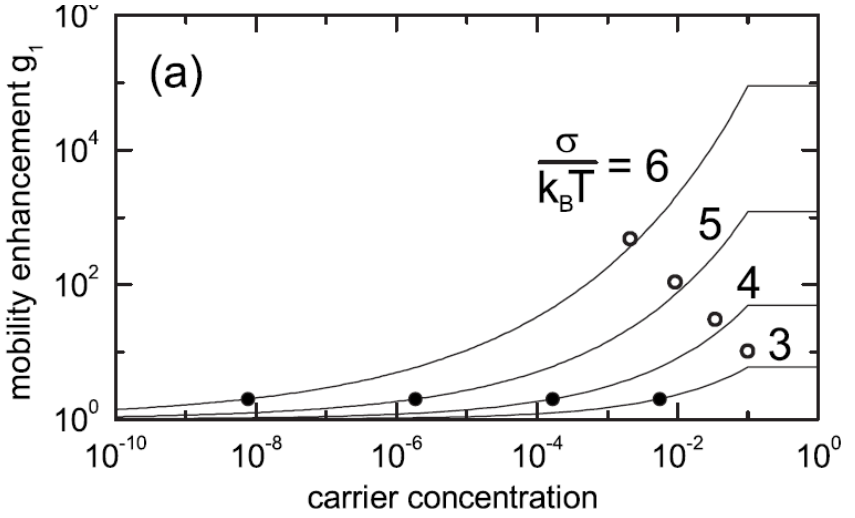
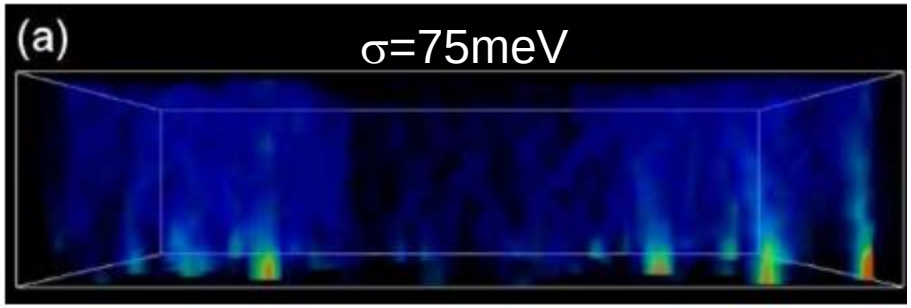
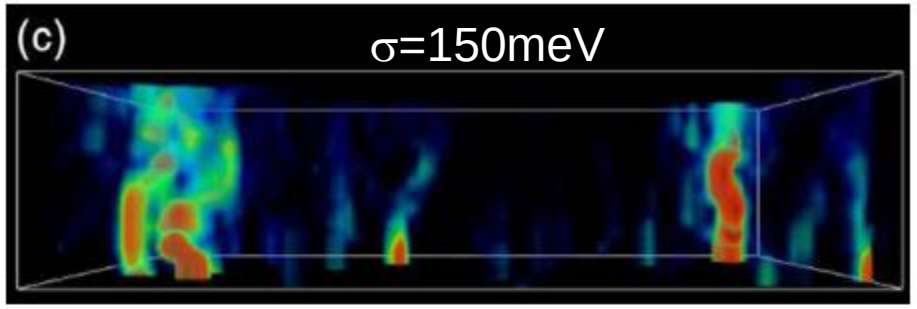
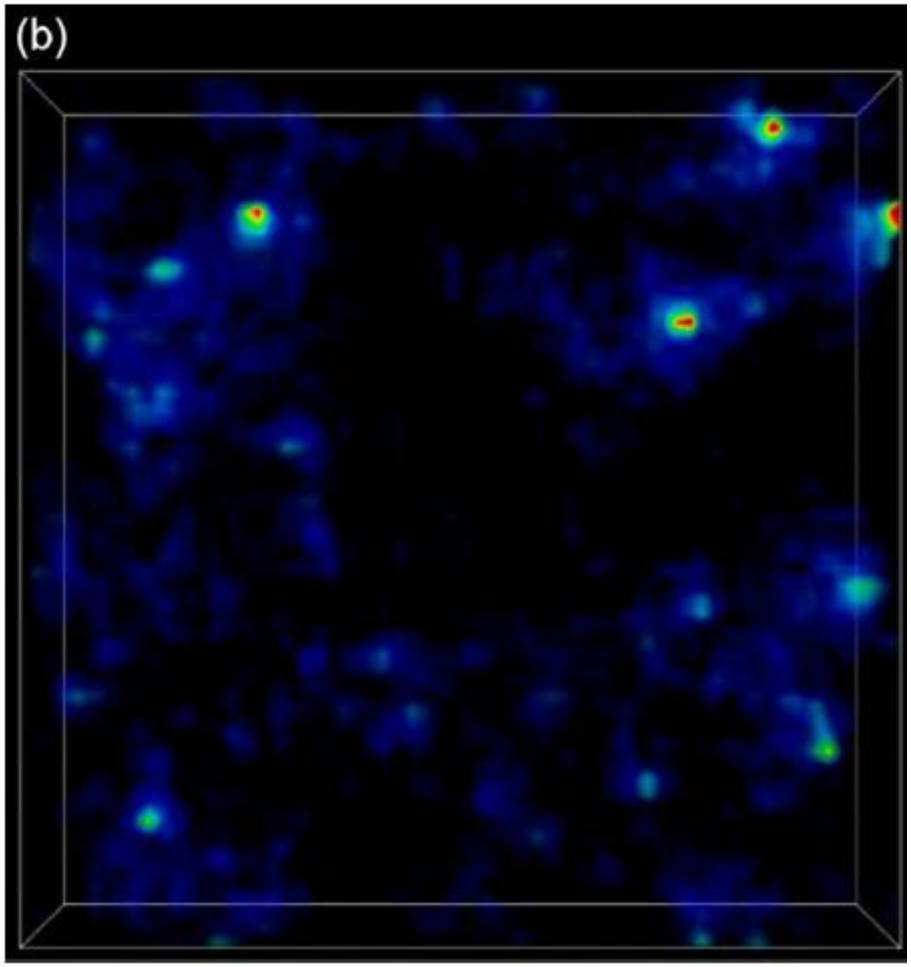
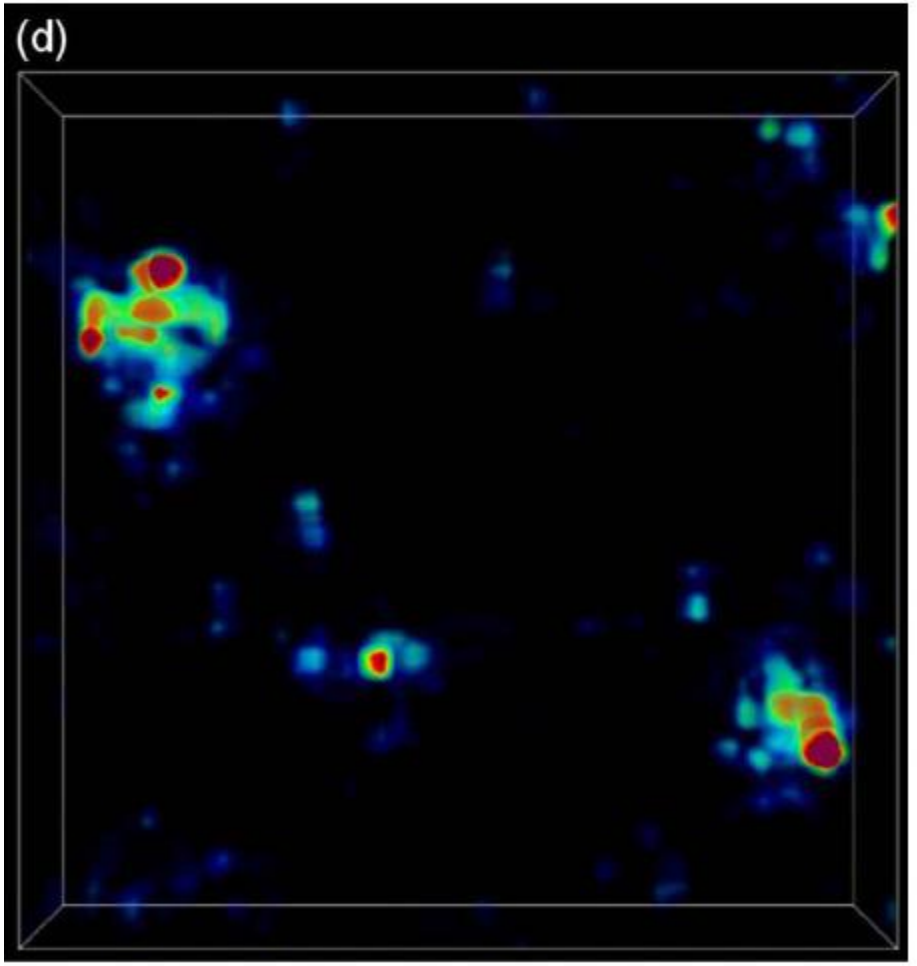


Hopping and spatial current distribution









Bobbert PHYSICAL REVIEW B **79, 085203 2009**

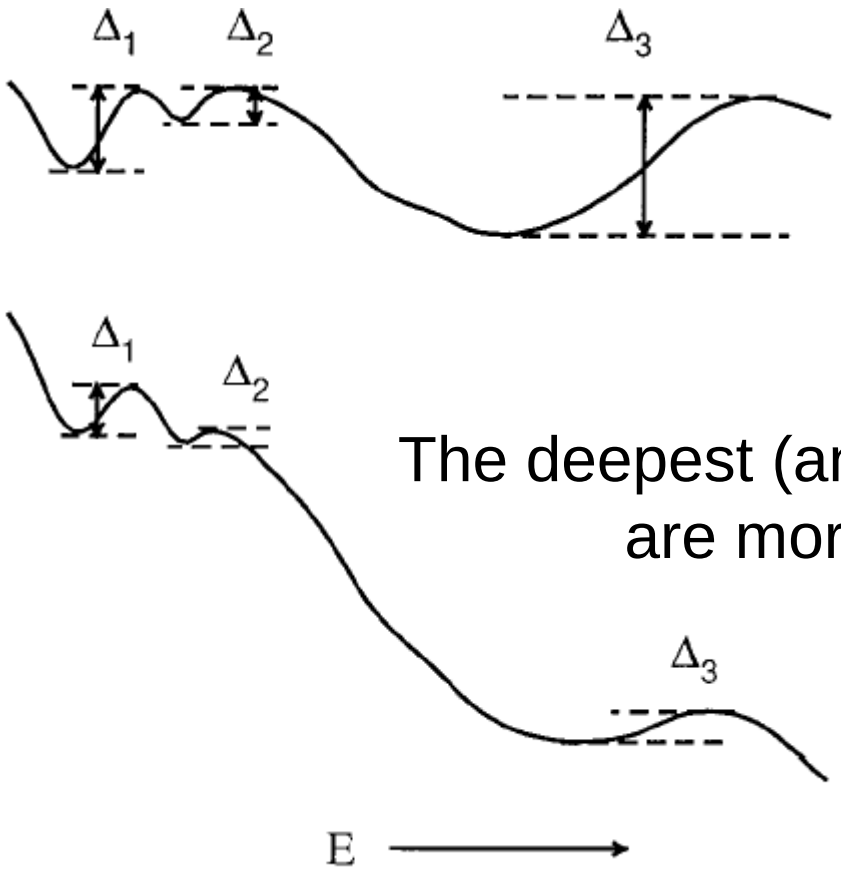
Correlated Gaussian Disorder Model(1)

The energetic disorder is *spatially* correlated

The deepest valley are the widest ones

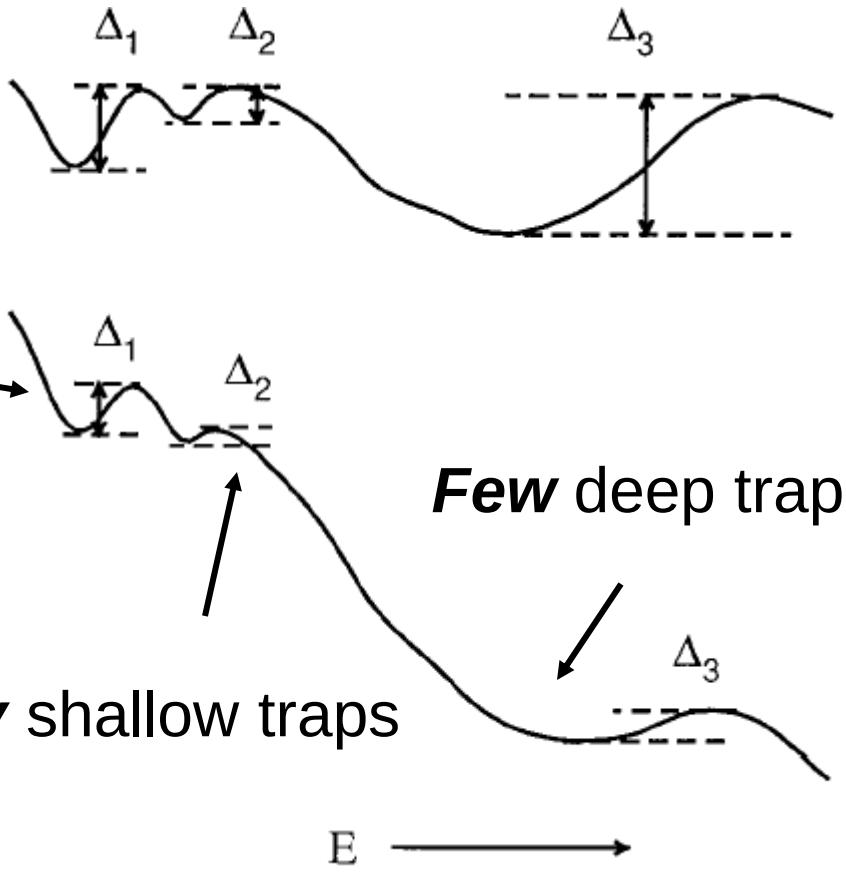
Correlated Gaussian Disorder Model(2)

The electric field lowers the escape barriers



The deepest (and widest) valleys are more affected

Correlated Gaussian Disorder Model(3)



Intermediate ***limiting*** traps

Few deep traps

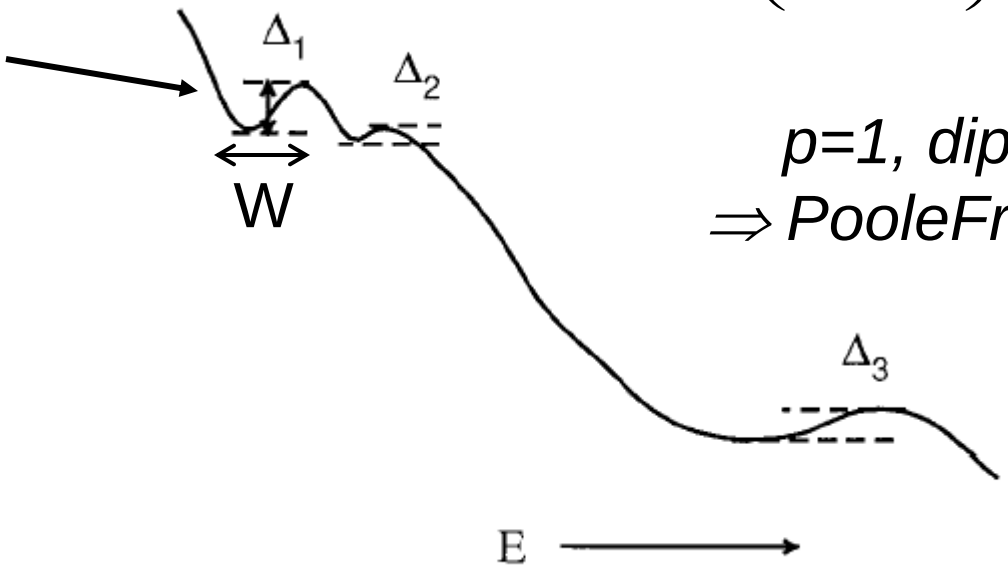
Many shallow traps

Correlated Gaussian Disorder Model(4)

Traps width W is electric field dependent:
for energy autocorrelation in the form $\frac{1}{r^p}$, $\rightarrow$ $W = E^{-\frac{1}{p+1}}$

Barrier lowering and hence μ is $\propto \exp\left(\frac{eEW}{kT}\right) \propto \exp\left(\beta E^{\frac{p}{p+1}}\right)$

Intermediate ***limiting*** traps

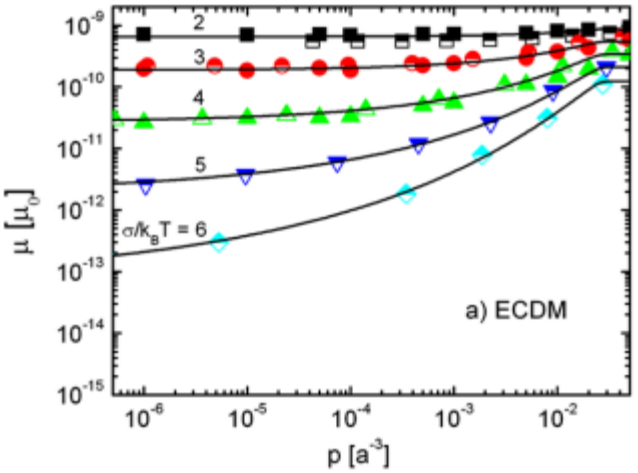


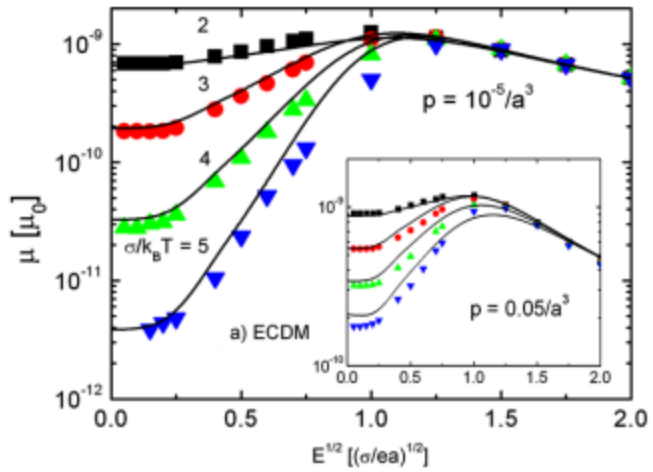
p=1, dipolar disorder
$\Rightarrow$ PooleFrenkel behavior

Parris, Phys. Stat. Sol. (b) 218, 47 (2000)

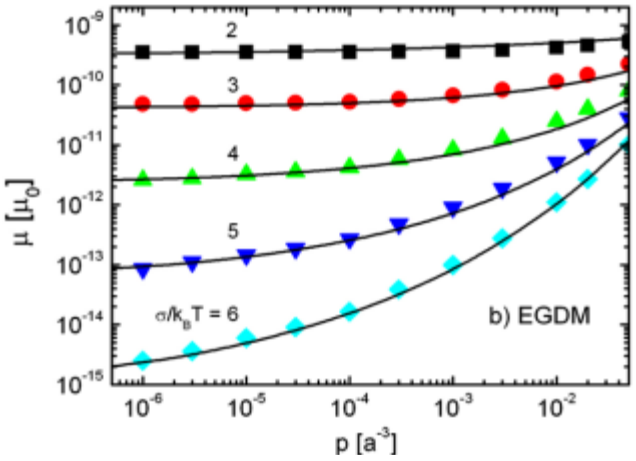
Correlated *vs* Uncorrelated

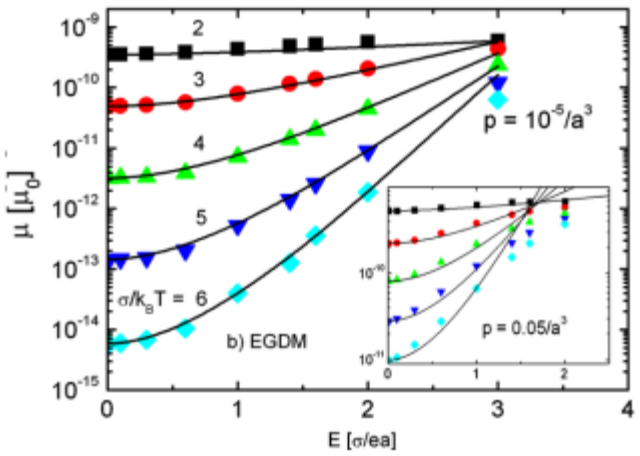
$$\mu(T, n, F) \approx \mu_0 \exp^{-2\alpha a} \exp^{-0.29\hat{\sigma}}$$





$$\mu(T, n, F) \approx \mu_0 \exp^{-2\alpha a} \exp^{-0.42\hat{\sigma}}$$

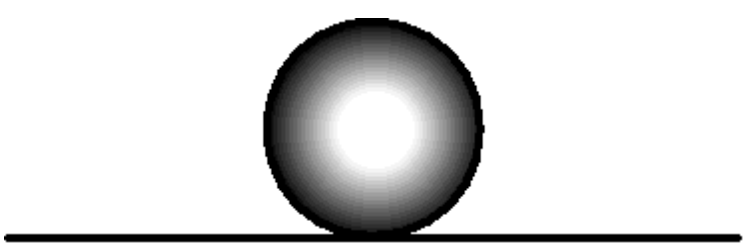


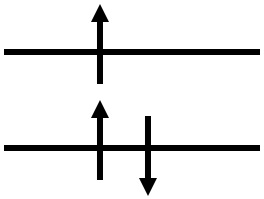


Bobbert Organic Electronics 10 (2009) 437–445

Polarons(1)

Relaxation of excess *slow* carriers…

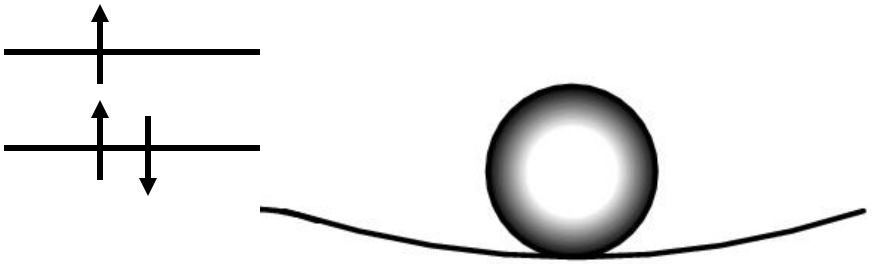


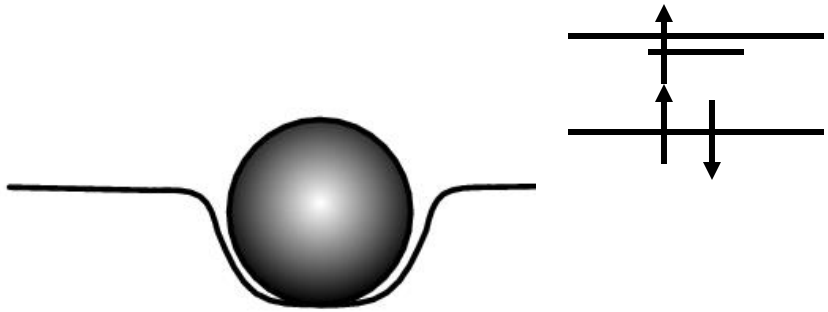


…due to **on-site e/p** coupling

Polarons(2)

Relaxation of excess *slow* carriers

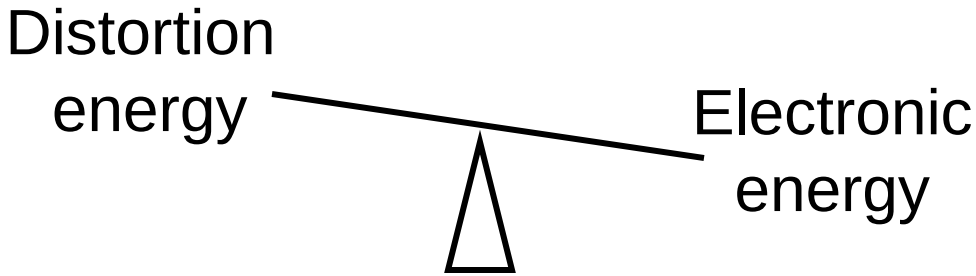




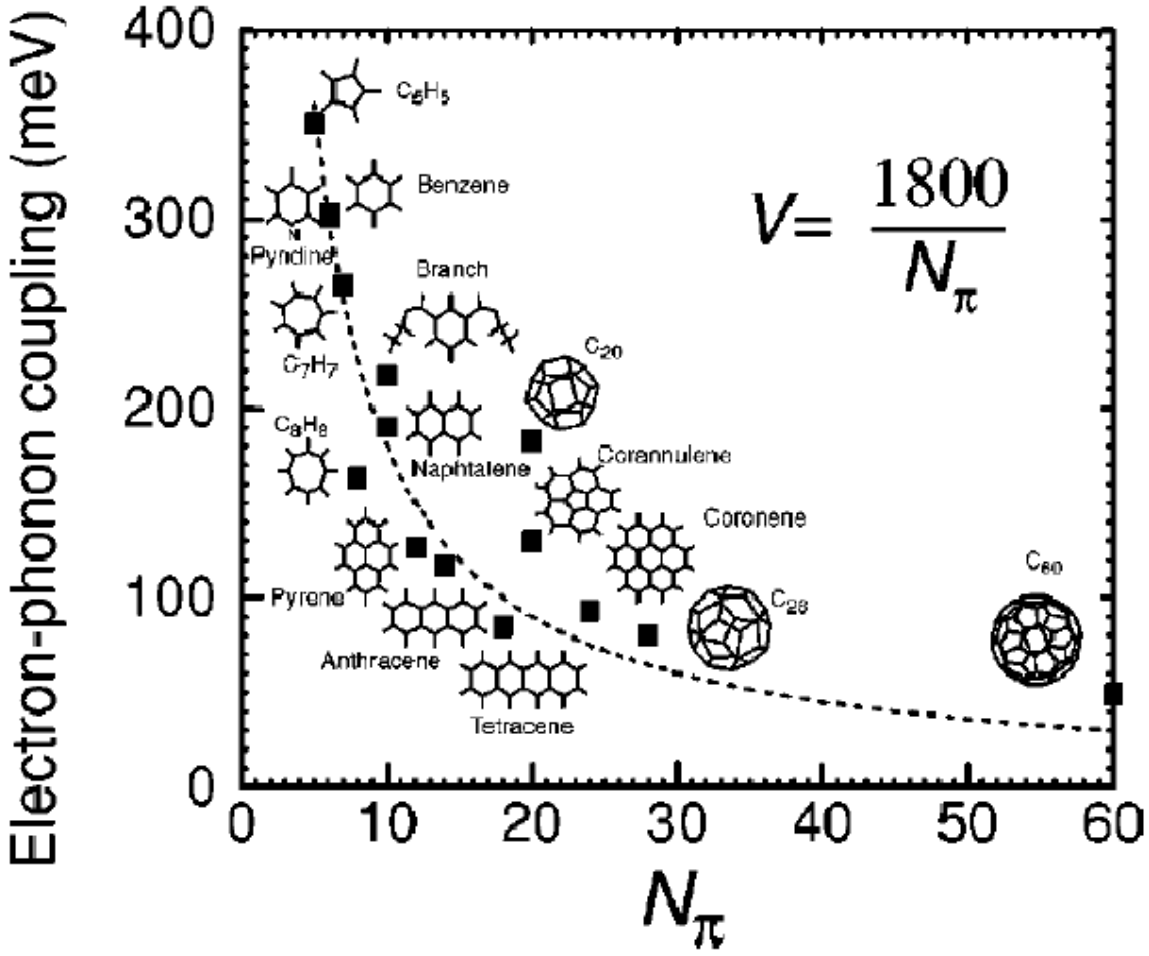
Large polaron:
Increased effective mass

Small polaron:
self-localized in a potential well

Sources:
- intramolecular vibrations
- Intermolecular vibrations
- Electronic polarization



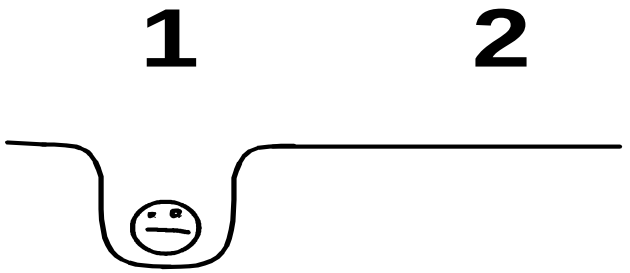
Polarons(3)



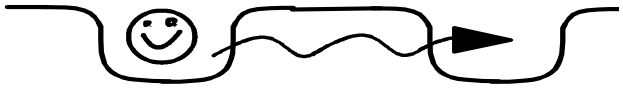
Role of the number of π carbon atoms

Burdett, Chemical Bonding in Solids, Oxford University press 1995

Polaron Hopping



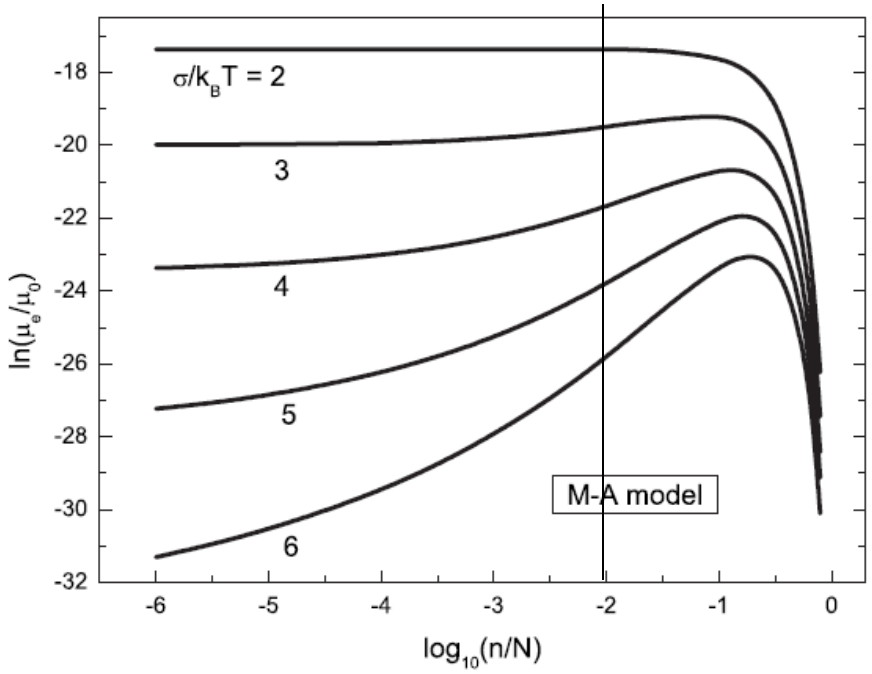
Thermal fluctuations create
Coincidence Event

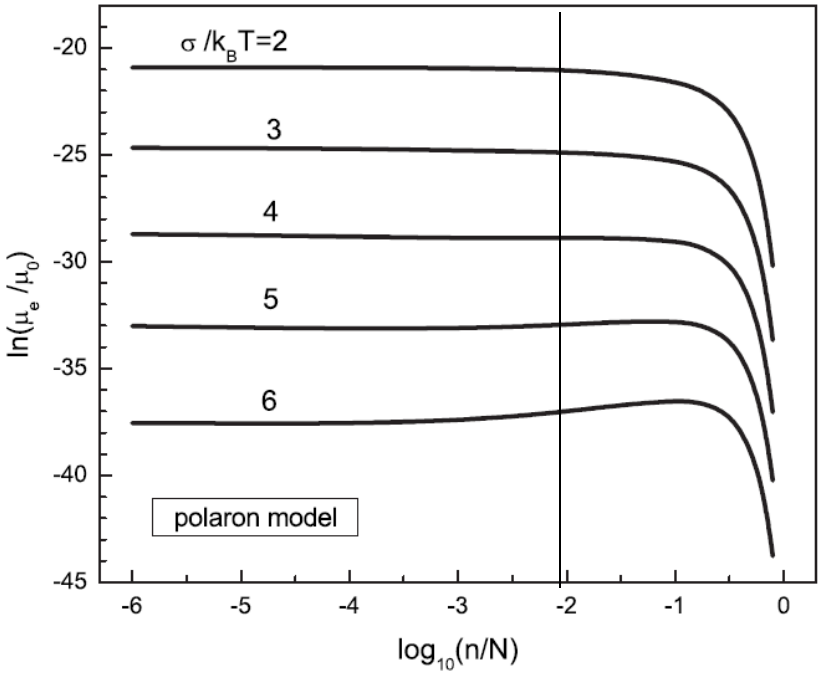


Holstein, Ann.Phys. 8 1959, 325

Disorder and polarons…Parris Phys.Rev.Lett. 87, 2001, 126601

Polaronic effect + Energetic Disorder

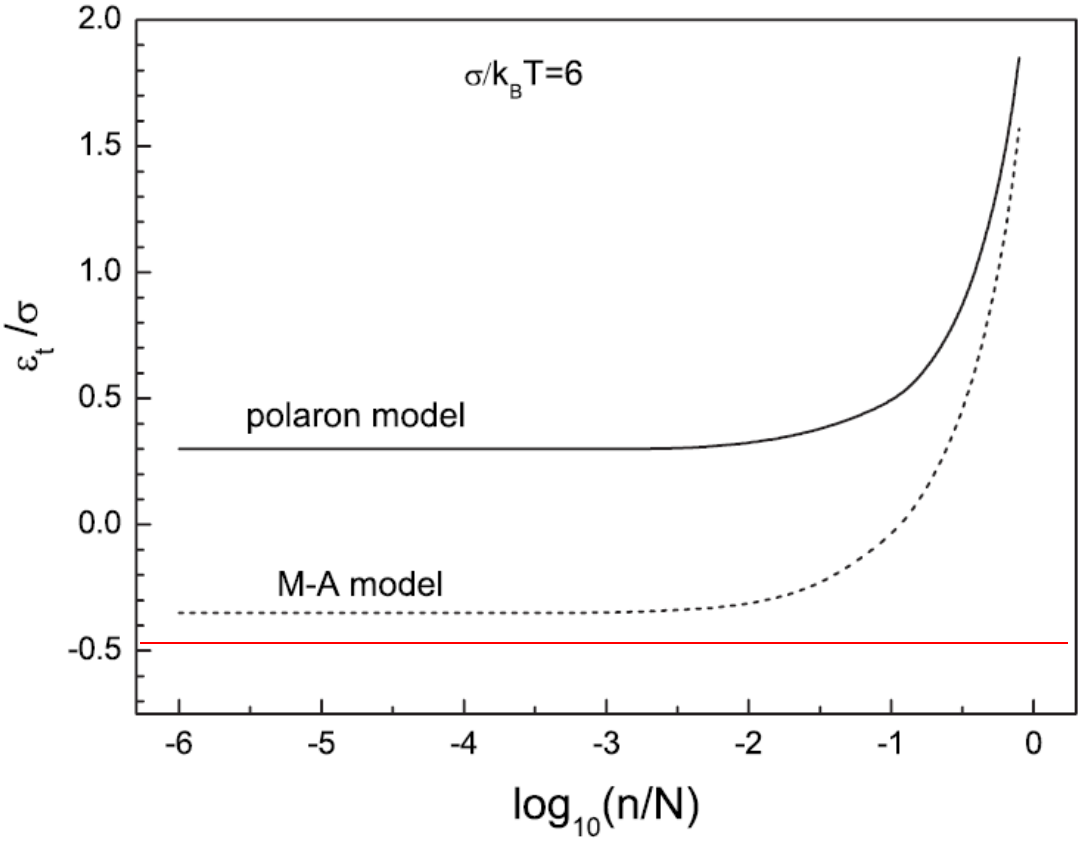




Charge density dependence almost supressed
in the polaron model

Fischuk PHYSICAL REVIEW B **76**, 045210 2007

Polaronic effect + Energetic Disorder

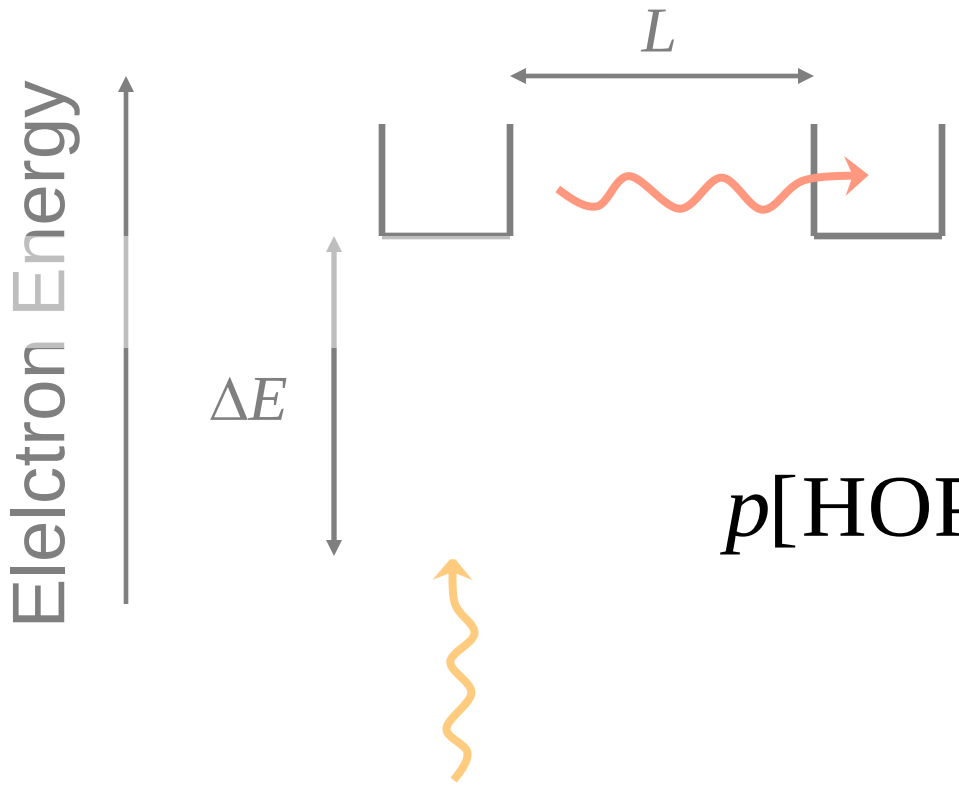


The transport energy lies higher in the polaron model ->
The relative change due tue Fermi level lifting is smaller

Fischuk PHYSICAL REVIEW B **76**, 045210 2007

Back to Hopping Rate

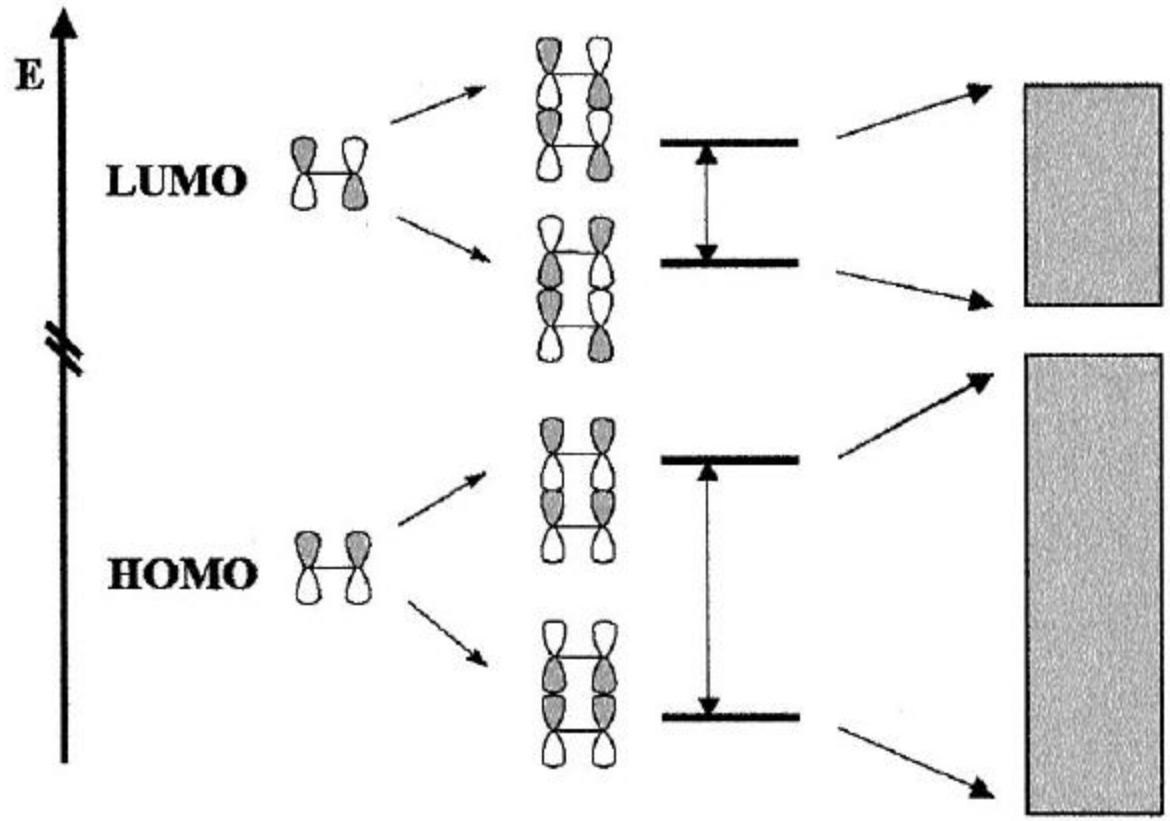
E’ un processo di **tunnelling** **termicamente attivato**



$$p[\mathrm{HOP}] \propto \exp^{-\frac{\Delta E}{kT}} \exp^{-\alpha L}$$

$$p[\mathrm{HOP}] \propto \exp^{-\frac{\Delta E}{kT}} \exp^{-\alpha L}$$

Xtal structure and transfer integral: two etylene molecules

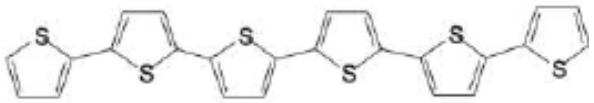


Mixed bonding/antibonding interaction

Full (anti)bonding interaction

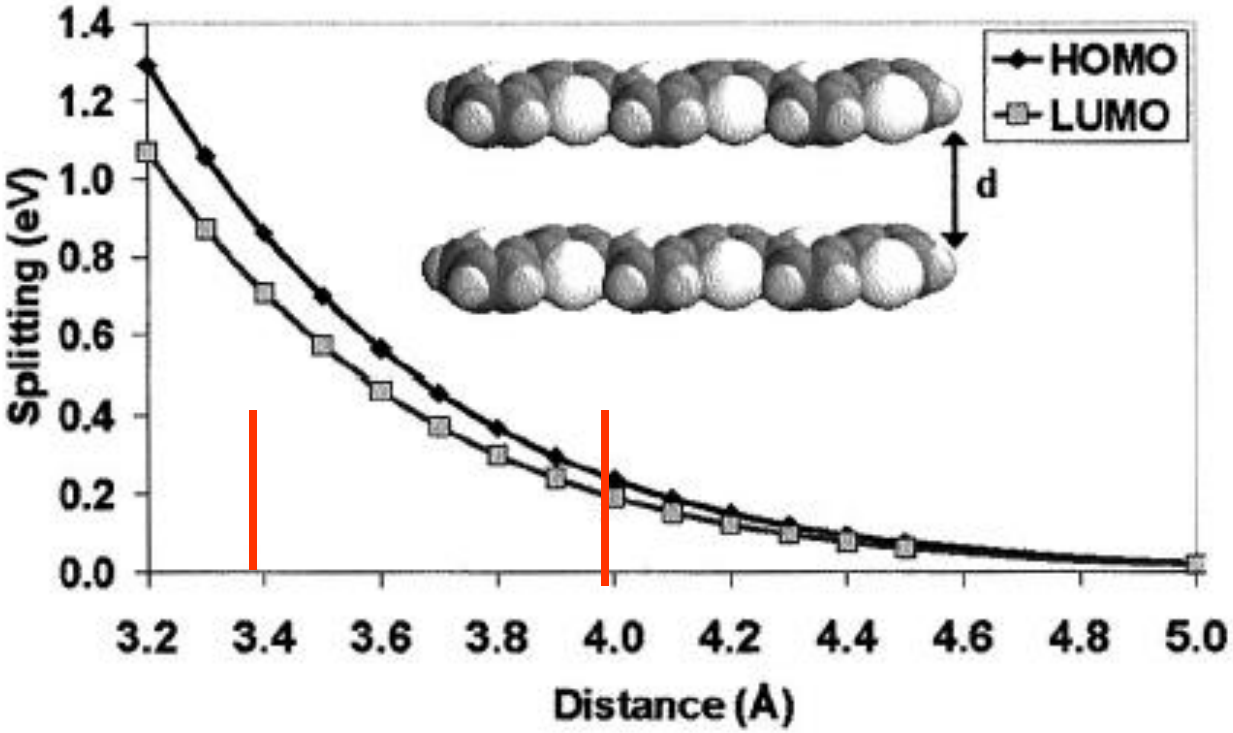
HOMO splitting larger than LUMO splitting

Bredas, Chem. Rev. **2004,** 104, 4971–5003; **2007**, 107, 926



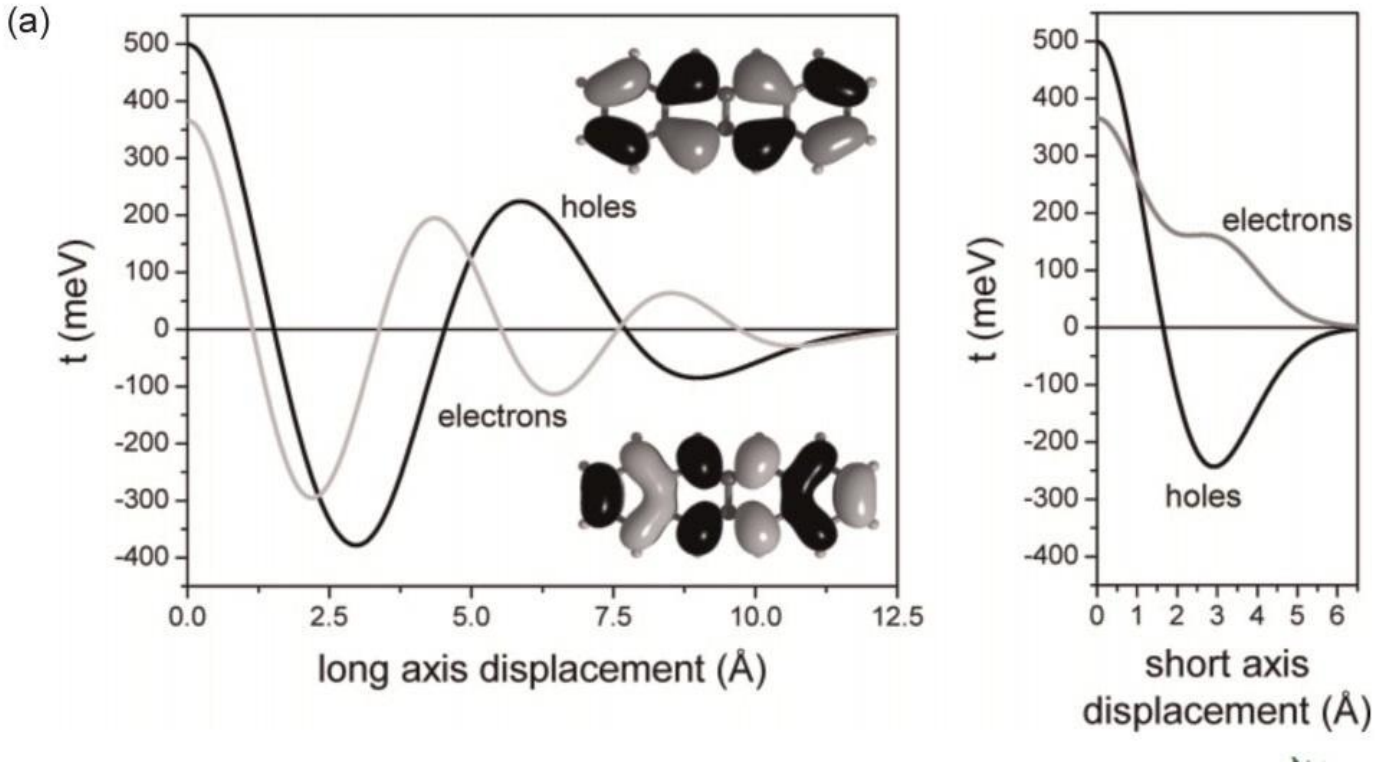
$$p[\mathrm{HOP}] \propto \exp^{-\frac{\Delta E}{kT}} \exp^{-\alpha L}$$

6T dimer: intermolecular distance effect



$$p[\mathrm{HOP}] \propto \exp^{-\frac{\Delta E}{kT}} \exp^{-\alpha L}$$

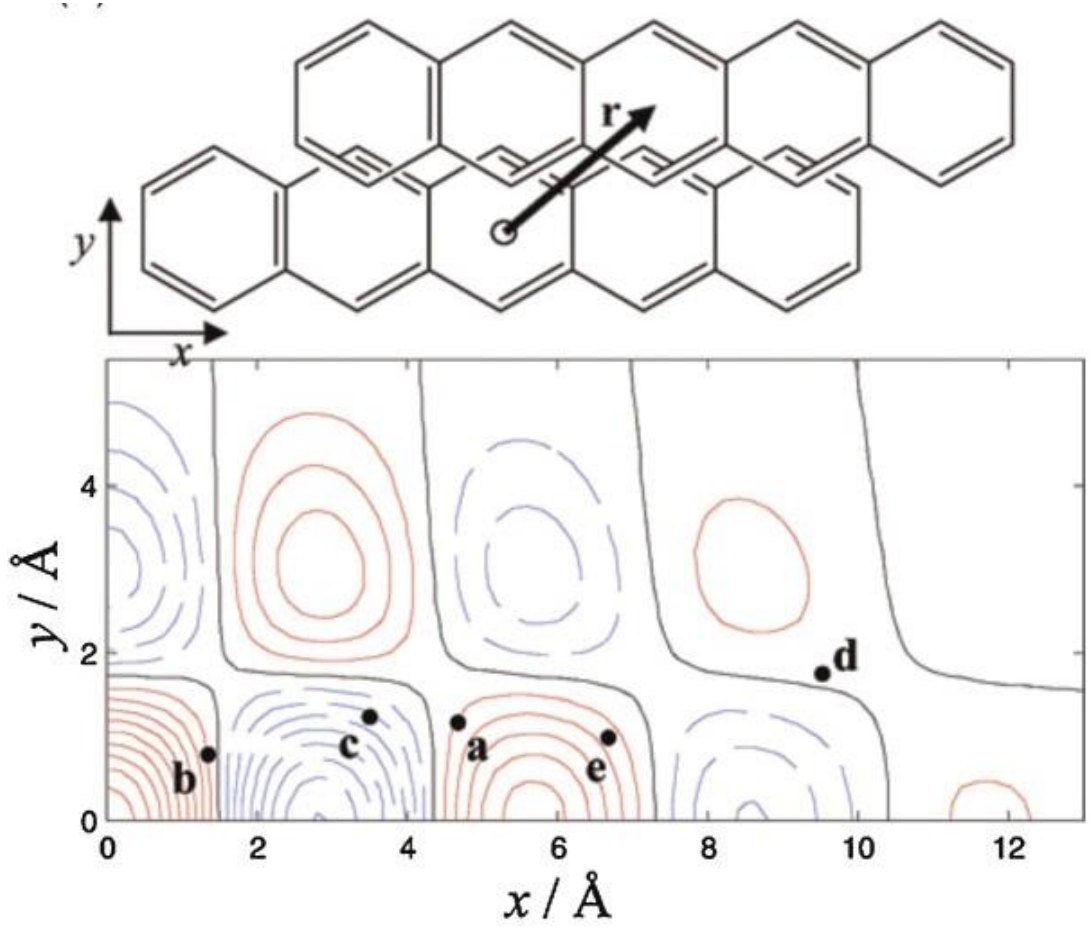
Tetracene dimer: long axis displacement



Chang et al. Phys. Status Solidi B 249, No. 9, 1655–1676 (2012)

$$p[\mathrm{HOP}] \propto \exp^{-\frac{\Delta E}{kT}} \exp^{-\alpha L}$$

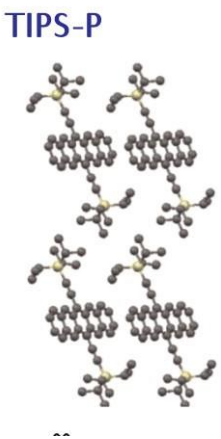
Pentacene

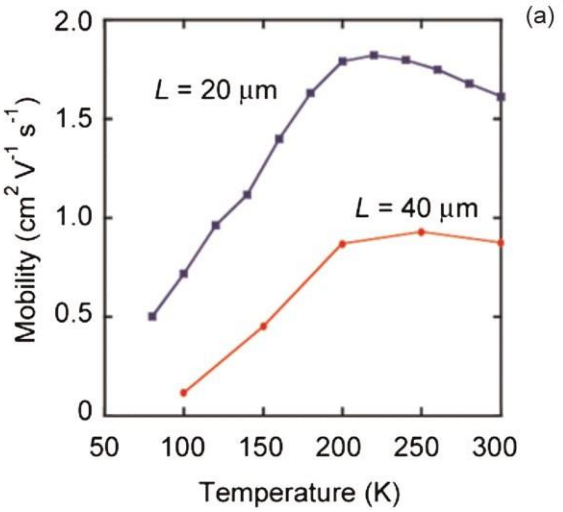


Equilibrium stacking does **not** correspond to a **max** of **transfer integral** ***!!!***

Sirringhaus et AL. Phys. Status Solidi B 249, No. 9, 1655–1676 (2012) / DOI 10.1002/pssb.201248143

Single Crystal & polycrystals: bandlike transport?



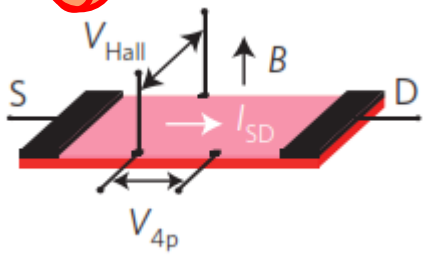


+

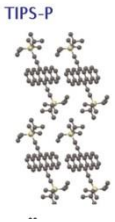
Ideal Hall effect measured!
->a momentum coupling with B can be defined!

μ(T) is band-like
(not thermally activated in 200K-RT)

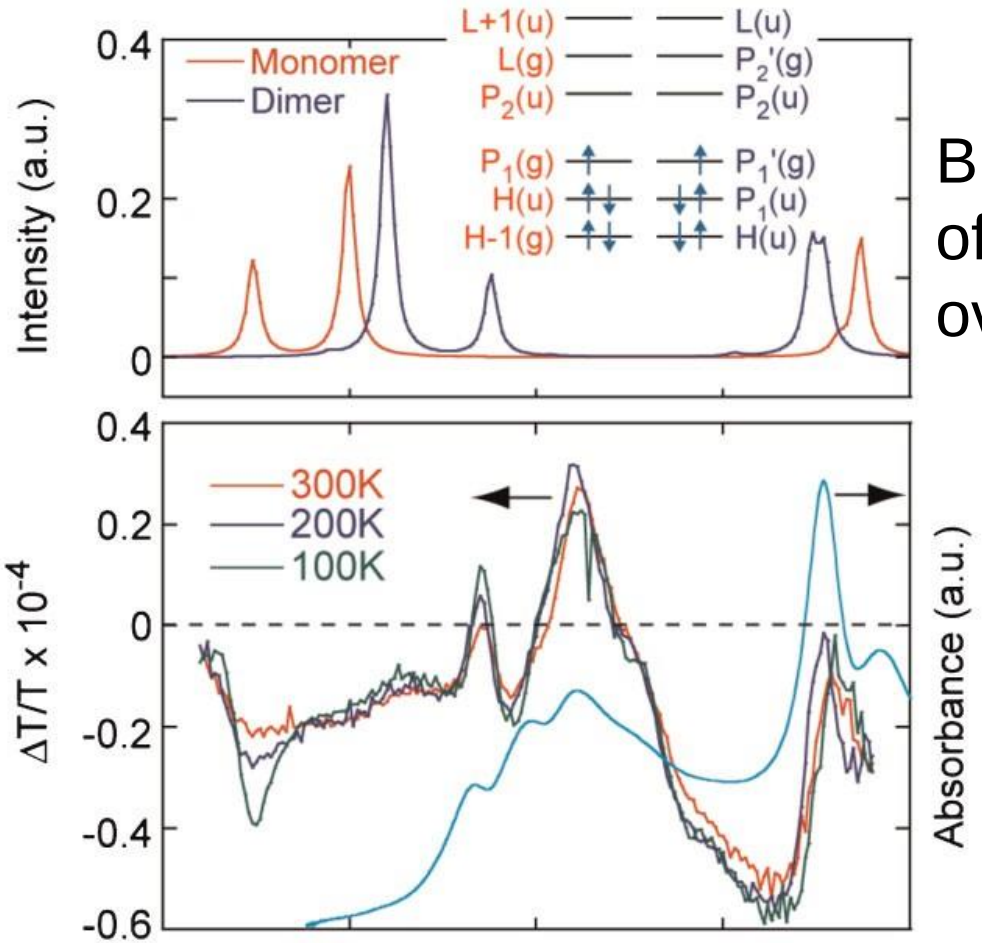
☺



Sirringhaus et al. Phys. Status Solidi B 249, No. 9, 1655–1676 (2012) / DOI 10.1002/pssb.201248143



Single Crystal & polycrystals: bandlike transport?

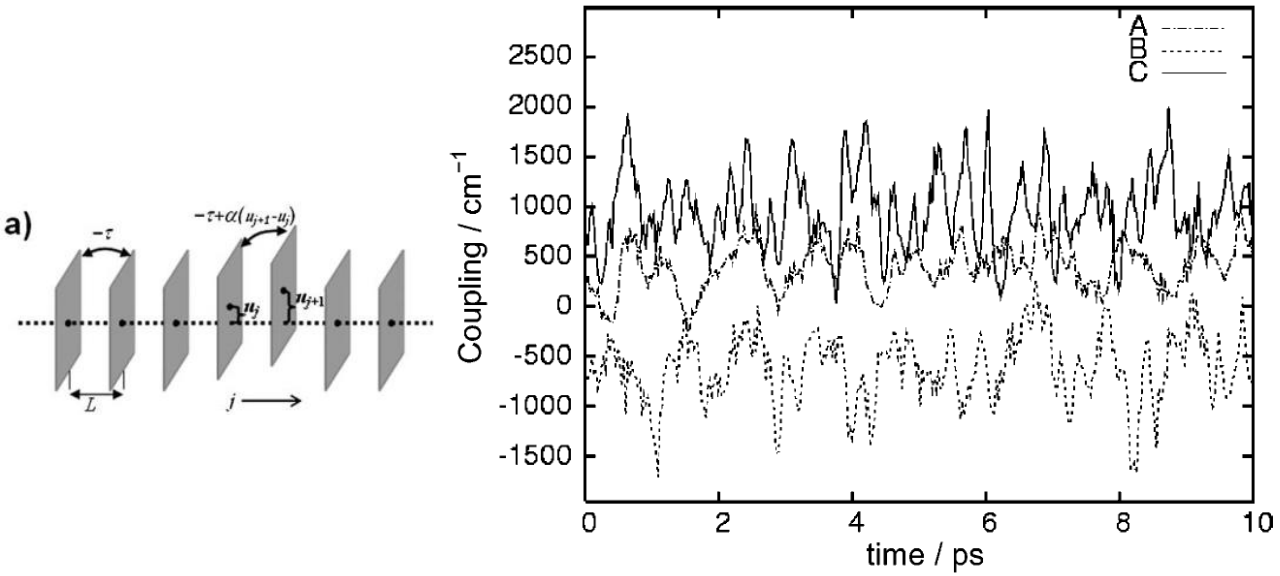


But spectroscopic fingerprints of charge localization over **few** molecules

Sirringhaus et AL. Phys. Status Solidi B 249, No. 9, 1655–1676 (2012) / DOI 10.1002/pssb.201248143

So what?

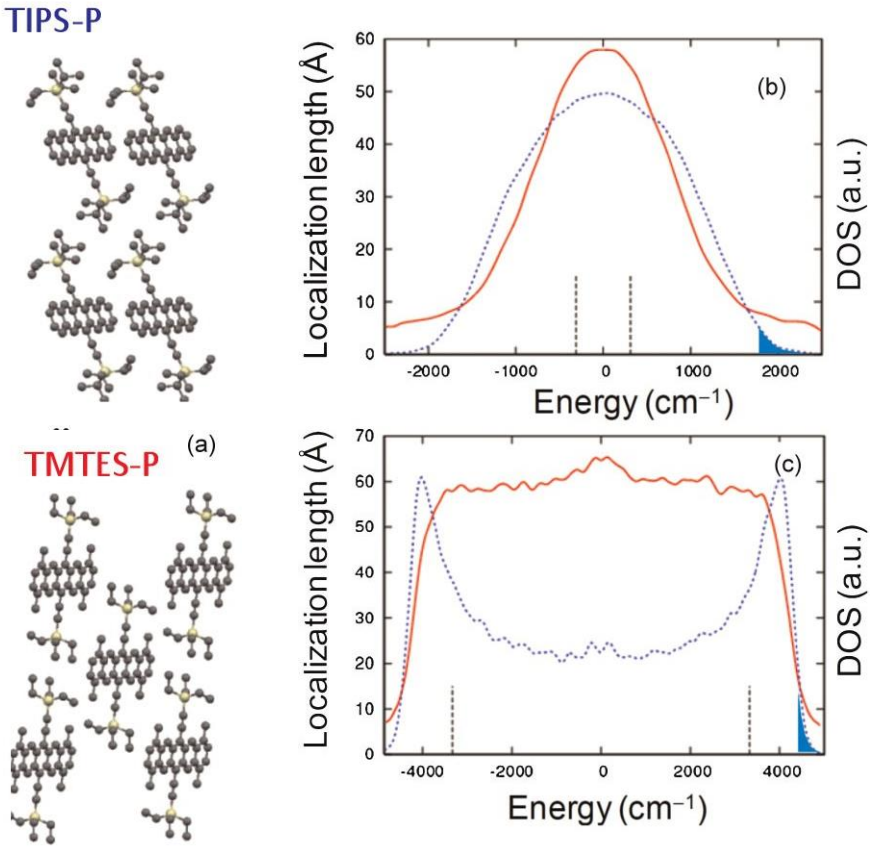
Single Crystal & polycrystals: bandlike transport?



Large transfer integral fluctuations (*non-local e/p coupling*)
-> dynamic disorder -> charge «localizaton»
*yet, **band like** temperature dependence, $\mu \propto T^{-n}$*

Troisi, *J. Phys. Chem. A* **2006,** *110,* 4065-4070, *Adv. Mater.* **2007**, *19*, 2000–2004

Our understanding so far



Wavefunction **localization** due to the dynamic disorder is **small enough** to give signature of localized states but **large enough** to allow observation of Hall effect

Sirringhaus et AL. Phys. Status Solidi B 249, No. 9, 1655–1676 (2012) / DOI 10.1002/pssb.201248143

What about high (>1cm^2/Vs) mobility polymers?

The (dis)order paradigm for high μ

Amorphous

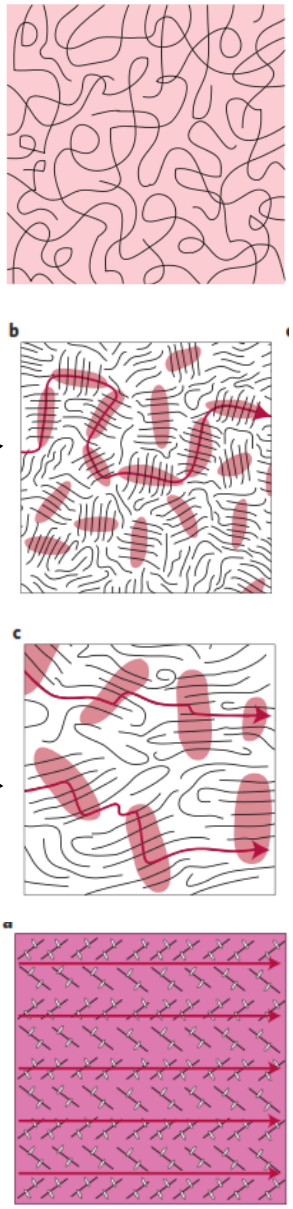
Hopping
$\mu < 10^{-1} cm^2/Vs$?
Troisi 10.1016/j.orgel.2011.08.020

Semi-amorphous

Semi-crystalline

Single crystals
(*ultrapure!*)

Dynamic localization
Troisi 2011 10.1039/c0cs00198h



aggregating

H. Sirringhaus, *Adv. Mater.*, vol. 26, no. 9, pp. 1319–35, Mar. 2014.
Venkateshvaran, et al.*Nature*, vol. 515, no. 7527, pp. 384–388, Nov. 2014.
Noriega et al Nat. Mat. 10.138/NMAT3722
V. Podzorov NATURE MATERIALS 12 NOVEMBER 2013 947

The (dis)order paradigm for high μ

Large size of molecular repeating units
and
Close π-stacking distance

Make interchain hopping
less sensitive to disorder

Amorphous

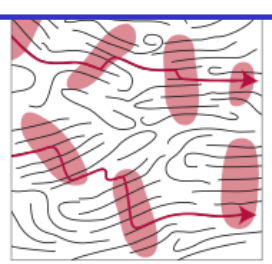
Semi-amorphous

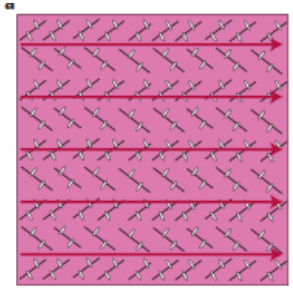
Semi-crystalline

Single crystals
(*ultrapure!*)

Dynamic localization

Troisi 2011 10.1039/c0cs00198h





ating

H. Sirringhaus, *Adv. Mater.*, vol. 26
Venkateshvaran, et al.*Nature*, vol. 5
Noriega et al Nat. Mat. 10.138/NMAT3
V. Podzorov NATURE MATERIALS 12 NOVEMBER 2013 947

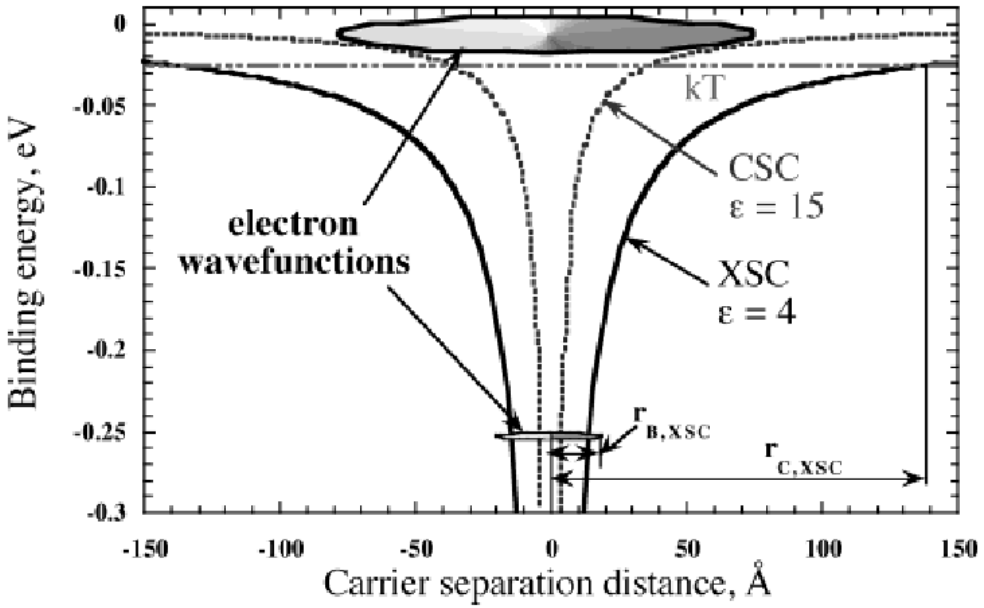
Doping

- **Interstitial**: the problem of stability for small dopants

(eg metals: Li^+, K^+, I_3^-..)

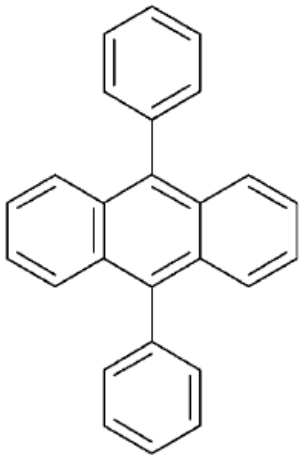
- **Molecular** doping is better
- The effect of the **dielectric constant**

(binding energy/dopant density)

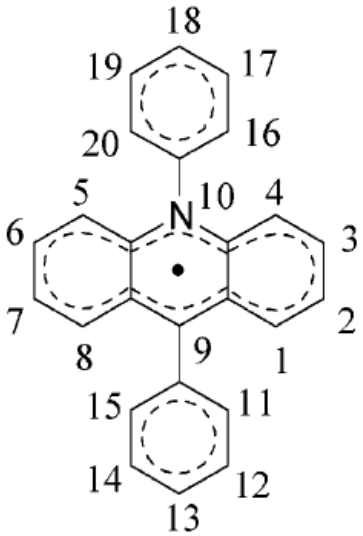


Gregg, *Chemistry of Materials*, 16, 2004, p 4586-4599

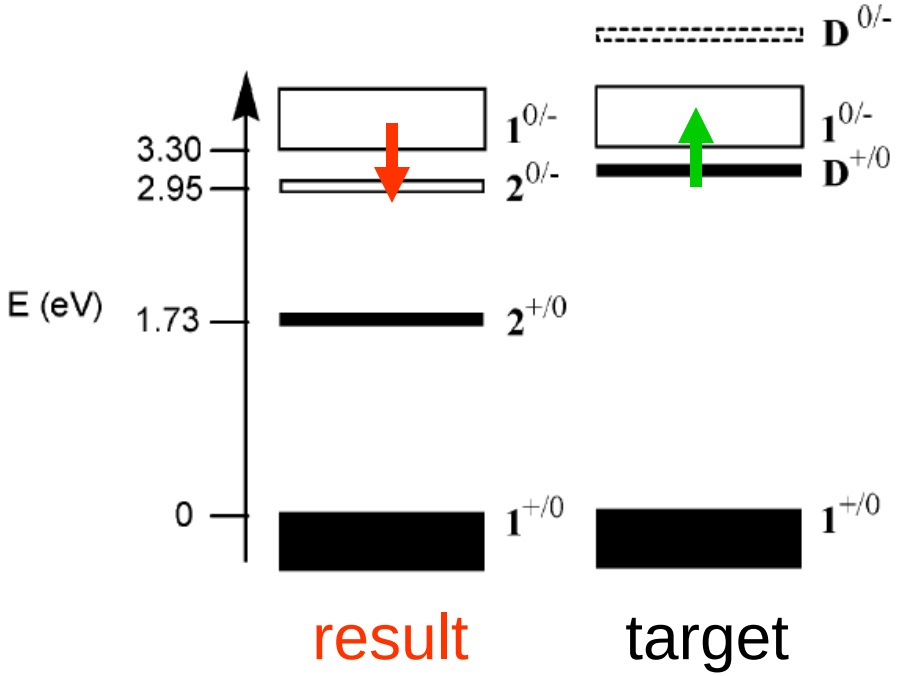
Doping:
C→N substitution *?!*



1



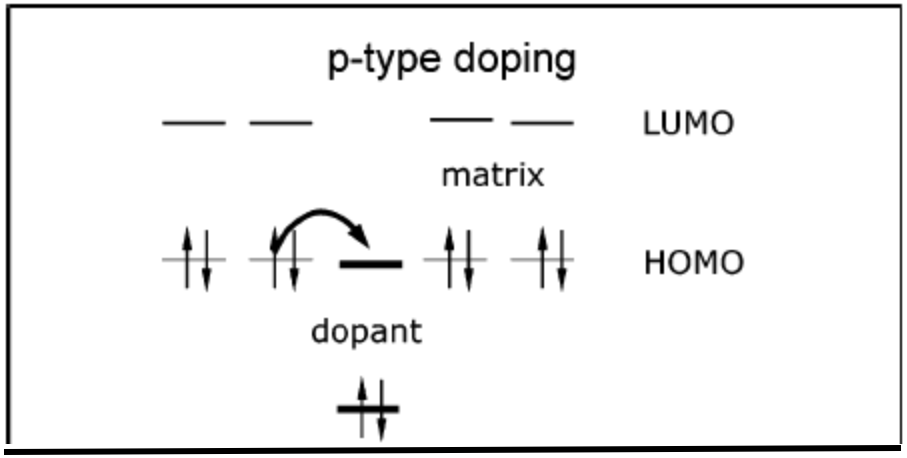
2

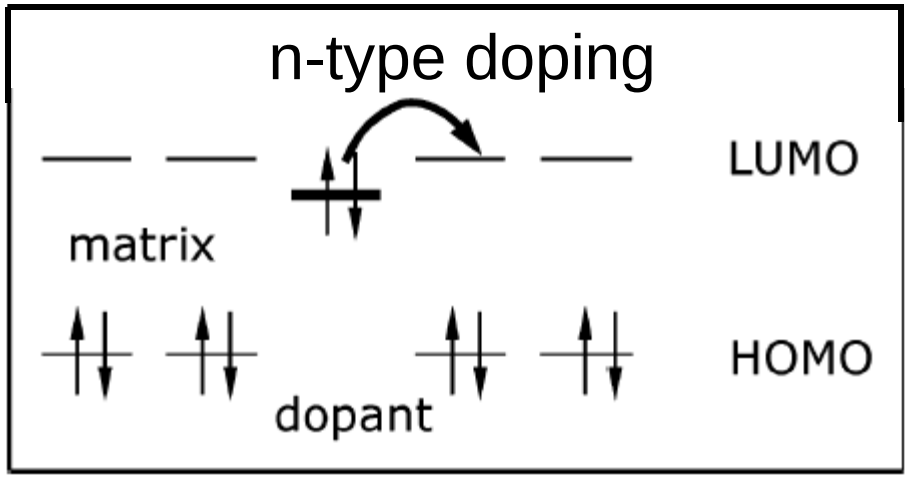


The supposed dopant acts as a trap!!!

Vaid, Chem.Mater 2003, 15, 4292

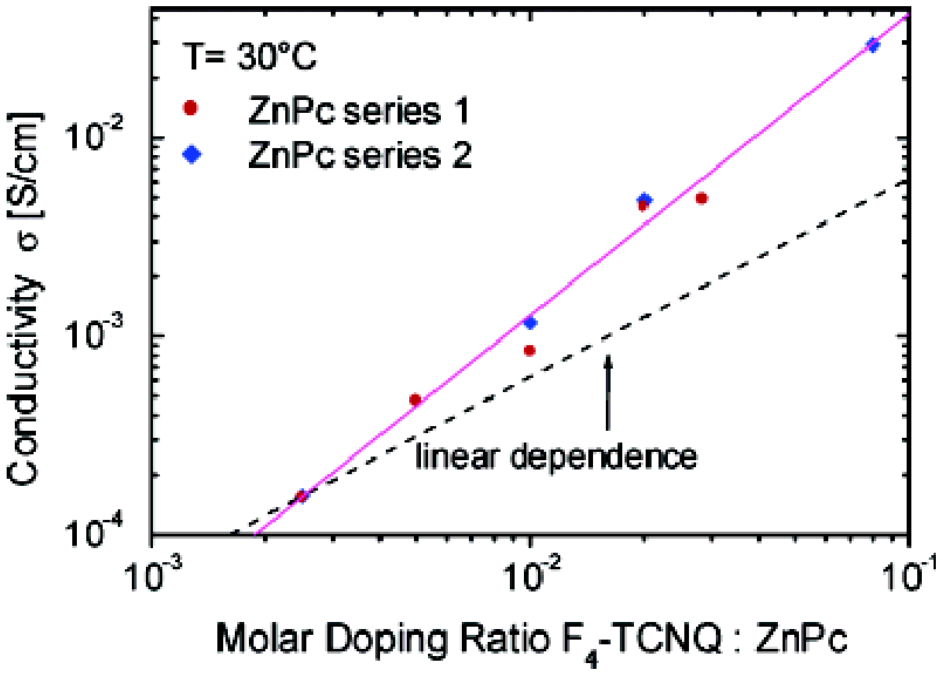
Molecular Doping(1)

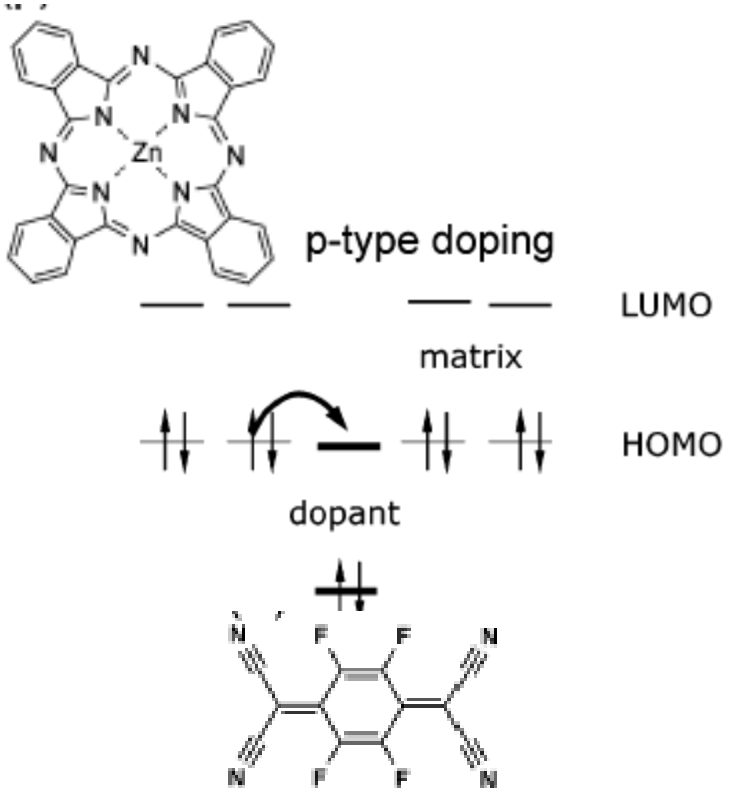




Leo et al. Chem. Rev. **2007,** 107, 1233–1271

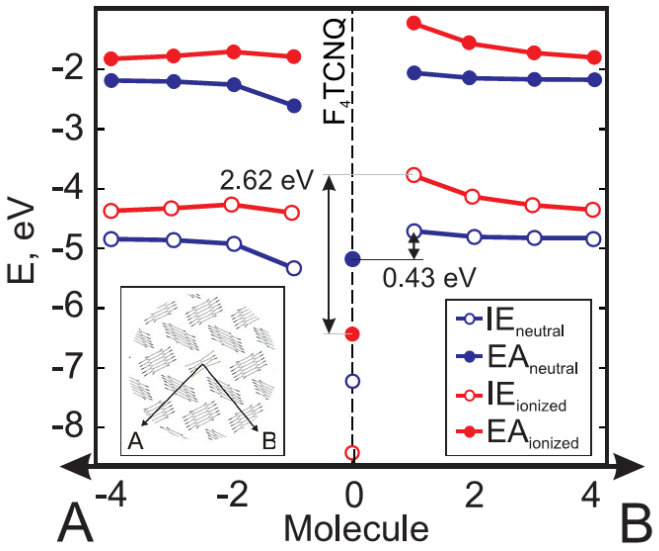
Molecular Doping(2)





Leo et al. Chem. Rev. **2007,** 107, 1233–1271

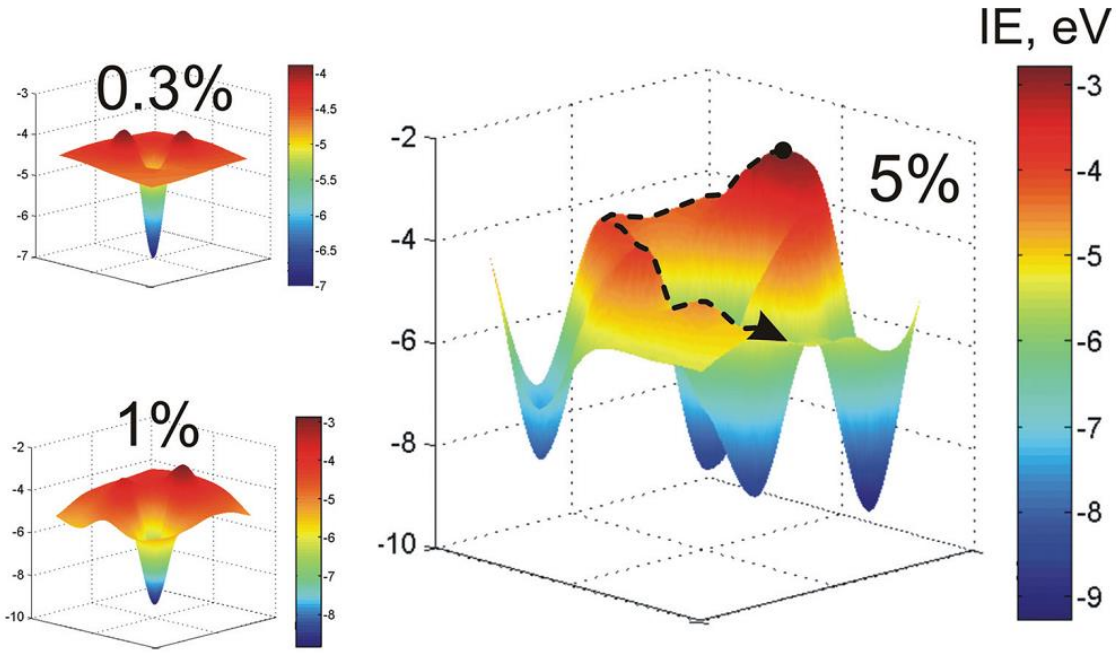
Doping: short-range interactions & doping-induced disorder



$$\rho = \rho_{\text{int}} + C \cdot N_{\text{mol}} \cdot \frac{P_{\text{ion}} \cdot P_{\text{dis}}}{1 - P_{\text{rec}}}$$

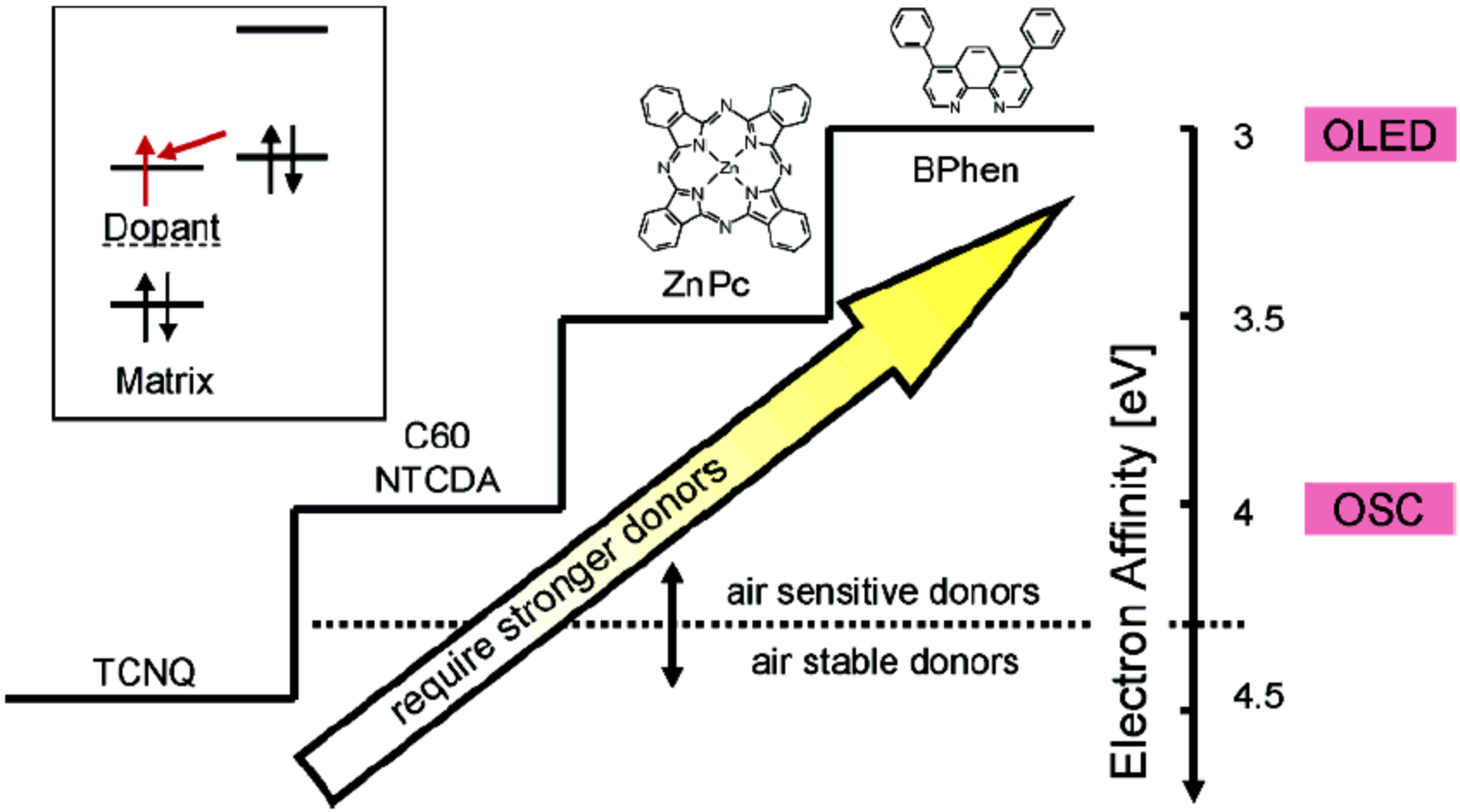
$P_{\text{dis}} \propto C$

–> ρ is superlinear on C

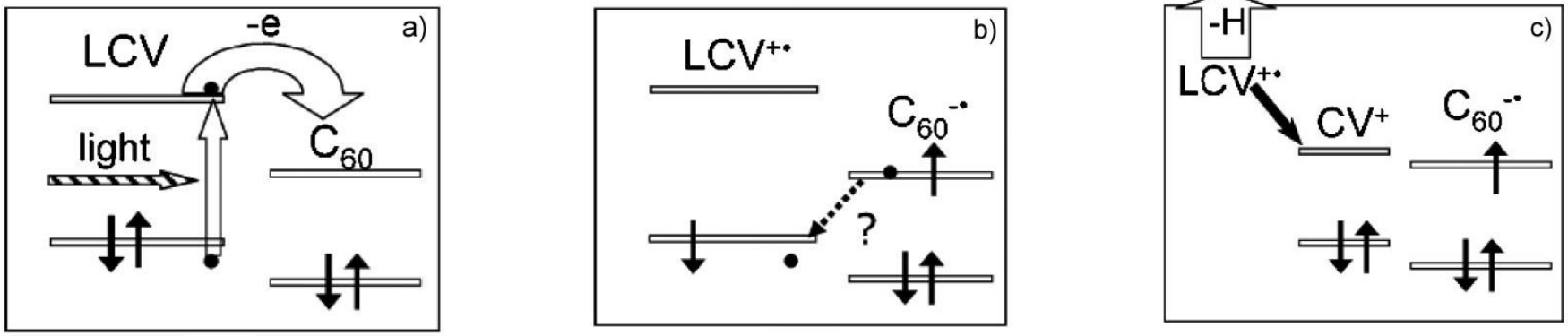


DOI: 10.1002/adma.201104269

N-type doping



N-type doping: the precursor way



Leo et al., Phys. Status Solidi A 210, No. 1, 9–43 (2013)

The End

Almost....The End

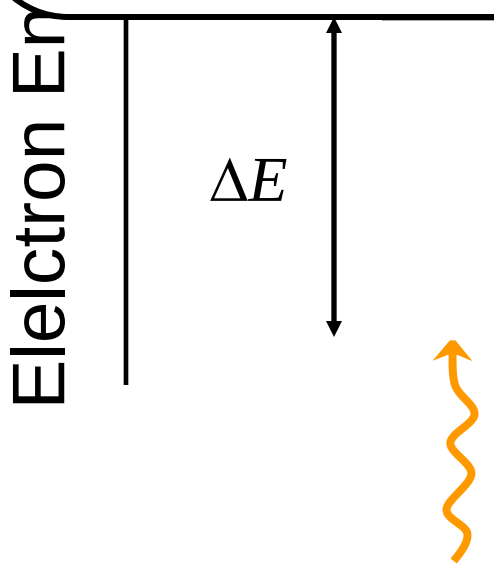
Tessler et al. Adv. Mater.2009, 21,2741–2761

Bobbert et al Phys. Status Solidi A209, 2354–2377 (2012)

Baranovskii,*Phys. Status Solidi*, vol. 251 pp. 487–525, 2014.

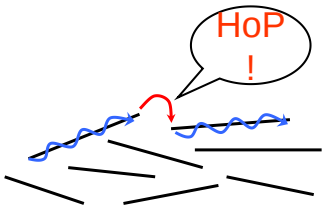
Hopping@low T

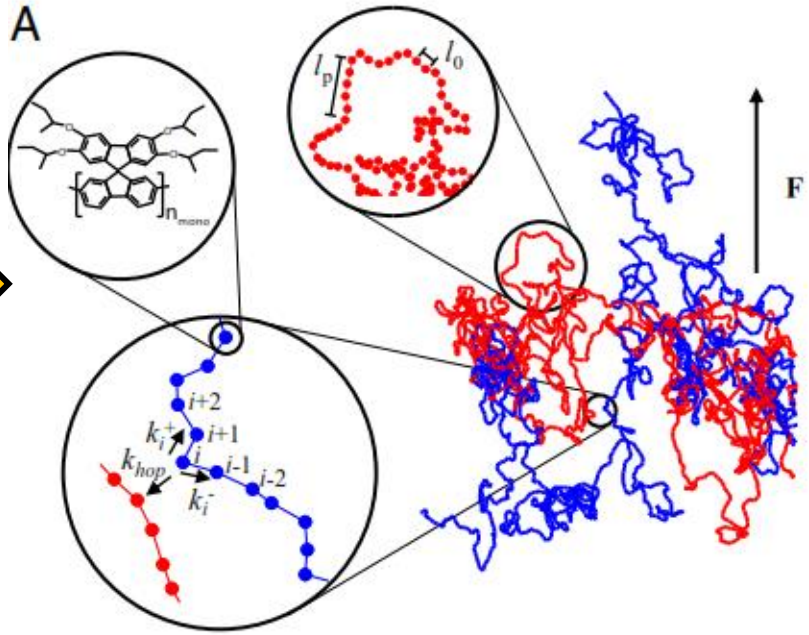
This is classical approximation,
predicting p[HOP]=0 @T=0K.
But a full treatment should take into consideration
zero-point oscillations!
See Asadi et al. 10.1038/ncomms2708

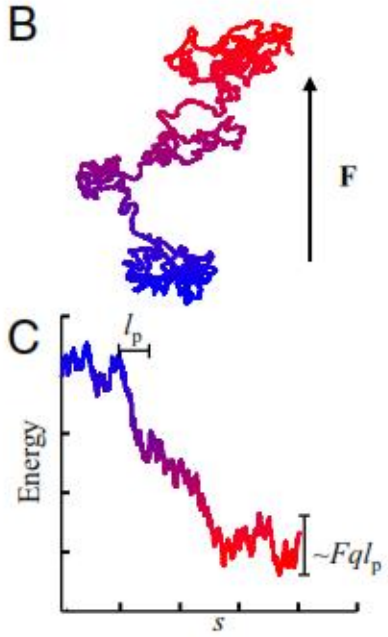


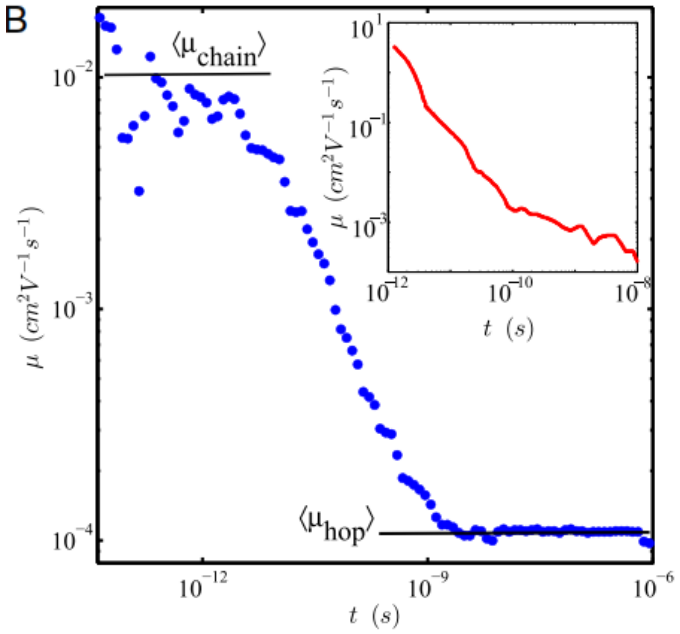
$$p[\mathrm{HOP}] \propto \exp^{-\frac{\Delta E}{\mathrm{k}T}} \exp^{-\alpha L}$$

Hopping revised: on-chain matters…





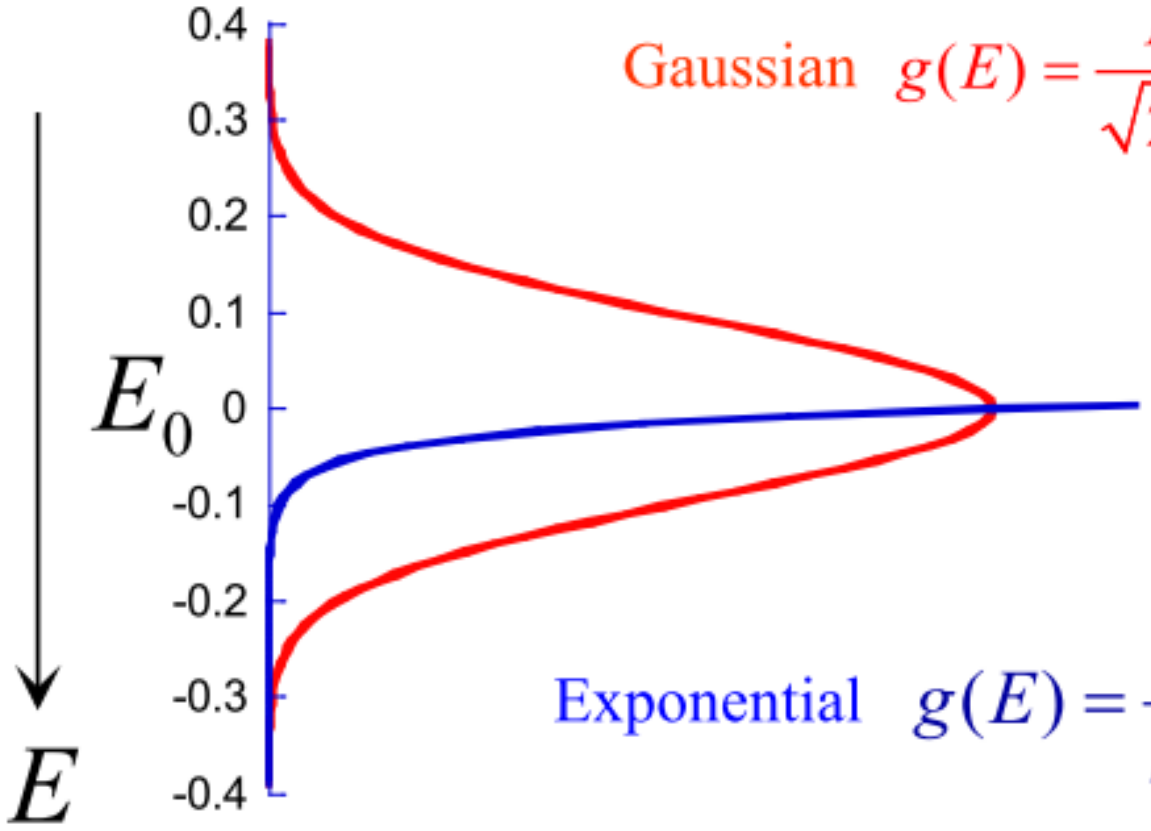




…at short timescale

Noriega et al. 10.1073/pnas.1307158110

Density of States



Gaussian $g(E) = \frac{N_V}{\sqrt{2\pi\sigma}} \exp\left[-\left(\frac{E - E_0}{\sqrt{2}\sigma}\right)^2\right]$

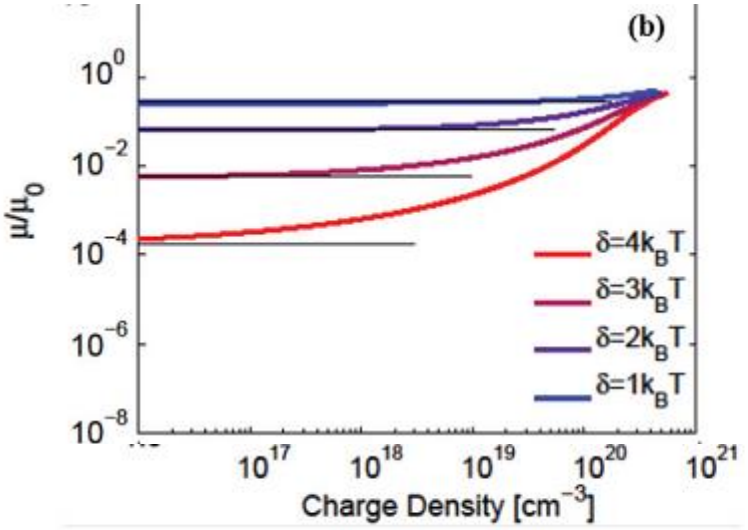
Exponential $g(E) = \frac{N_t}{kT_0} \exp\left(-\frac{E}{kT_0}\right)$

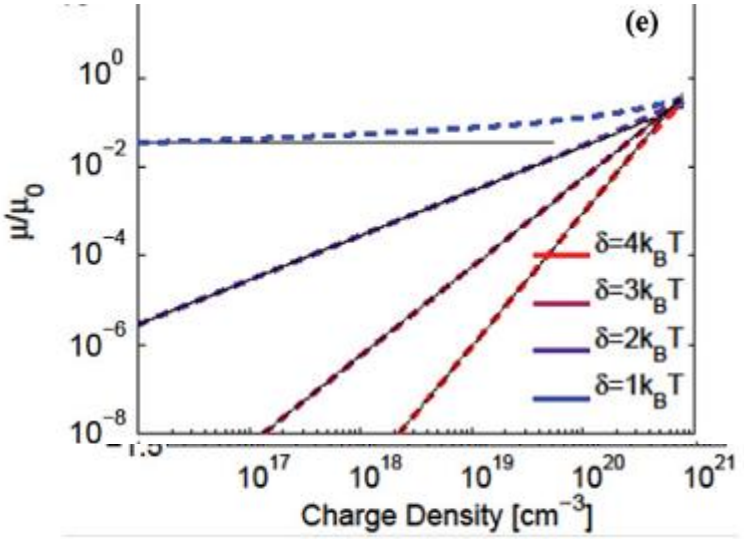
Bassler, Phys. Stat. Sol. B 175(1993) 15

(debate ongoing Vukmirovic J. Phys. Chem. B, 2011, 115 (8), pp 1792–1797

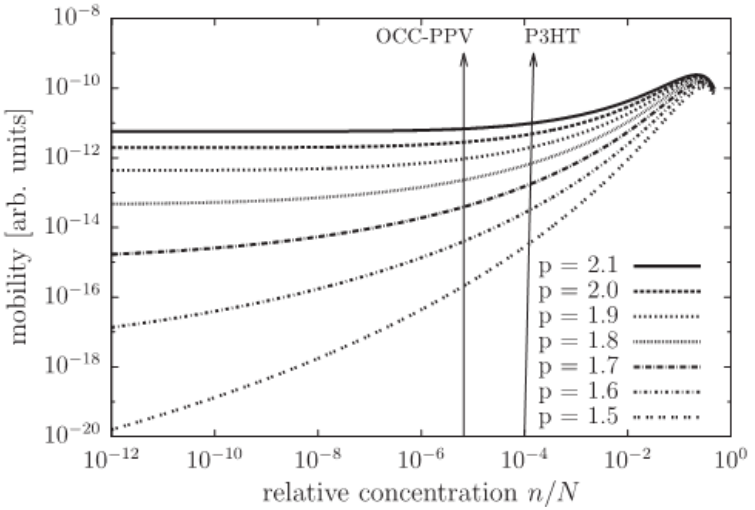
DOS: Gauss vs exp

Bredas et alPHYSICAL REVIEW B87, 195209 (2013)





In a pure exp DOS μ->0 for n->0,
Which is not experimentally found



$$g(\varepsilon) = \frac{N}{C}\exp\left[-\left(\frac{\varepsilon}{\sigma}\right)^p\right], \qquad p > 0,$$

Baranovski et al PRL108,226403 (2012