Lattice field theory of organic semiconductors

[based on ArXiv:2312.14914, to appear in Phys.Rev.Applied]

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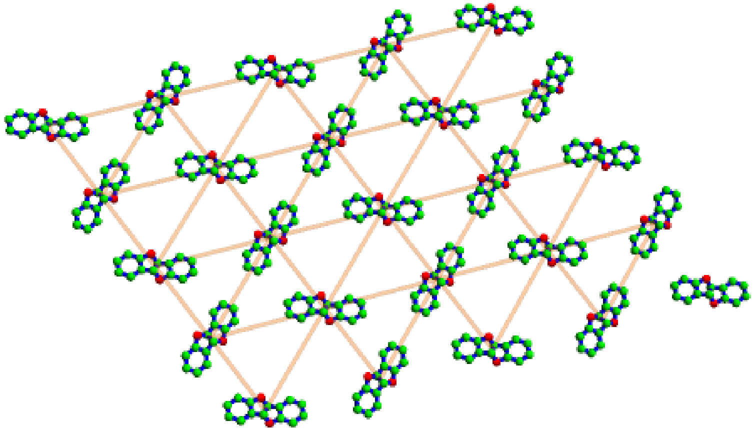
Molecular semiconductors (pentacene, rubrene)

- Promising candidates for organic-based electronics/photovoltaics
- Large device area
- 3D printable
- Recyclable, soluble

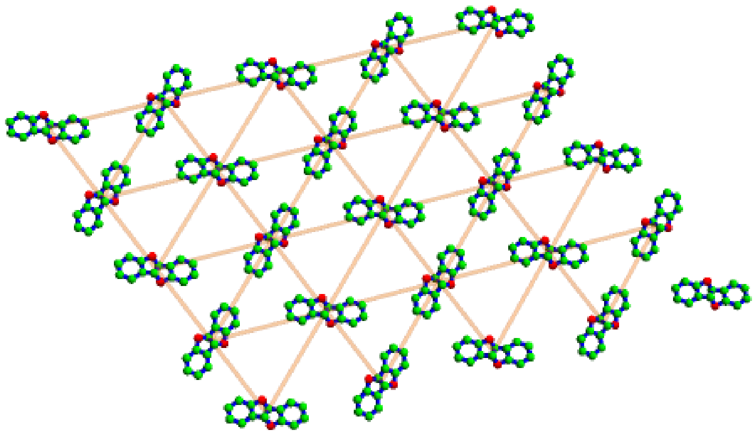


Goal: find compounds with high mobilities

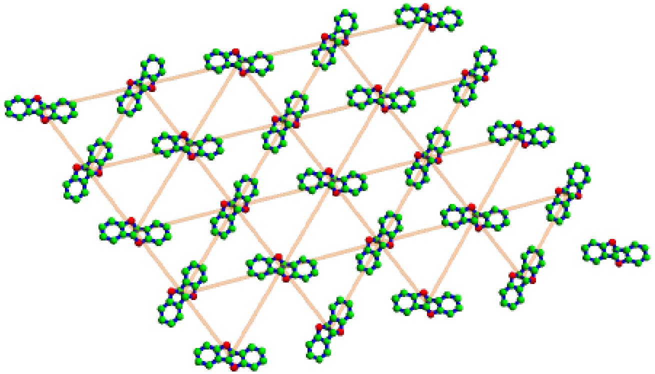
Model description

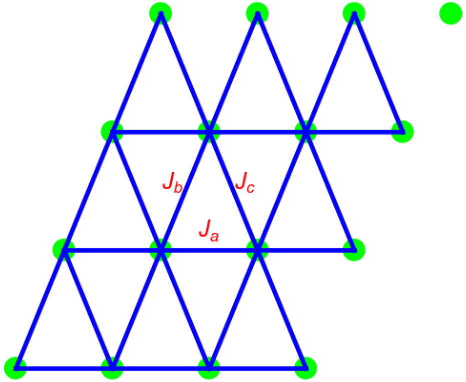
[Fratini et al., Nature Mat. 16, 998–1002 (2017)] – **reasonably good model description for ~4000 compounds:**

- **Triangular lattice, nearest-neighbor hoppings**
- **Phonons live on bonds, are independent and harmonic**
- **Linear hopping modulation**



Tight binding model





Tight-binding model on **two-dimensional triangular lattice**

$$\hat{H} = -\sum_{i,a,\sigma} J_a \left(1 - \lambda_a \hat{x}_{ia}\right) \left(\hat{c}^{\dagger}_{i,\sigma}\hat{c}_{i+a,\sigma} + \hat{c}^{\dagger}_{i+a,\sigma}\hat{c}_{i,\sigma}\right) - \mu \sum_{i,\sigma} \hat{c}^{\dagger}_{i,\sigma}\hat{c}_{i,\sigma} + \sum_{i,a} \left(\frac{1}{2m}\hat{p}^2_{ia} + \frac{m}{2}\omega_0^2 \hat{x}^2_{ia}\right)$$

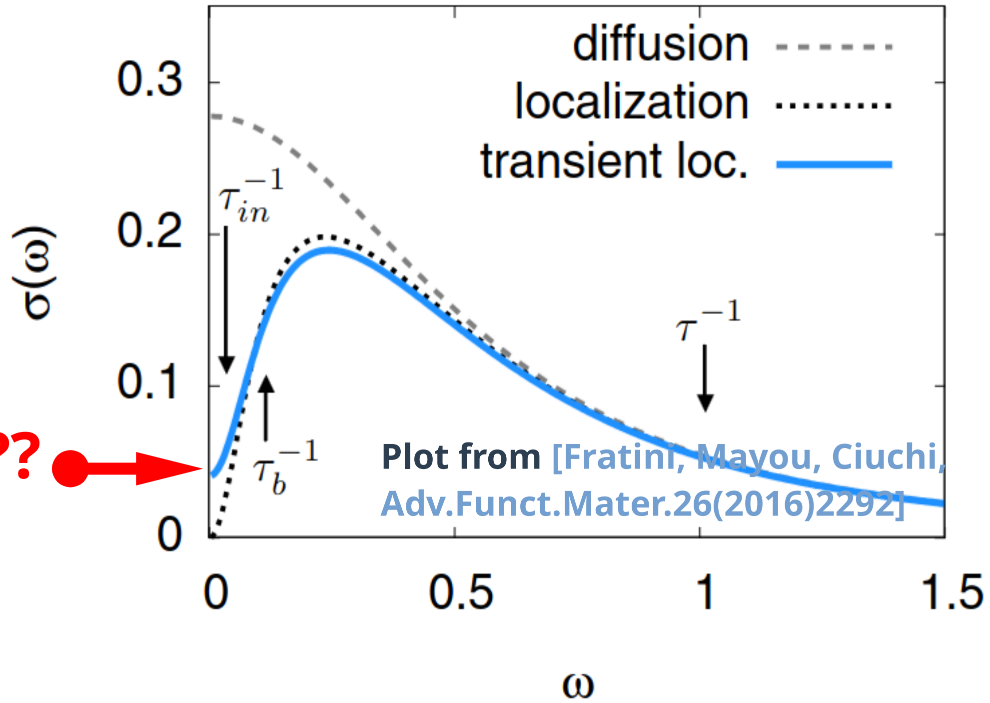
Single-particle Hamiltonian in phonon background

$$\hat{H} = \sum_{k,l,\sigma} \hat{c}^{\dagger}_{k,\sigma} h_{kl}\left(\hat{x}_{ia}\right) \hat{c}_{l,\sigma} + \hat{H}_B\left(\hat{p}_{ia}, \hat{x}_{ia}\right)$$

Dynamical thermal disorder

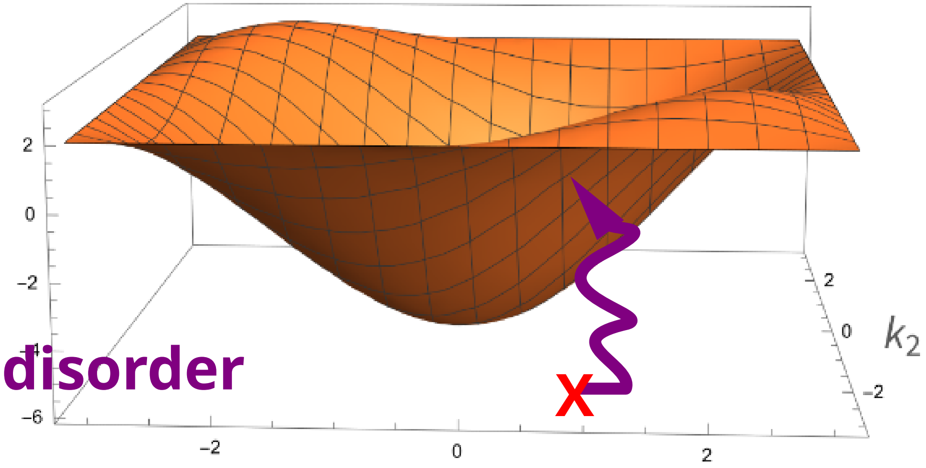
- Typical phonon ω_0~0.005 eV
- ω_0/T ~ 0.2 – nearly classical (room temp. T~0.025 eV)
- Transfer integrals/hopping amplitudes J~0.1 eV
- Disorder modulation ΔJ/J ~ 0.5
- Strong dynamical disorder
- No intrinsic small parameter, neither hopping nor band theory work

Optical conductivity



Plot from [Fratini, Mayou, Ciuchi, Adv.Funct.Mater.26(2016)2292]

- "Free limit": no AC conductivity at all
- "Static phonons": no DC conductivity,
- Anderson localization (1D/2D)



Charge transport driven by dynamical disorder

Numerical approaches so far

Quite similar to methods for real-time simulations of glasma/early-stage HIC

- **Ehrenfest dynamics** (fermions fully quantum, bosons classical)

  [Troisi, Orlandi PRL 96 (2006) 086601]

- **Surface hopping** (FOB-SH)

  [J. Spencer, F. Gajdos, J. Blumberger, J. Chem. Phys. 2016, 145, 064102]

- **Relaxation time approximation**

  [Fratini, Mayou, Ciuchi]

- **Quantum Monte-Carlo** (Worldline + DiagMC) in 1D

  [Mischenko et al., PRL 114 (2015) 146401]

No first-principle approaches for 2D so far!

Quantum Monte-Carlo: path integral

$$\mathcal{Z} = \int \mathcal{D}x_{ia}(\tau) \left[\det\left(I + \mathcal{T}\exp\left(-\int_0^\beta d\tau\, h\left(x_{ia}(\tau)\right)\right)\right)\right]^{N_\sigma} \times$$

$$\times \exp\left(-\int_0^\beta d\tau \left(\frac{m}{2}\dot{x}_{ia}^2(\tau) + \frac{m\,\omega_0^2}{2}x_{ia}^2(\tau)\right)\right)$$

Euclidean (imaginary) time

Time-ordered exponent

Single-particle Hamiltonian background of phonon fields

Phonon field (nuclei displacements)

Euclidean action of phonon fields

$$\mathcal{U}_E(\tau_1, \tau_2) := \mathcal{T}\exp\left(-\int_{\tau_1}^{\tau_2} d\tau\, h\left(x_{ia}(\tau)\right)\right)$$

Physical observables

Electric current operator

$$\hat{\mathcal{J}}_a = -i \sum_{i,\sigma} J_a \left(1 - \lambda_a \hat{x}_{ia}\right) \left(\hat{c}^\dagger_{i,\sigma} \hat{c}_{i+a,\sigma} - \hat{c}^\dagger_{i+a,\sigma} \hat{c}_{i,\sigma}\right) = \sum_{k,l} \hat{c}^\dagger_k \left(\mathcal{J}_a\right)_{kl} \hat{c}_l$$

Current-current correlators

$$G^E_{ab}\left(\tau\right) = \mathcal{Z}^{-1} \operatorname{Tr}\left(\hat{\mathcal{J}}_a e^{-\tau \hat{H}} \hat{\mathcal{J}}_b e^{-(\beta-\tau)\hat{H}}\right)$$

$$G^E_{ab}\left(\tau\right) = \mathcal{Z}^{-1} \int \mathcal{D}x_{ia}\left(\tau\right) \mathcal{W}_E\left[x_{ia}\left(\tau\right)\right] \operatorname{Tr}\left(\mathcal{J}_a \mathcal{G}\left(0,\tau\right) \mathcal{J}_a \mathcal{G}\left(\tau,\beta\right)\right)$$

Single-particle current operator

Fermionic Green's functions

$$\mathcal{G}\left(\tau_1,\tau_2\right) = \mathcal{U}_E\left(\tau_1,\tau_2\right) - \mathcal{U}_E\left(\tau_1,\beta\right)\mathcal{U}_E\left(\beta,0\right)\mathcal{U}_E\left(0,\tau_2\right) + \ldots \simeq$$
$$\simeq \frac{\mathcal{U}_E\left(\tau_1,\tau_2\right)}{I + \mathcal{U}_E\left(0,\beta\right)}$$

Green-Kubo relations for optical conductivity

$$G^E_{ab}\left(\tau\right) = \hbar \int_0^{+\infty} \frac{dw}{2\pi} \frac{2w \cosh\left(w\left(\tau - \beta/2\right)\right)}{\sinh\left(\beta\, w/2\right)} \sigma\left(w\right)$$

Limit of low charge carrier densities

- We send $\mu \to +\infty$
- Carrier concentration $\langle n \rangle \sim e^{-\mu/T}$
- Fermion determinant does not depend on phonons

$$\mathcal{U}_E(0,\beta) \sim e^{-\beta\mu}$$

$$\left[\det\left(I + \mathcal{U}_E(0,\beta)\right)\right]^{N_\sigma} = 1 + O\left(e^{-\beta\mu}\right)$$

Path integral weight becomes a Gaussian functional of $x_{ia}(\tau)$:

$$\mathcal{W}\left[x_{ia}(\tau)\right] = \exp\left(-\int_0^\beta d\tau \left(\frac{m}{2}\dot{x}_{ia}^2(\tau) + \frac{m\,\omega_0^2}{2} x_{ia}^2(\tau)\right)\right) + O\left(e^{-\beta\mu}\right)$$

Can be sampled **without any autocorrelations**! (Ideal case for normalizing flow!!!)

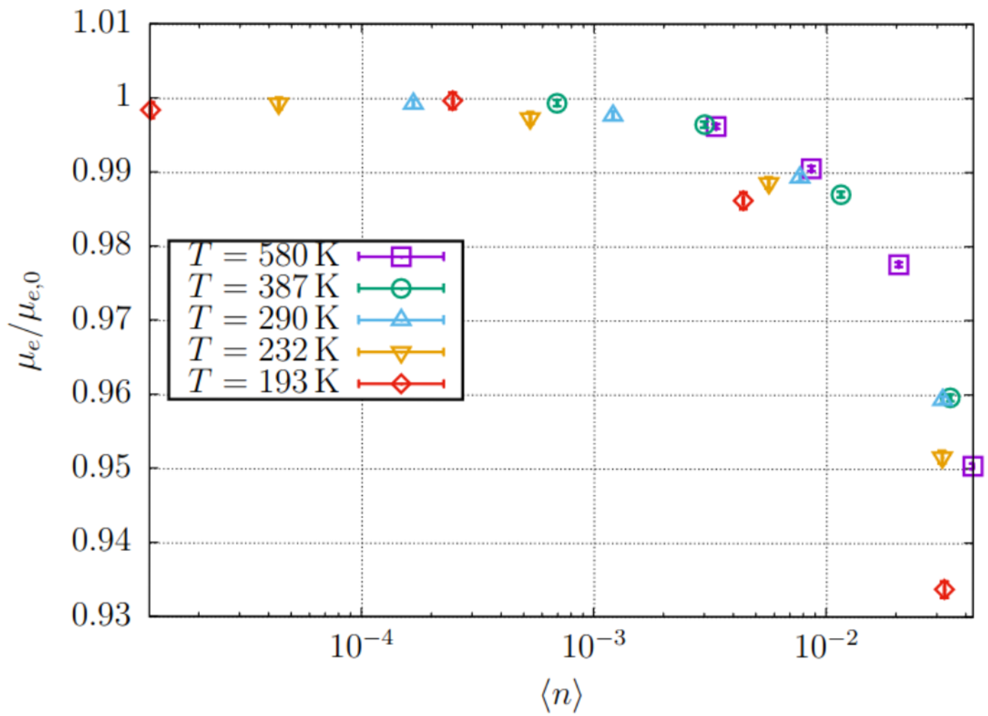
Current-current correlators saturated by single-particle states

$$G_{ab}^E(\tau) = \mathcal{Z}^{-1}\int \mathcal{D}x_{ia}(\tau)\, \mathcal{W}_E\left[x_{ia}(\tau)\right] \mathrm{Tr}\left(\mathcal{J}_a \mathcal{U}_E(0,\tau)\; \mathcal{J}_a \mathcal{U}_E(\tau,\beta)\right) + O\left(e^{-2\beta\mu}\right)$$

$$\mathcal{U}_E(\tau_1,\tau_2) \sim e^{-(\tau_2-\tau_1)\mu}$$

Conductivity $\sigma \sim e^{-\mu/T}$ density $\langle n \rangle \sim e^{-\mu/T}$ → mobility $\mu_e = \sigma / \langle n \rangle$ finite

When can single-particle picture be trusted?



[Characteristic parameters for OSs]

- Charge carrier concentration ***<n>~0.01*** (per unit cell) for most realistic compounds in transistor applications

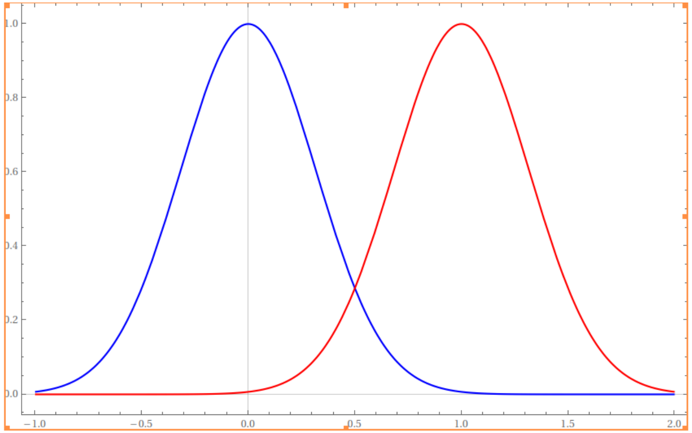
Noise reduction and log-normal distribution

$$G^E_{ab}(\tau) = \mathcal{Z}^{-1} \int \mathcal{D}x_{ia}(\tau)\, \mathcal{W}_E[x_{ia}(\tau)]\, \mathrm{Tr}\left(\mathcal{J}_a \mathcal{U}_E(0,\tau)\, \mathcal{J}_a \mathcal{U}_E(\tau,\beta)\right) + O\left(e^{-2\beta\mu}\right)$$

~Exp(-X²) ~Exp(-a X)

$$P(x) \sim e^{-x^2/2}, \quad y = e^{\alpha x}$$

$$P(y) \sim y^{-1} \exp\left(-\frac{1}{2\alpha^2}\log^2(y)\right)$$



[Endres,Kaplan,Lee,Nicholson,ArXiv:1106.0073]

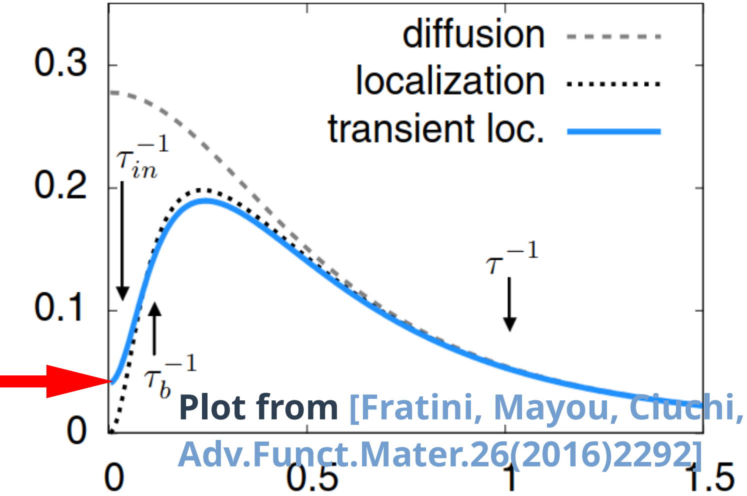
Sampled using HMC [further tricks in J. Ostmeyer's talk]

$$G^E_{ab}(\tau) = \mathcal{Z}^{-1} \int \mathcal{D}x_{ia}(\tau)\, \mathcal{W}_E[x_{ia}(\tau)]\, \mathrm{Tr}\left(\mathcal{U}_E(0,\beta)\right) \frac{\mathrm{Tr}\left(\mathcal{J}_a \mathcal{U}_E(0,\tau)\, \mathcal{J}_b \mathcal{U}_E(\mathcal{U}_E(0,\tau))\right)}{\mathrm{Tr}\left(\mathcal{U}_E(0,\beta)\right)}$$

Observable

Static approximation and **beyond**...

- ***w_0/T ~ 0.2***, path integral dominated by **static, τ-independent** phonon configurations
- **Quantum fermions** propagating in **static boson background**
- **Spectral function exactly calculable** from single-particle Hamiltonian ***$h[x_{i\alpha}]$ ($O(V^3)$)***
- **We know that static limit is not enough – do we see the difference in QMC?**



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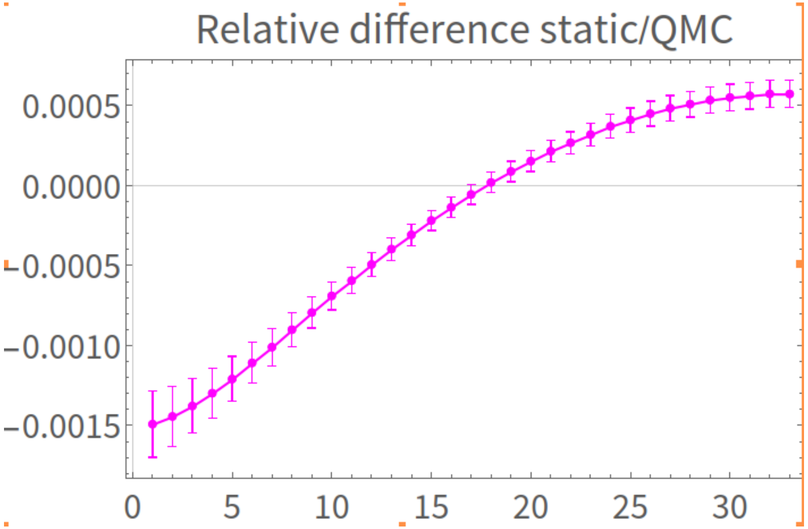
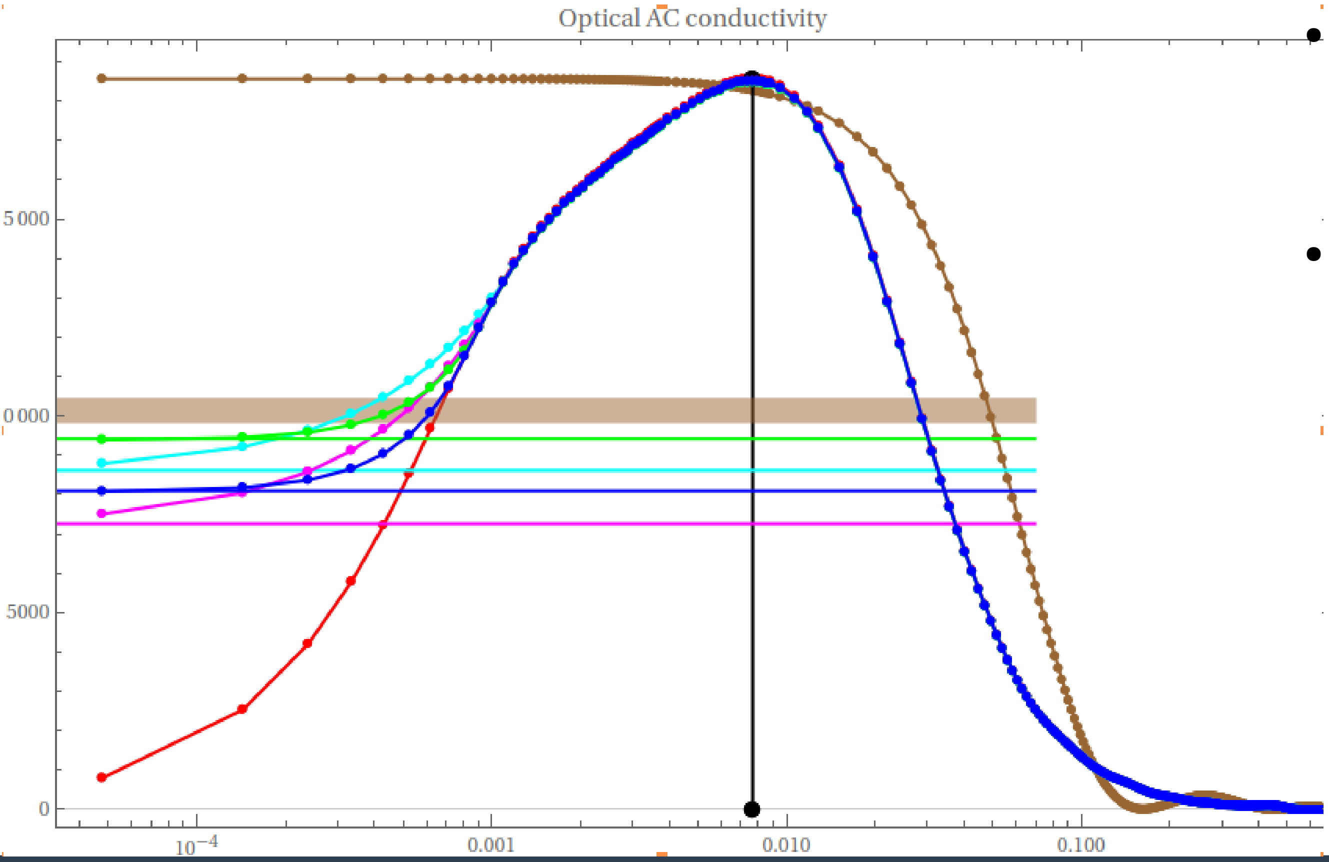


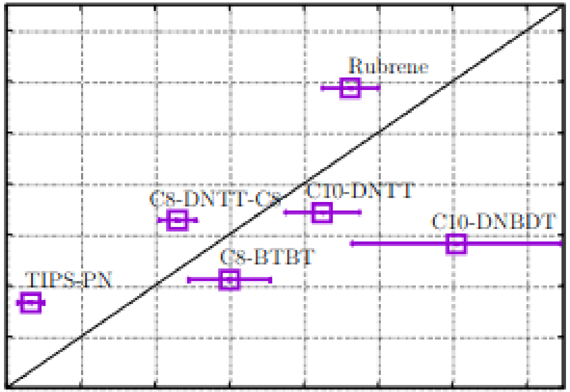
Contribution to **$G_E(\tau)$**

$$\sim \exp\left(-\frac{\pi T}{w}\right)$$

Static approximation and **beyond**...

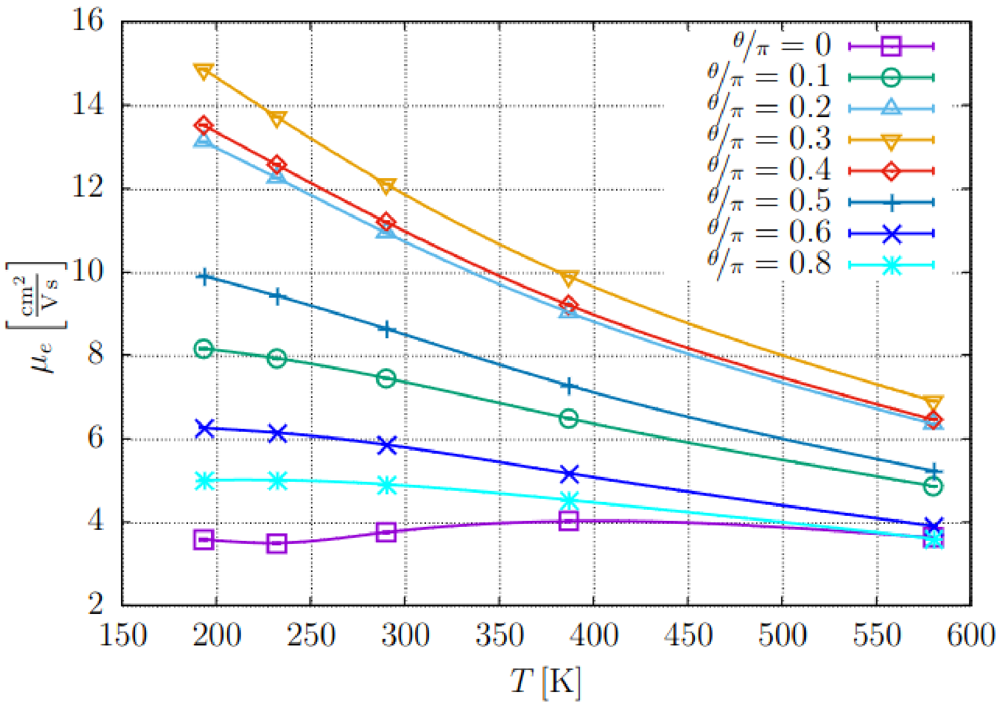


- **Precision** just enough to start tackling the **low-frequency region**
- Good agreement with **experimental data** (often imprecise/controversial)



Temperature dependence of mobility

$$J_1 = J\cos\theta \text{ and } J_2 = J_3 = J/\sqrt{2}\sin\theta$$



Power-law decay:

signature of **band transport picture**

Exponential suppression:

Anderson localization,

thermally activated transport

Monte-Carlo data consistent

with **power-law decay**

Conclusions

- **Hybrid Monte-Carlo**: computationally cheap first-principle approach to simulate organic semiconductors
- Range of **parameters is very favorable** for HMC simulations (in contrast to **superconductor physics** etc.)
- Extremely high precision for current-current correlators allows to tackle the physics of slow dynamical disorder

Outlook

- **Static approximation** is also good for current-current correlators in **high-T lattice QCD** – can we use it to improve spectral function reconstruction?