Fragment orbital-based surface hopping (FOB-SH): Method, Implementation, Application

Jochen Blumberger

University College London
Department of Physics and Astronomy

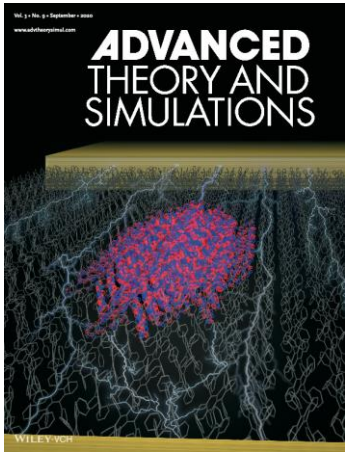
Vista Seminar Series

22.10.2020

Content

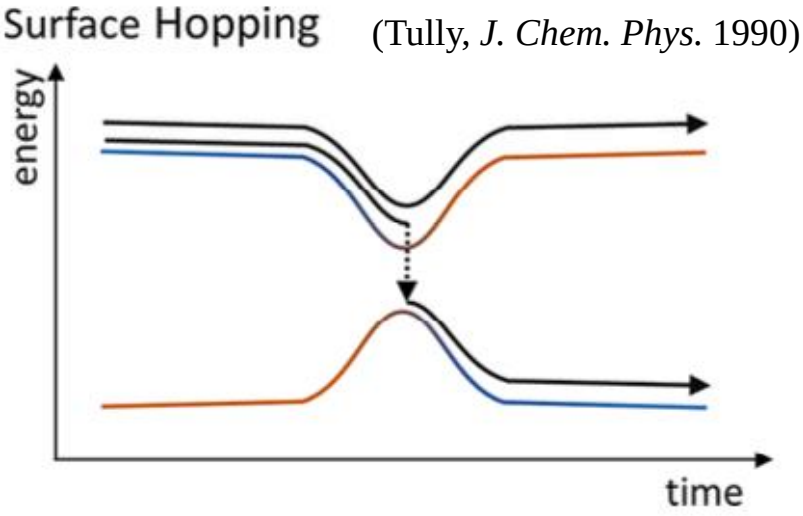
- FOB-SH: a tool for simulating electronic transport processes in truly nanoscale molecular materials

- Application to charge transport in organic crystals and the emergence of large ``flickering'' polarons



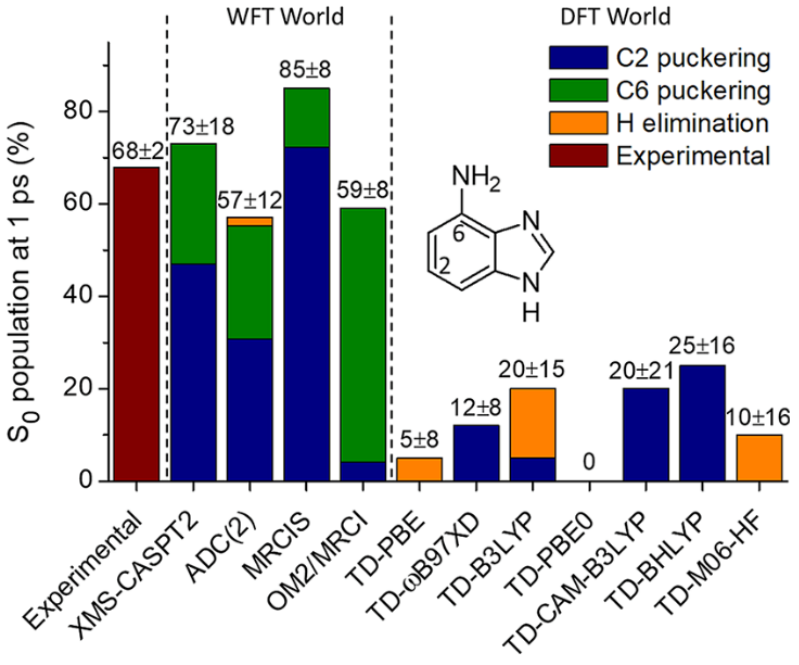
- Tricks of the Trade: importance of decoherence correction, trivial crossing detection and all that

Workhorse for photochemistry



(Tully, *J. Chem. Phys.* 1990)

Crespo-Otero and Barbatti
Chem. Rev. 118, 7026 (2018)



But: ad-hoc/intuitive, no nuclear tunneling,….

Challenge 1: Ascending (another) Jacob's ladder

.

.

.

Multiconfigurational time-dependent Hartree (Meyer,…)

(Classical limit of) Exact factorisation of molecular wavefunction (Gross,…)

Ab-initio multiple spawning (Martinez,…)

Ring-polymer MD with non-adiabatic transitions (T. Miller,…)

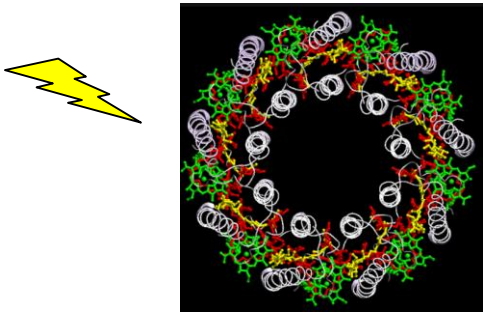
Fewest switches surface hopping (Tully,…)

Ehrenfest dynamics (Ehrenfest)

Challenge 2 (this talk): Going bigger

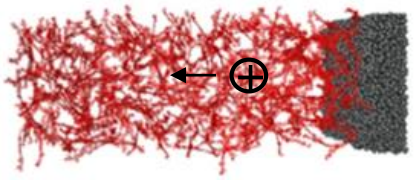
Non-adiabatic dynamics at the true nanoscale (> 5 nm):

Light harvesting



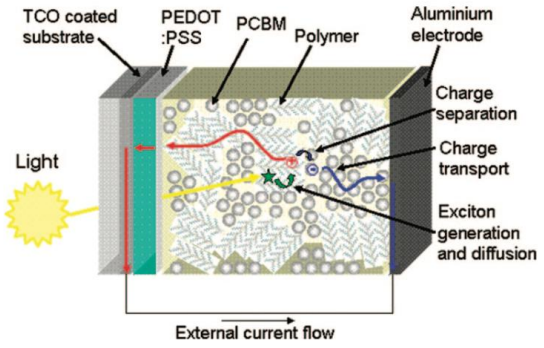
Energy transfer

Organic Transistors



Charge transport

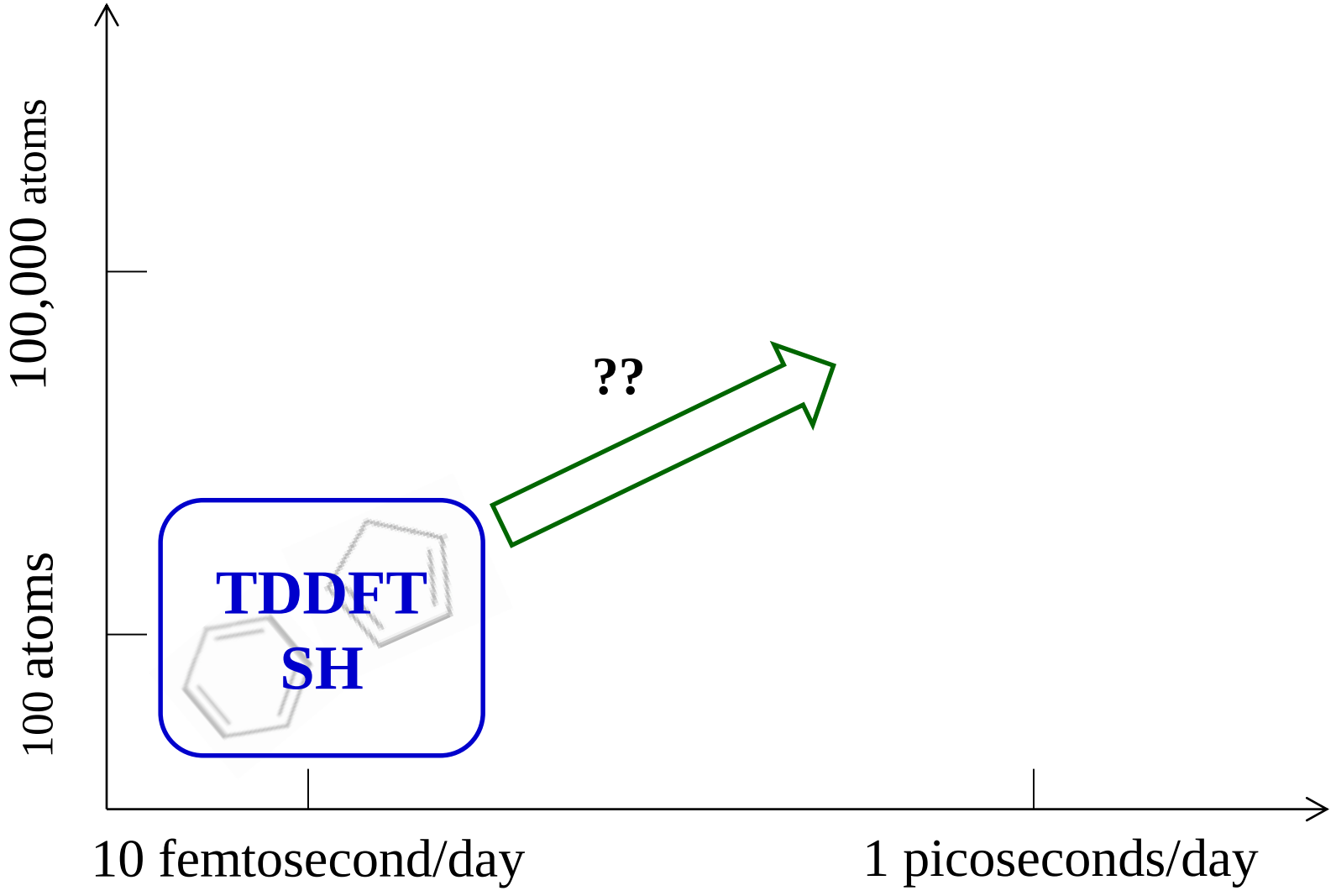
Solar Cells



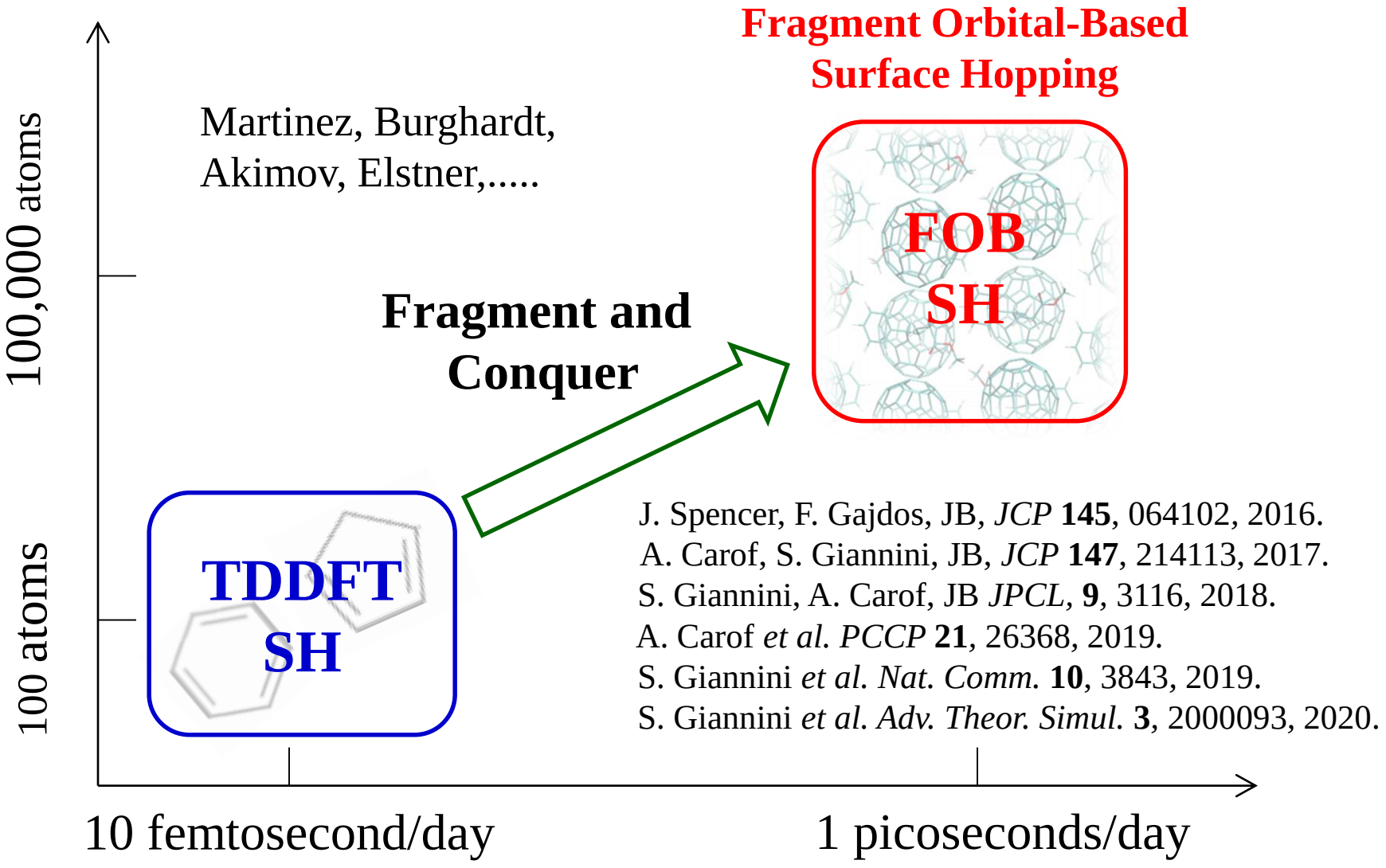
Exciton dissociation to charges, recombination

Electronic processes can be strongly delocalized in space (no QM/MM) and non-periodic (no periodic supercells)

Molecular → True Nanoscale: How?



Molecular → True Nanoscale



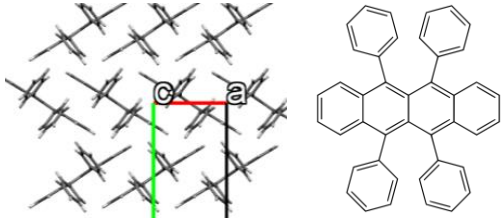
J. Spencer, F. Gajdos, JB, *JCP* **145**, 064102, 2016.
A. Carof, S. Giannini, JB, *JCP* **147**, 214113, 2017.
S. Giannini, A. Carof, JB *JPCL*, **9**, 3116, 2018.
A. Carof *et al. PCCP* **21**, 26368, 2019.
S. Giannini *et al. Nat. Comm.* **10**, 3843, 2019.
S. Giannini *et al. Adv. Theor. Simul.* **3**, 2000093, 2020.

FOB-SH implemented for:

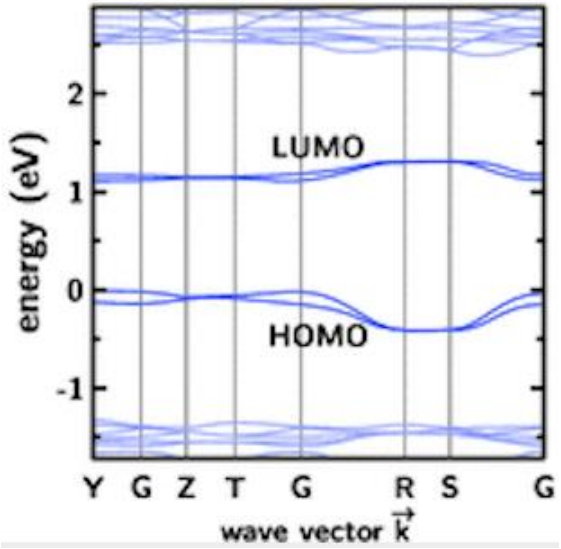
- Charge transport in molecular materials (this talk)
- Exciton transport in molecular materials (upcoming VISTA talk by Samuele Giannini(?))
- Exciton dissociation and charge recombination at nanoscale materials interfaces (in progress)

Charge transport in molecular materials

DFT band structure



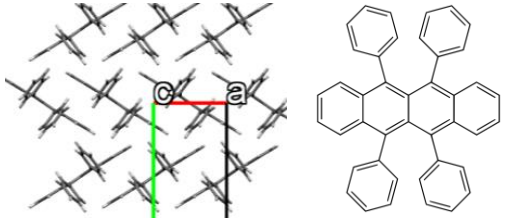
rubrene



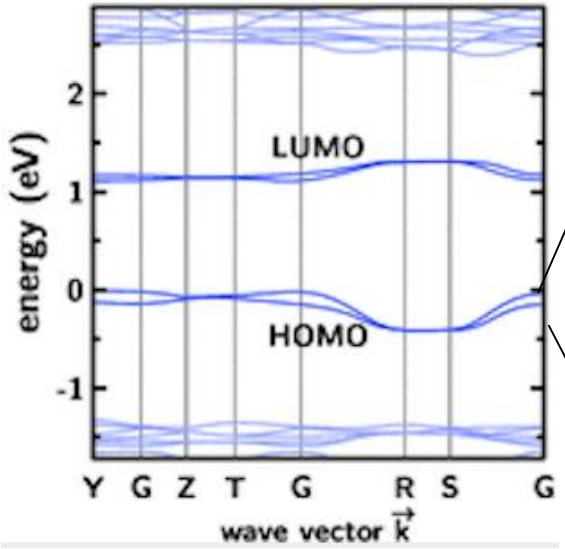
→ narrow bands

Charge transport in molecular materials

DFT band structure

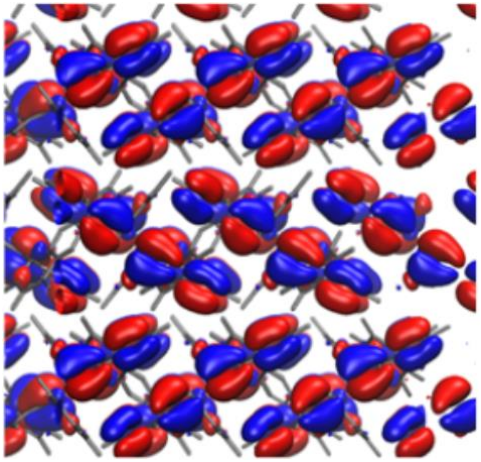


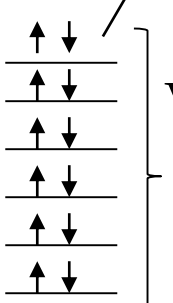
rubrene



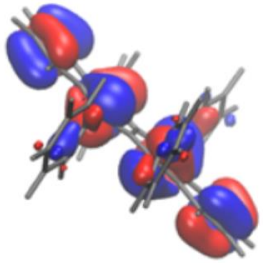
→ narrow bands

Valence Band (VB)



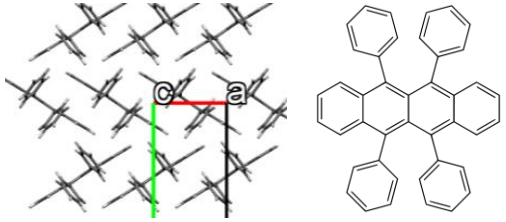


VB ≃ linear combinations of HOMOs

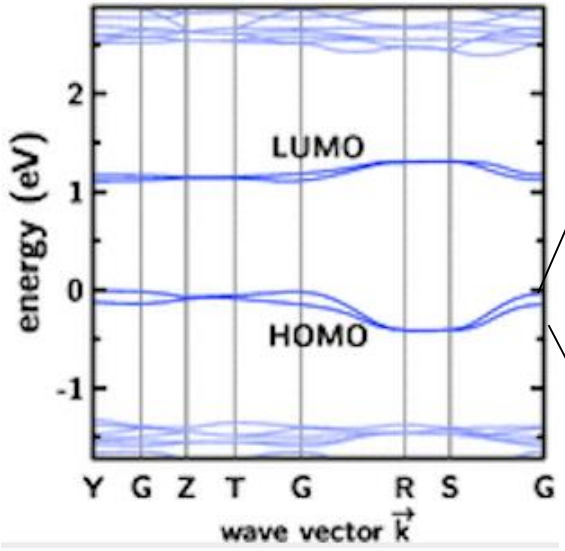


Charge transport in molecular materials

DFT band structure

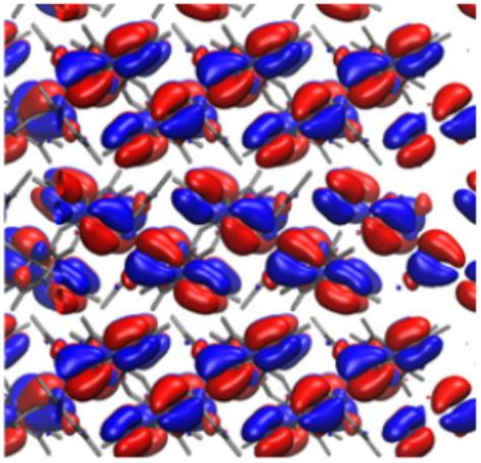


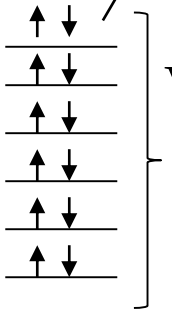
rubrene



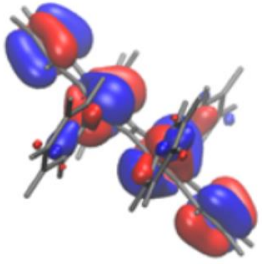
→ narrow bands

Valence Band (VB)

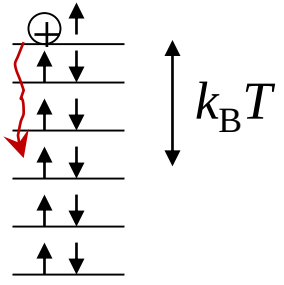




VB ≃ linear combinations of HOMOs



Hole Transport in VB



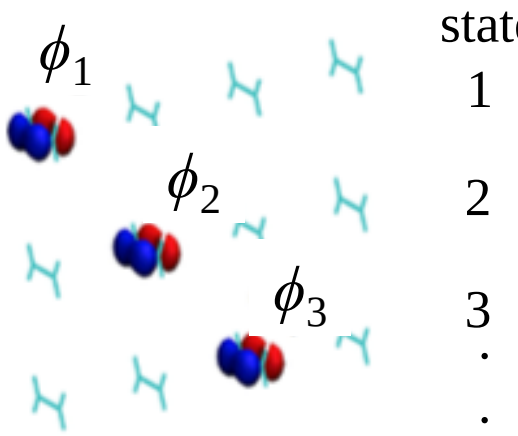
Non-adiabatic dynamics of hole in valence band

FOB-SH for charge transport

JCP **145**, 064102 (2016), *JCP* **147**, 214113 (2017), *JPCL* **9**, 3116 (2018), *PCCP* **21**, 26368 (2019)

electron hole

State basis of HOMO orbitals



Hole wavefunction:

$$\psi(\mathbf{r},t) = \sum_k u_k(t) f_k(\mathbf{r}, \mathbf{R}_I(t))$$

Schrodinger equation for hole:

$$i\hbar \dot{u}_k = \sum_l u_l \left(H_{kl} - i\hbar \left\langle \phi_k \middle| \dot{\phi}_l \right\rangle \right)$$

nuclei

Classical nuclear dynamics

$$\mathbf{F}_{I,i} = -\frac{\partial}{\partial \mathbf{R}_I} E_i \qquad E_i = H_{ii}^{diag}$$

*i*th adiabatic electronic state

Stochastic hopping from surface $E_i \rightarrow E_j$ with probability

$$p_{j \leftarrow i}(u_k, H_{kl}, d_{kl})$$

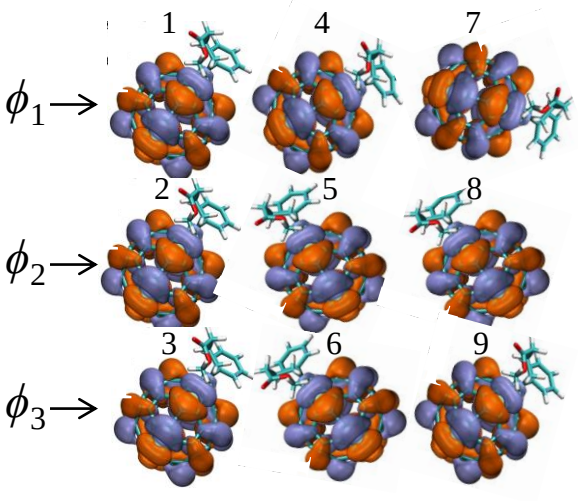
Antoine Carof

1. Fast calculation of Hole Hamiltonian

J. Spencer, F. Gajdos, JB, *JCP* **145**, 064102, 2016.

Hole Hamiltonian (``Tight binding"):

$$H_{kl} = \langle f_k | H | f_l \rangle$$



force field

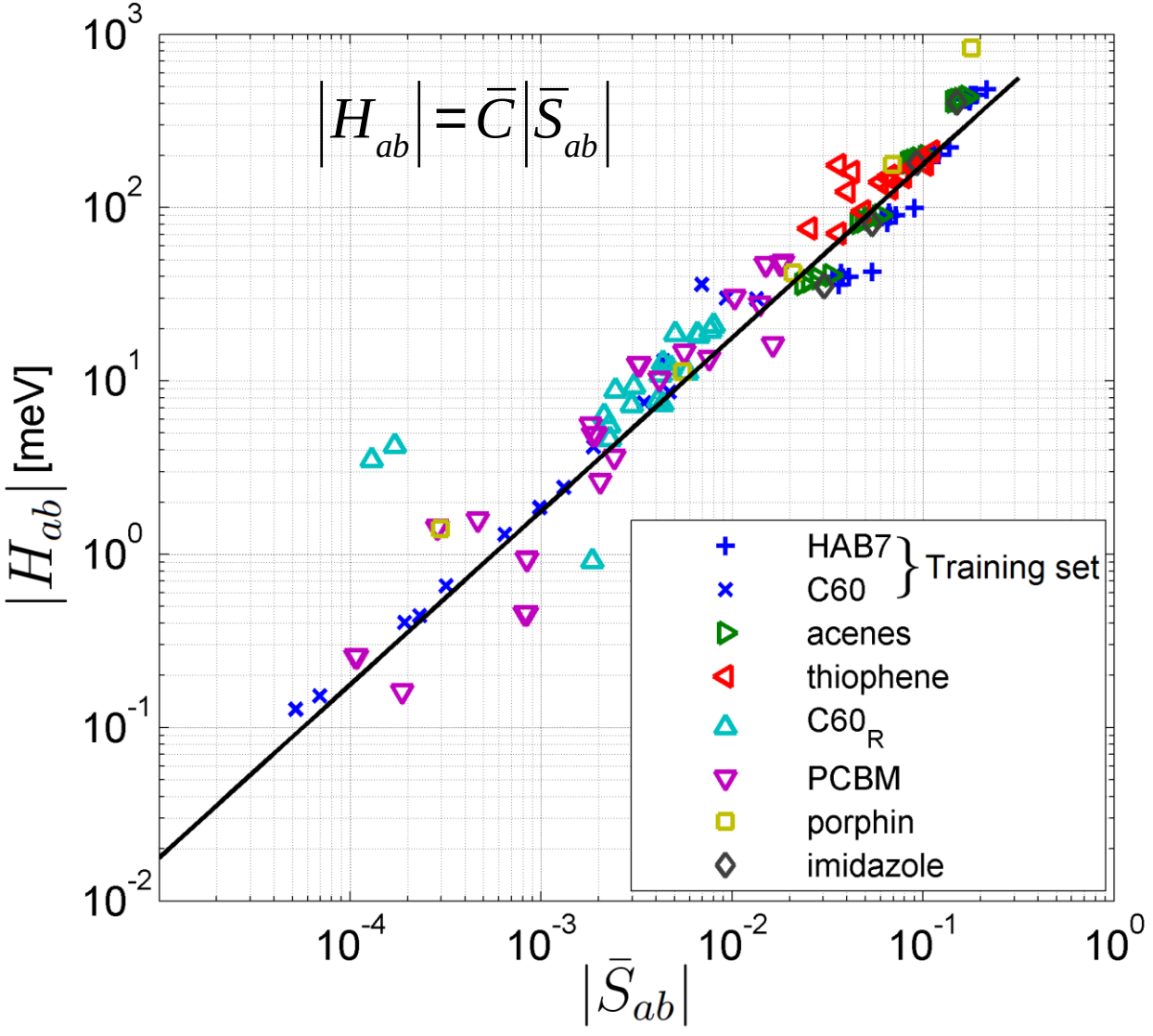
Analytic overlap method (AOM)

$$H_{kl} = \bar{C}\,\bar{S}_{kl}$$

$$H = \begin{pmatrix} H_{11} & H_{12} & 0 & H_{14} & 0 & 0 & 0 & 0 & 0 \\ H_{21} & H_{22} & H_{23} & 0 & H_{25} & 0 & 0 & 0 & 0 \\ 0 & H_{32} & H_{33} & 0 & 0 & H_{36} & 0 & 0 & 0 \\ H_{41} & 0 & 0 & H_{44} & H_{45} & 0 & H_{47} & 0 & 0 \\ 0 & H_{52} & 0 & H_{54} & H_{55} & H_{56} & 0 & H_{58} & 0 \\ 0 & 0 & H_{63} & 0 & H_{65} & H_{66} & 0 & 0 & H_{69} \\ 0 & 0 & 0 & H_{74} & 0 & 0 & H_{77} & H_{78} & 0 \\ 0 & 0 & 0 & 0 & H_{85} & 0 & H_{87} & H_{88} & H_{89} \\ 0 & 0 & 0 & 0 & 0 & H_{96} & 0 & H_{98} & H_{99} \end{pmatrix}$$

Ultrafast estimation of electronic couplings

F. Gajdos, JB *et al. J. Chem. Theor. Comput.* **10**, 4653 (2014).



blue symbols
=
Training set

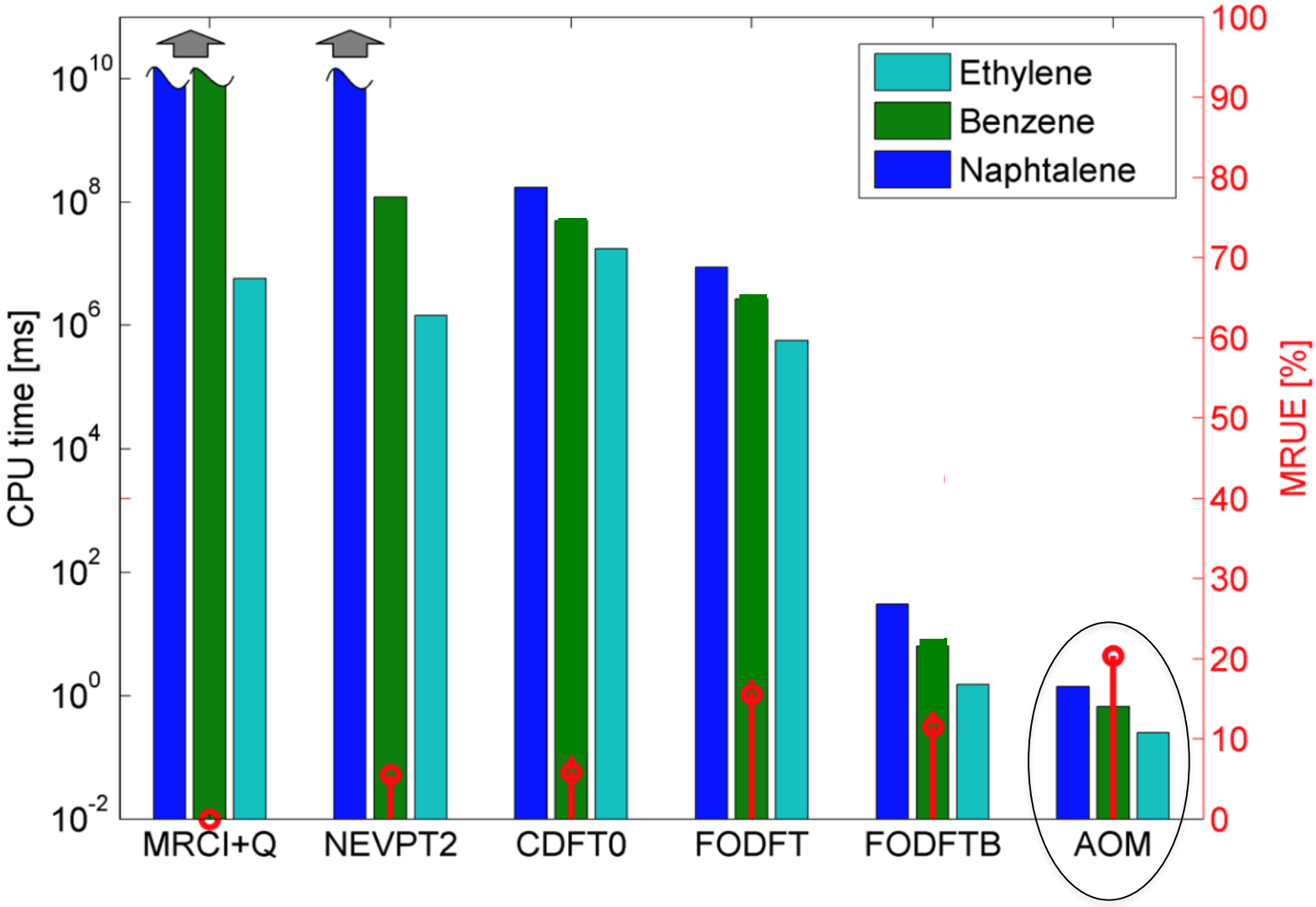
$\bar{C} = 1.819\ \text{eV}\ (R^2 = 0.974)$
(black line)

other symbols
=
Test sets

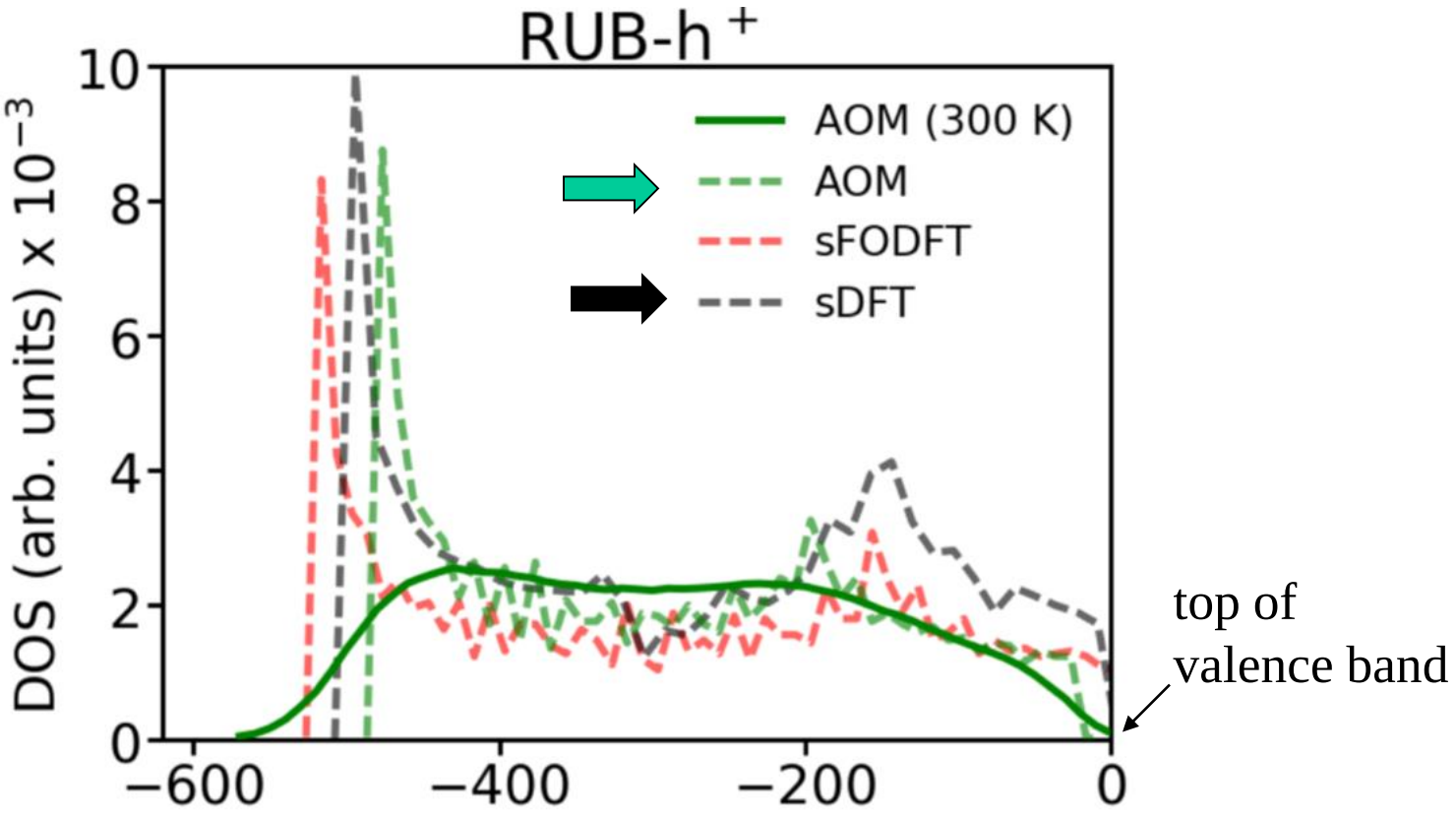
mean error = factor 1.9
over 5 decades!

Speed-up of 6 orders of magnitude, 20% loss of accuracy

F. Gajdos, JB *et al. J. Chem. Theor. Comput.* **10**, 4653 (2014).



Density of states rubrene valence band



→ Good agreement AOM vs sDFT for peak position and band width (0.5 eV)

2. Fast calculation of nuclear gradients

J. Spencer, F. Gajdos, JB, *JCP* **145**, 064102, 2016
A. Carof, S. Giannini, JB, *JCP* **147**, 214113, 2017

$$F^{ad}_{I,i} = -\sum_{kl} U^{T*}_{ik} \nabla_I H_{kl} U_{li} \qquad d^{ad}_{I,ij} = \frac{1}{E_j - E_i} \sum_{kl} U^{T*}_{ik} \nabla_I H_{kl} U_{lj} + \ldots$$

nuclear force on adiabatic PES *i*

NACV between PESs *i,j*

$$\nabla_I H_{kl} = C \nabla_I S_{kl}$$

off-diagonal gradients in HOMO basis (diagonal gradient from force field)

$$\nabla_I S_{kl} = \boldsymbol{d}_{I,kl} + \boldsymbol{d}^*_{I,lk}$$

overlap gradients in HOMO basis

$$\boldsymbol{d}_{I,kl} = \left\langle j_k \middle| \nabla_I j_l \right\rangle$$

NACV in HOMO basis (finite difference)

Antoine Carof

3. Making surface hopping work

- **Decoherence correction:** damping of inactive states using frozen Gaussian approximation

$$c_i \to c_i \exp(-\tau_{ia}^{-1}\Delta t) \qquad \tau_{ia}^{-1} = \sum_I \frac{\left|F_{I,i}(t) - F_{I,a}(t)\right|}{2\hbar a_I^{1/2}}$$

Schwartz, Bittner, Prezhdo, Rossky, *JCP* 104, 5942 (1996)

- **Detection of trivial crossing:** (i) State tracking algorithm

Giannini, Carof, JB *JPCL* (2018) similar to Tretiak's algorithm

(ii) Enforcing sum rule: $\sum_i g_{ia} = -\frac{d\left|c_a\right|^2}{dt}\left|c_a\right|^{-2} dt \qquad g_{ja} = \sum_i g_{ia} - \sum_{i \neq j} g_{ia}$

Wang and Prezhdo, *JPCL* 5, 713 (2014)

- **Removal of decoherence-correction induced artificial long-range CT** via projection of wavefunction in moving active region

Giannini, Carof, JB *JPCL* (2018)

Content

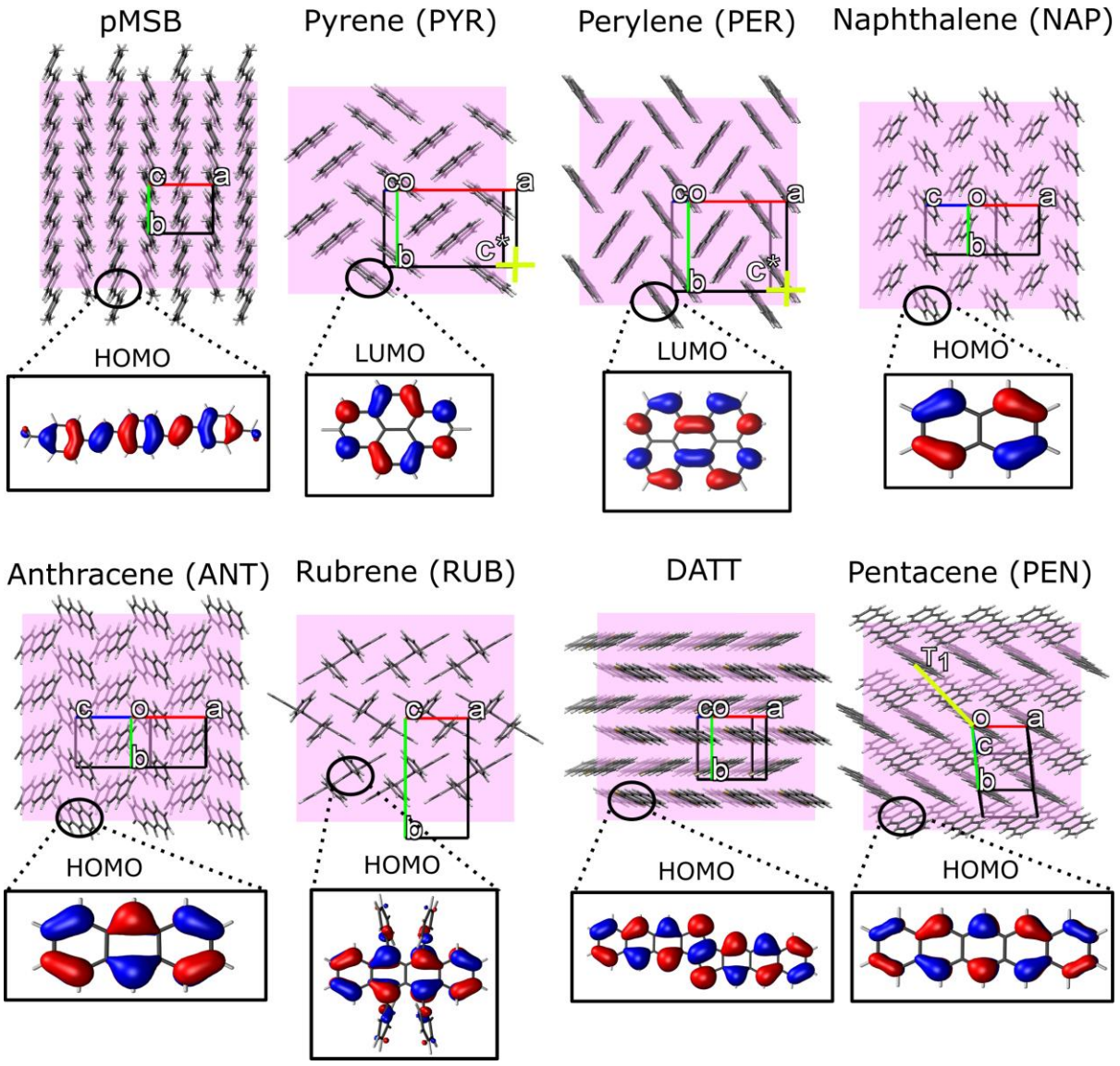
- FOB-SH: a tool for simulating electronic transport processes in truly nanoscale molecular materials

- Application to charge transport in organic crystals and the emergence of large ``flickering'' polarons

- Tricks of the Trade: importance of decoherence correction, trivial crossing detection and all that

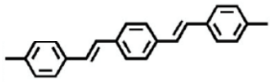
Organic Single Crystals

Samuele Giannini



Hole transport in conductive plane at 300K

Giannini *et al*. *Nature Comm.* **10**, 3843, 2019; *Adv. Theor. Simul.* **3**, 2000093, 2020.

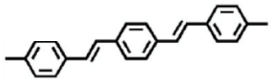
pMSB 

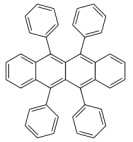
small polaron hopping

$$\xi = \frac{2\langle|H_{ab}|\rangle}{\lambda} < 1$$

Hole transport in conductive plane at 300K

Giannini *et al*. *Nature Comm.* **10**, 3843, 2019; *Adv. Theor. Simul.* **3**, 2000093, 2020.

pMSB 

rubrene 

small polaron hopping

$$\xi = \frac{2\langle|H_{ab}|\rangle}{\lambda} < 1$$

large (``flickering") polaron

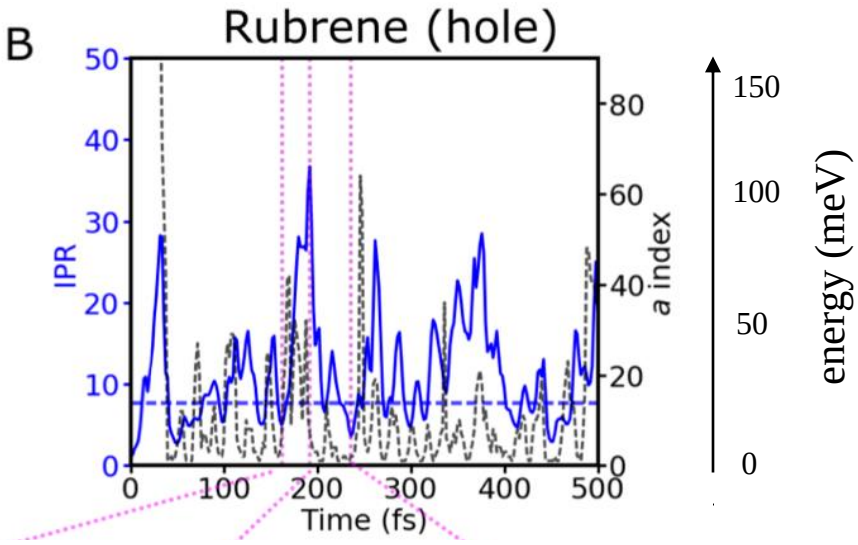
$$\xi = \frac{2\langle|H_{ab}|\rangle}{\lambda} > 1$$

Transport Mechanism from FOB-SH

Giannini *et al*. *Adv. Theor. Simul*. **3**, 2000093, 2020.

IPR = inverse participation ratio (number of molecules over which charge is delocalized)

a index = active state PES in FOB-SH

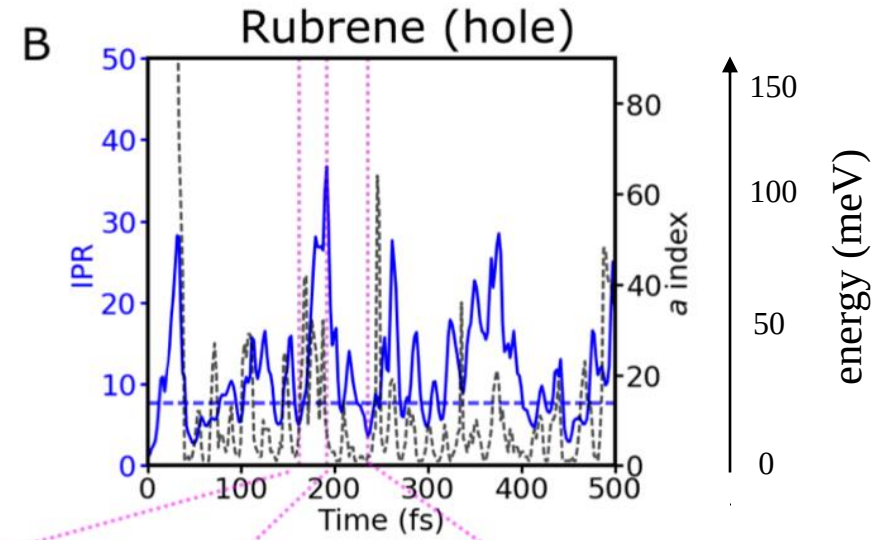


Transport Mechanism from FOB-SH

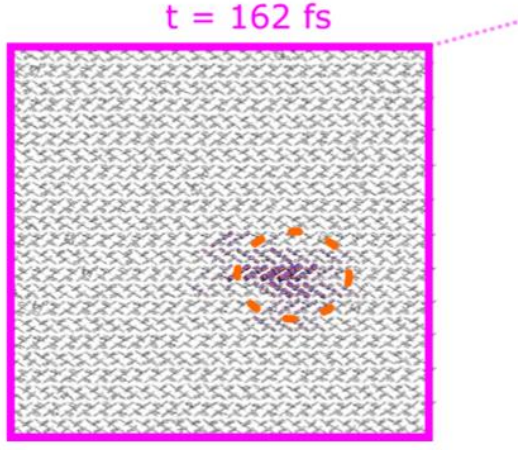
Giannini *et al*. *Adv. Theor. Simul*. **3**, 2000093, 2020.

IPR = inverse participation ratio (number of molecules over which charge is delocalized)

a index = active state PES in FOB-SH



C

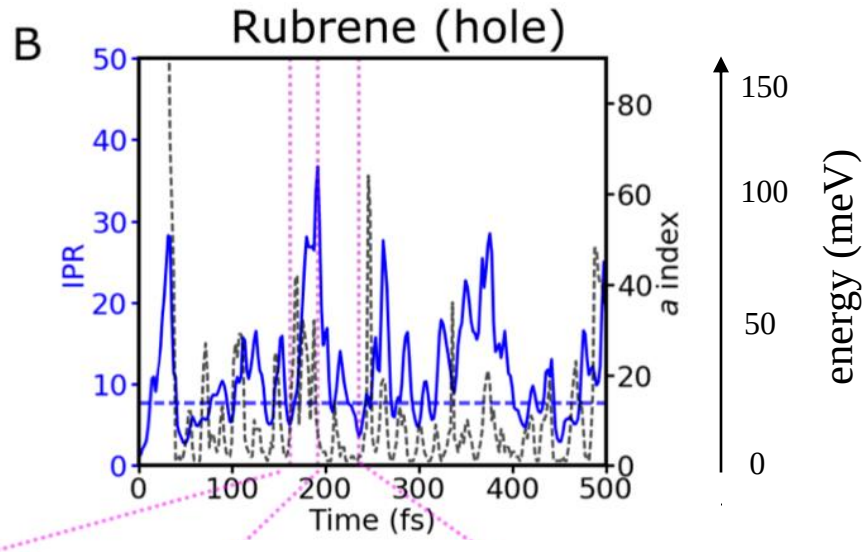


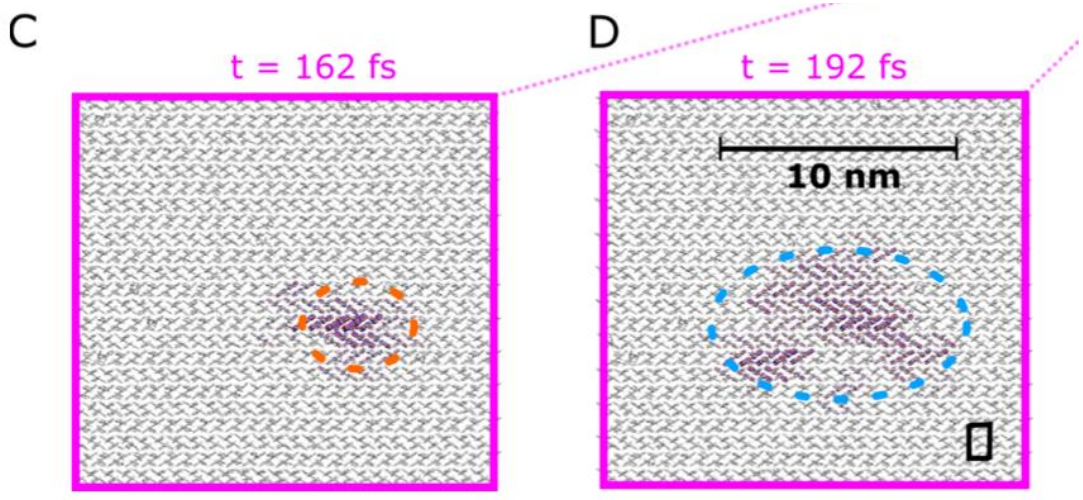
Transport Mechanism from FOB-SH

Giannini *et al*. *Adv. Theor. Simul*. **3**, 2000093, 2020.

IPR = inverse participation ratio (number of molecules over which charge is delocalized)

a index = active state PES in FOB-SH



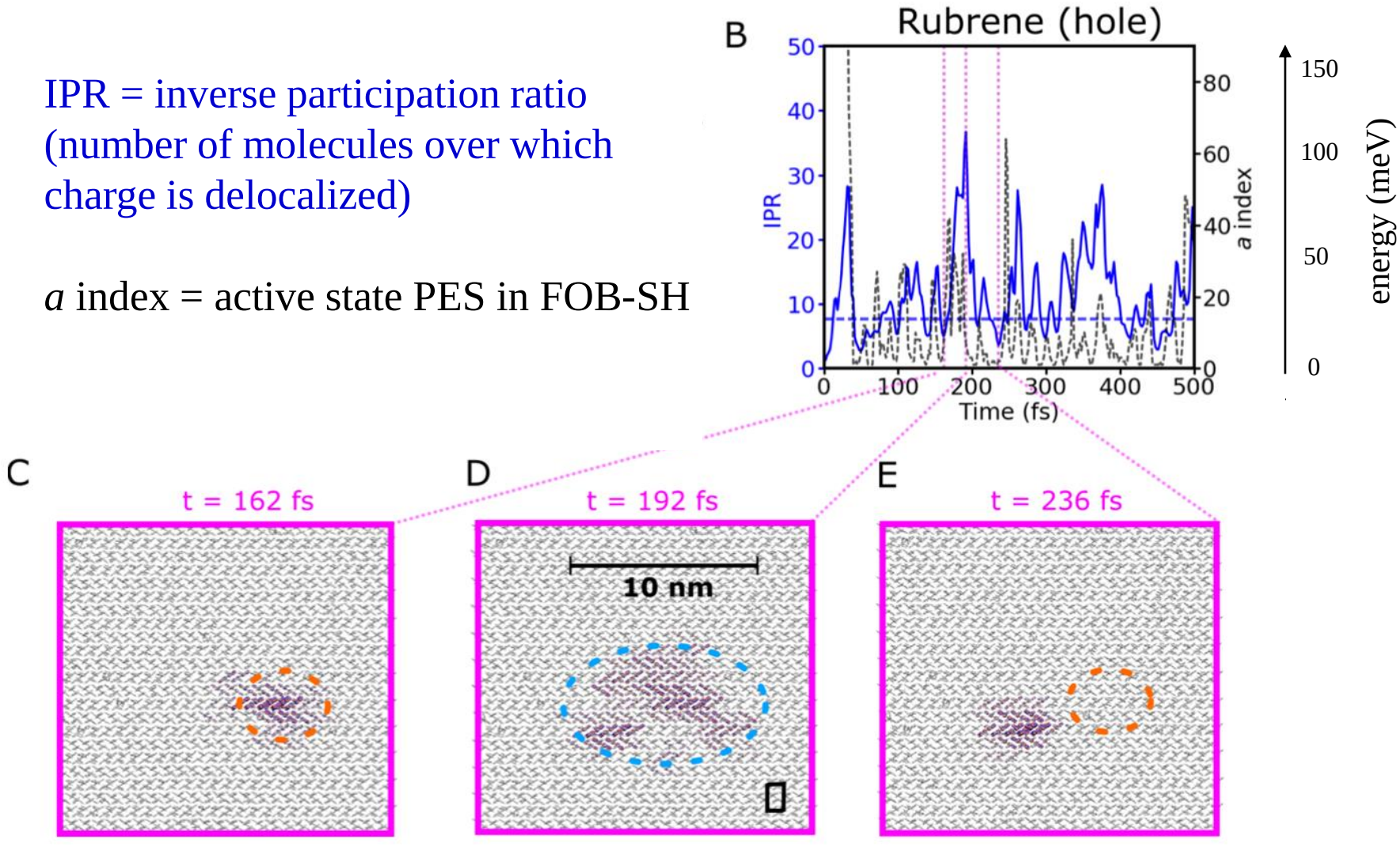


Transport Mechanism from FOB-SH

Giannini *et al*. *Adv. Theor. Simul*. **3**, 2000093, 2020.

IPR = inverse participation ratio (number of molecules over which charge is delocalized)

a index = active state PES in FOB-SH



From trajectories to charge mobilities

Mean-Square Displacement

$$MSD(t) = \frac{1}{N_{traj}} \sum_{n}^{traj} \langle \Psi_n(t) | (x - x_0)^2 | \Psi_n(t) \rangle$$

⇩

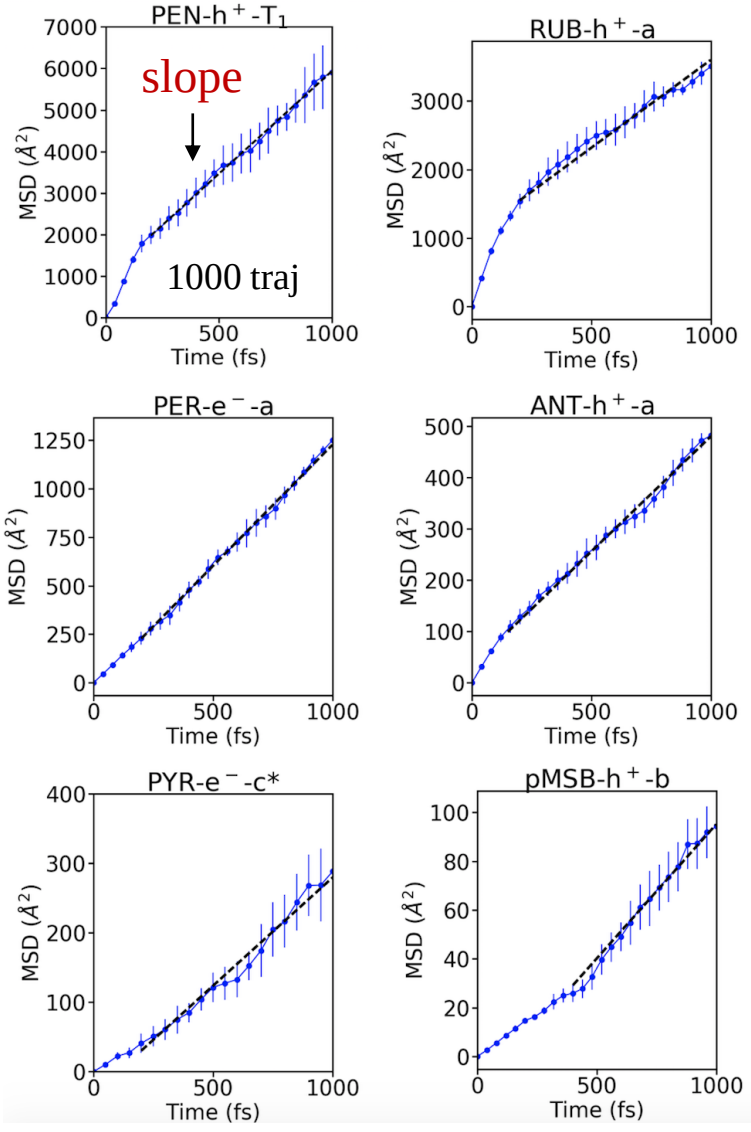
Diffusion coefficient

$$D = \frac{1}{2} \frac{d}{dt} MSD(t)$$

⇩

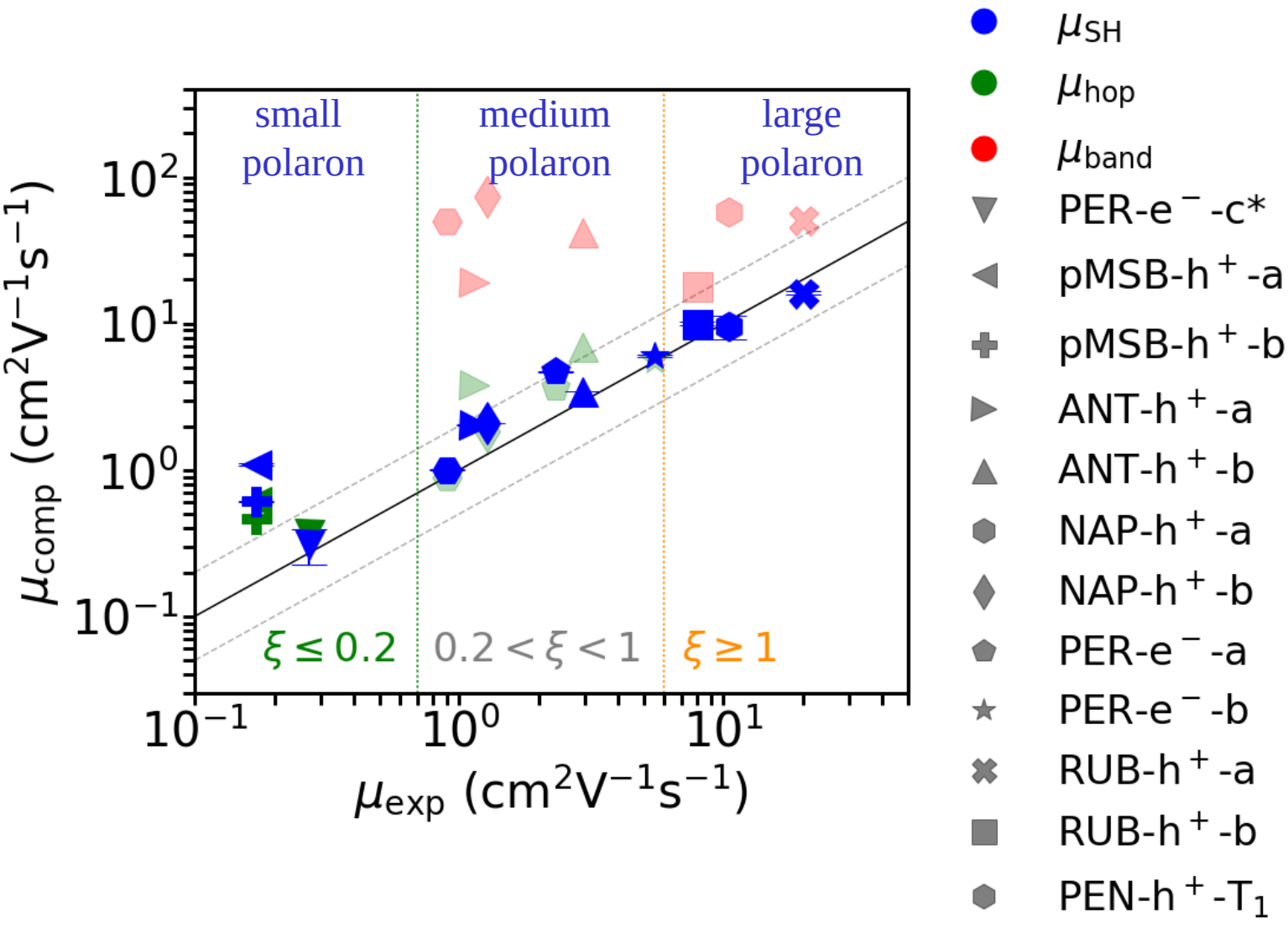
Charge mobility

$$m = \frac{eD}{k_B T}$$



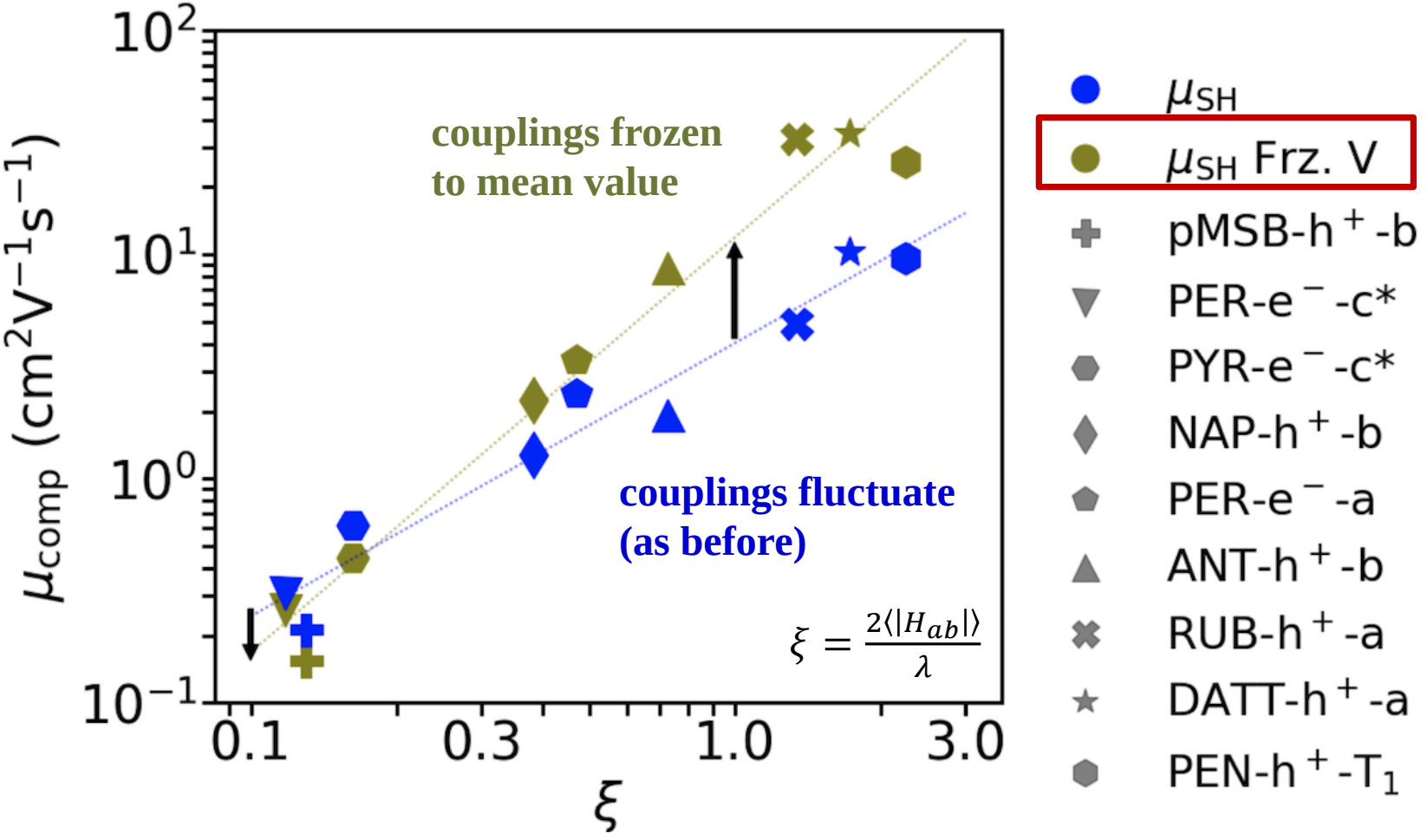
Charge mobility: FOB-SH vs Experiment

Giannini *et al. Nature Comm.* **10**, 3843, 2019; *Adv. Theor. Simul.* **3**, 2000093, 2020.



What limits charge mobility in organic crystals? Thermal fluctuations of electronic coupling

Giannini *et al. Nature Comm.* **10**, 3843, 2019.



Content

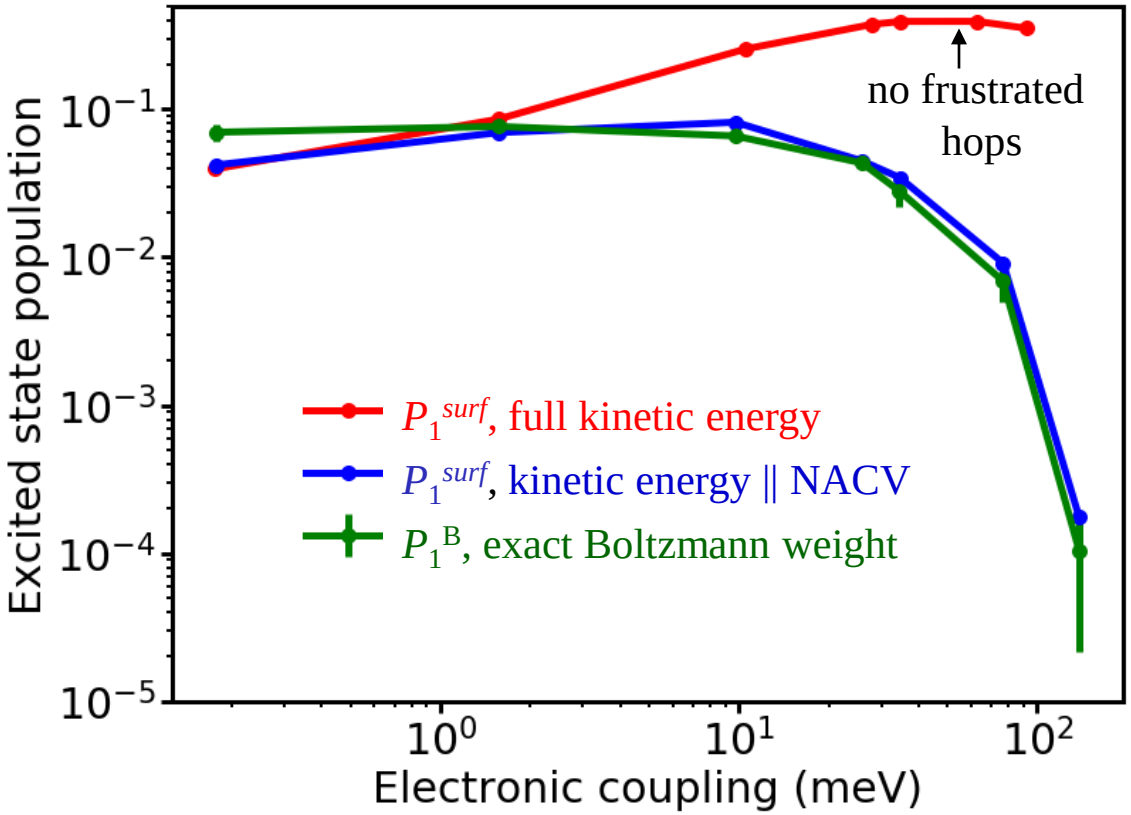
- FOB-SH: a tool for simulating electronic transport processes in truly nanoscale molecular materials

- Application to charge transport in organic crystals and the emergence of large ``flickering'' polarons

- Tricks of the Trade: importance of decoherence correction, trivial crossing detection and all that

1. Energy criterion for hops: Kinetic energy || NACV → Detailed balance

JCP **147**, 214113 (2017)

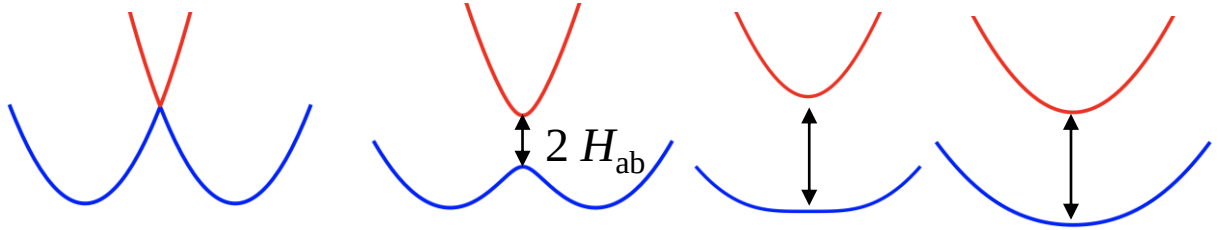


Detailed balance:

$$P_1^{surf} = P_1^{B}$$

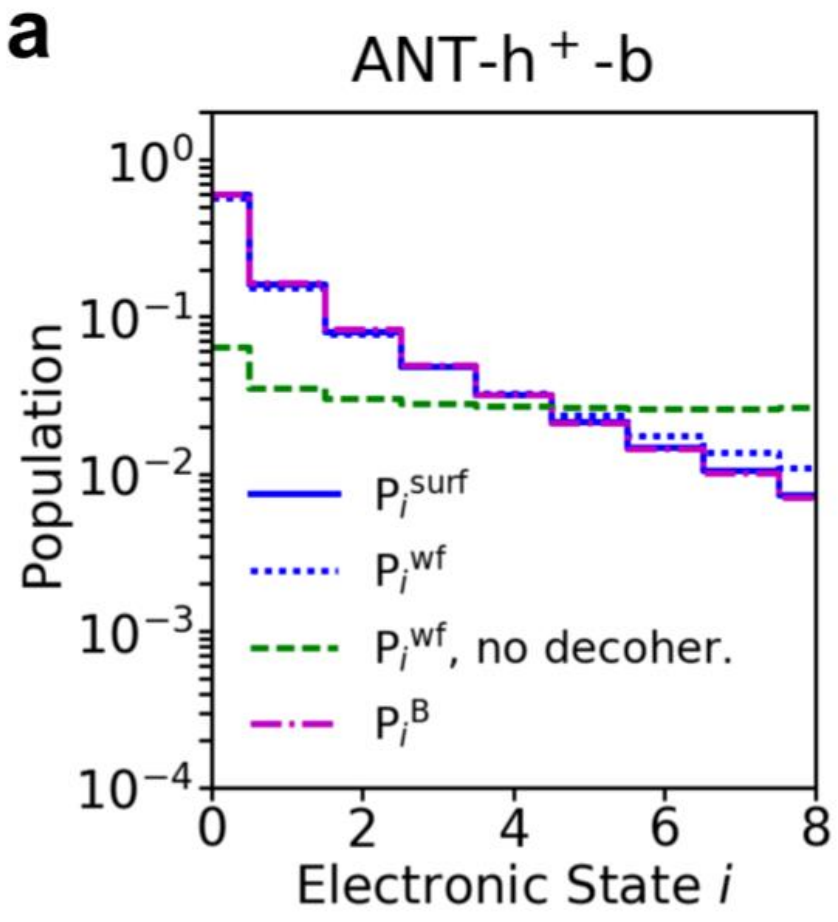
P_1^{surf} = population of excited state PES in FOB-SH

$$P_1^{B} = \langle exp(-\beta(E_1 - E_0)\rangle_0$$



2a Decoherence correction → Internal consistency

Giannini *et al*. *Nature Comm.* **10**, 3843, 2019.



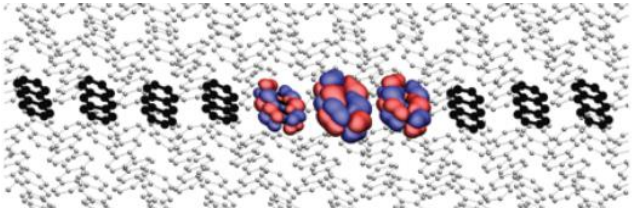
Internal consistency

$$P_i^{surf} = P_i^{wf}$$

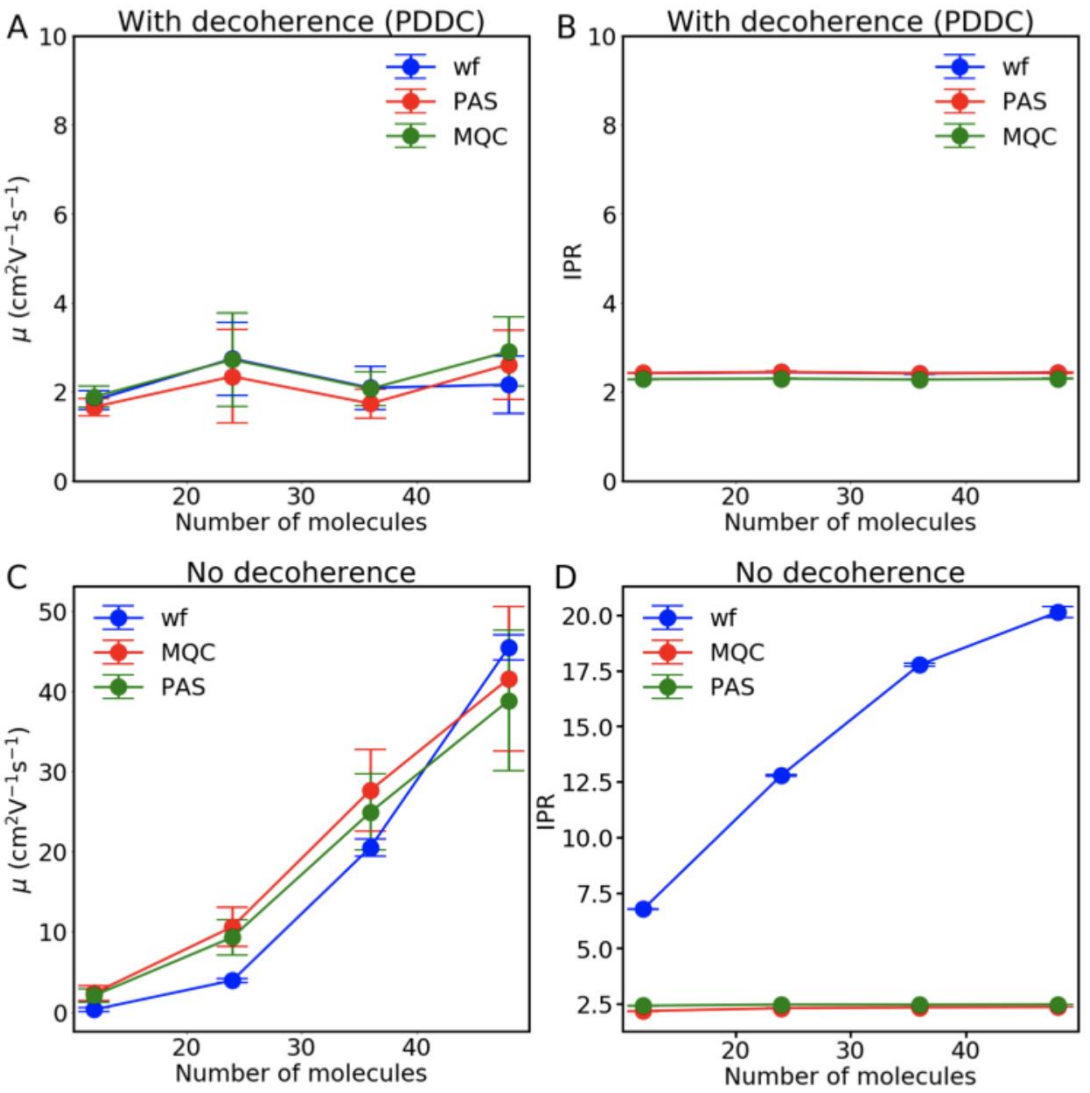
P_i^{surf} = population of adiabatic PES i in FOB-SH

P_i^{wf} = population of electronic adiabatic wavefunction i in FOB-SH

$$P_i^{B} = \langle exp(-\beta(E_i - E_0)\rangle_0$$



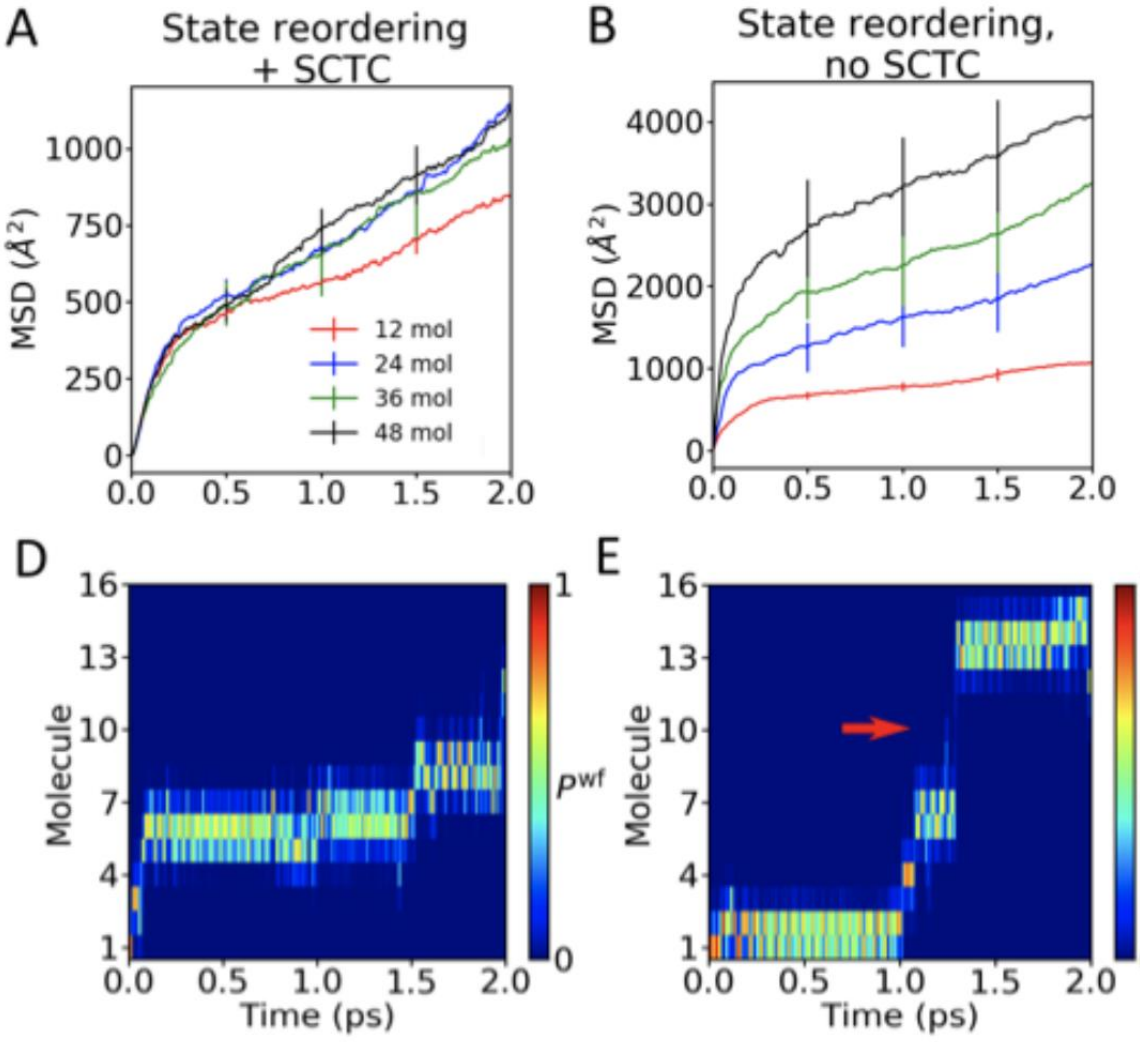
2b Decoherence correction → convergence of mobility



PCCP **21**, 26368 (2019)

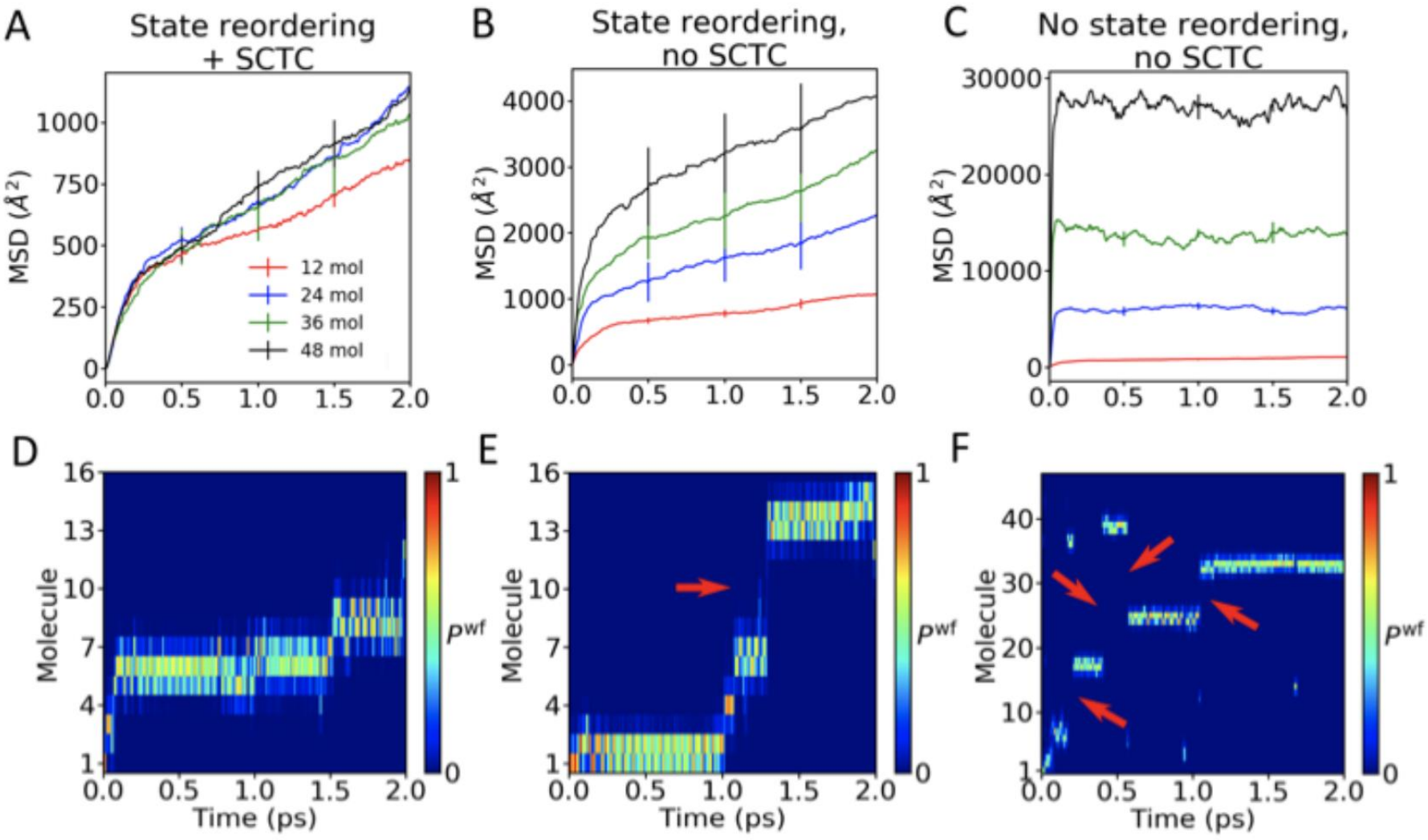
→ **Mobilities diverge with system size without decoherence**

3. Spurious charge transfer correction (SCTC) → physical CT dynamics



4. Detection of trivial crossings → physical CT dynamics

PCCP **21**, 26368 (2019)



Summary

- Developed a non-adiabatic MD method for real-time propagation of charge carriers in ``soft" materials

- Practical: -large systems (1000 sites $\triangleq 10^5$ valence electrons)
  -convergence: 10^3 trjs 1ps each in 1 day on 10^3 cores

- Predictive: Experimental mobilities well reproduced

- New picture of charge carriers in ``soft" materials: not hopping, not band

- Provides numerical benchmarks for new theories
  e.g. transient localization theory, stochastic Liouville

- Useful: Prediction of charge mobility in new materials

Outlook

- Extending state space of electronic Hamiltonian in FOB-SH

→ Exciton transport (VISTA talk by Samuele Giannini (?))

→ Charge separation and recombination at n-p type interfaces (excitonic solar cells)

→ Exciton dissociation at n-p type interfaces

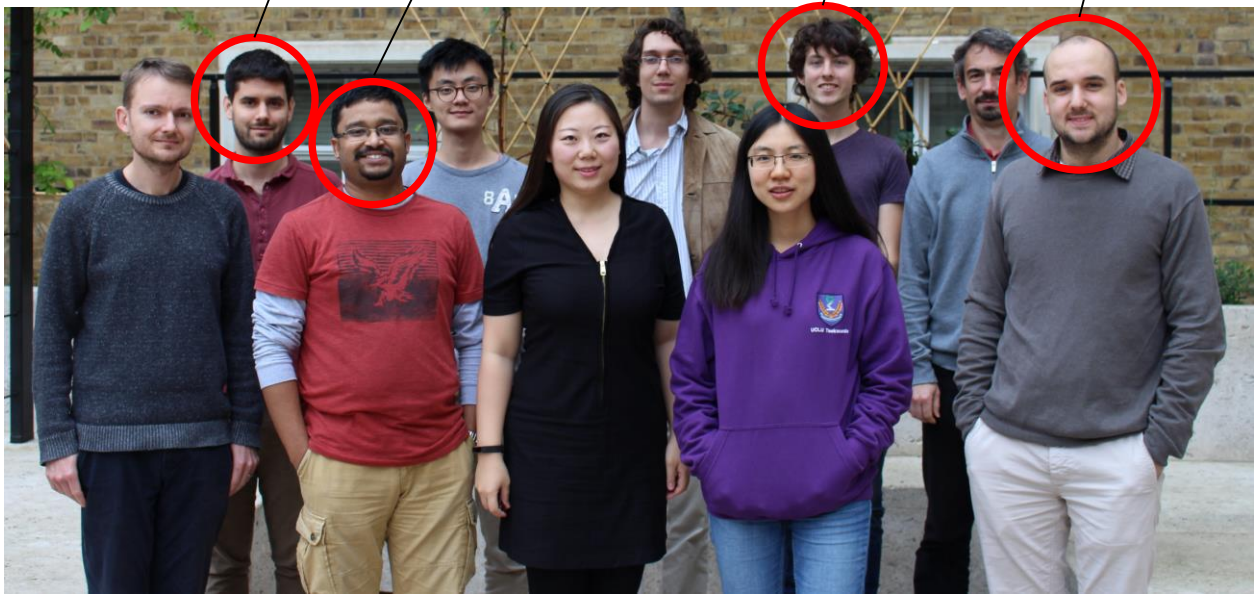
- Beyond Surface Hopping

→ Classical limit of exact factorisation (Abedi, Gross, Agostini,…)
Ehrenfest + quantum momentum terms
Problem: Divergence of quantum momentum in Eq. S28 of *Min* et al. *JPCL* 2017

→ Surface Hopping with Quantum Nuclei/RPMD (Tully, Shushkov, Miller,…)
Problem: Many beads but only one electronic SE. Expensive.

Acknowledgements

Antoine Carof Soumya Ghosh Matt Ellis Samuele Giannini



European Research Council

European Commission

Pacific Northwest NATIONAL LABORATORY

THE THOMAS YOUNG CENTRE TYC

IAS TUM Institute for Advanced Study

EPSRC Engineering and Physical Sciences Research Council

UCL

Acknowledgements

Orestis Ziogos Wei-Tao Peng Jan Elsner

European Research Council

European Commission

Pacific Northwest NATIONAL LABORATORY

THE THOMAS YOUNG CENTRE TYC

IAS TUM Institute for Advanced Study

EPSRC Engineering and Physical Sciences Research Council

UCL

23-25 June 2021

Face-to-face, Virtual or Hybrid


TRTWORLD
PARDON ME SIR, MAY I SUGGEST YOU TO TAKE A PARACHUTE WITH YOU ?
THANKS, THE FLAG WILL DO !

Fragment orbital-based surface hopping (FOB-SH)

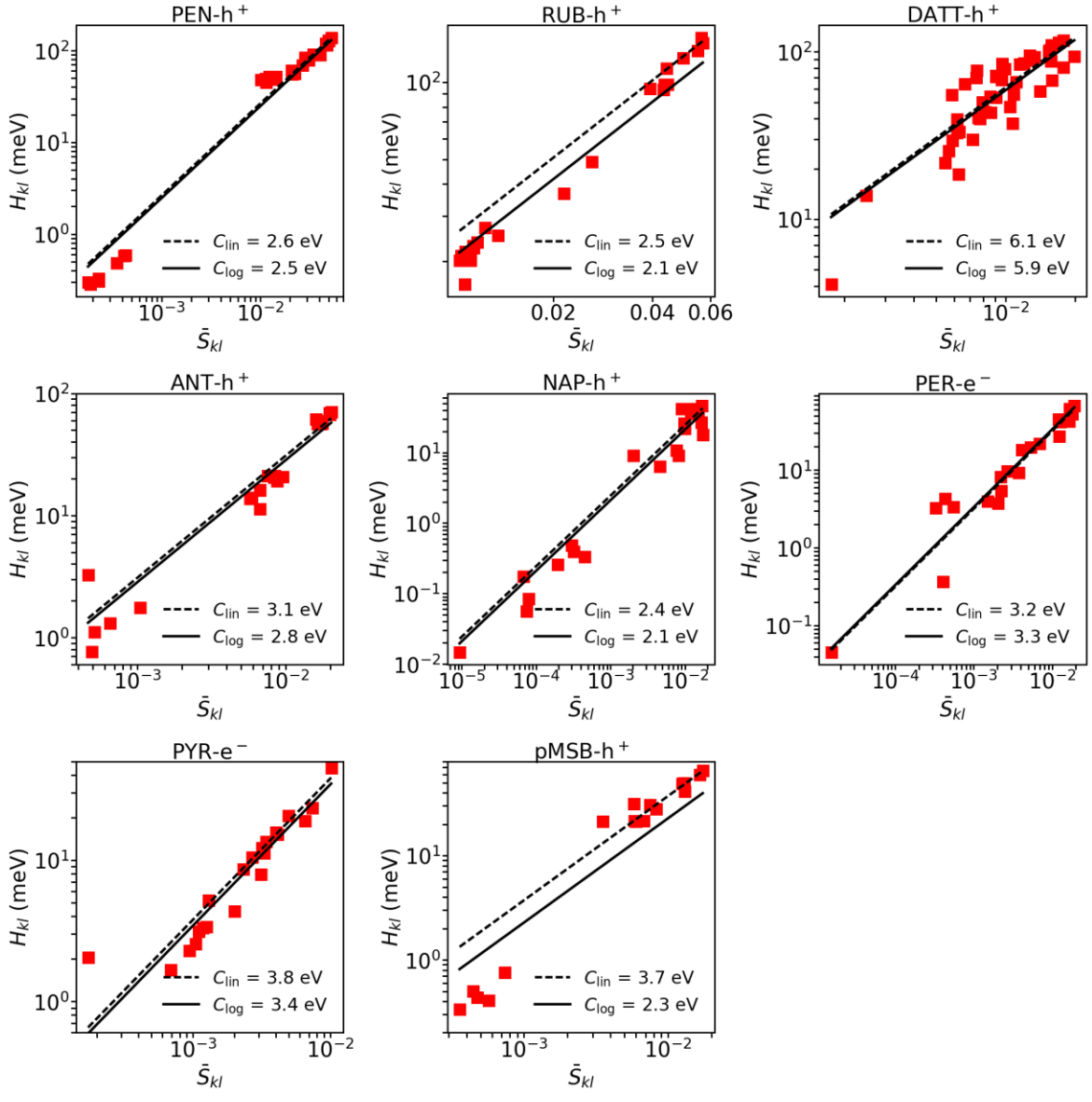
2 major approximations:

1. Exact electron-nuclear quantum dynamics replaced by
   mixed quantum-classical dynamics

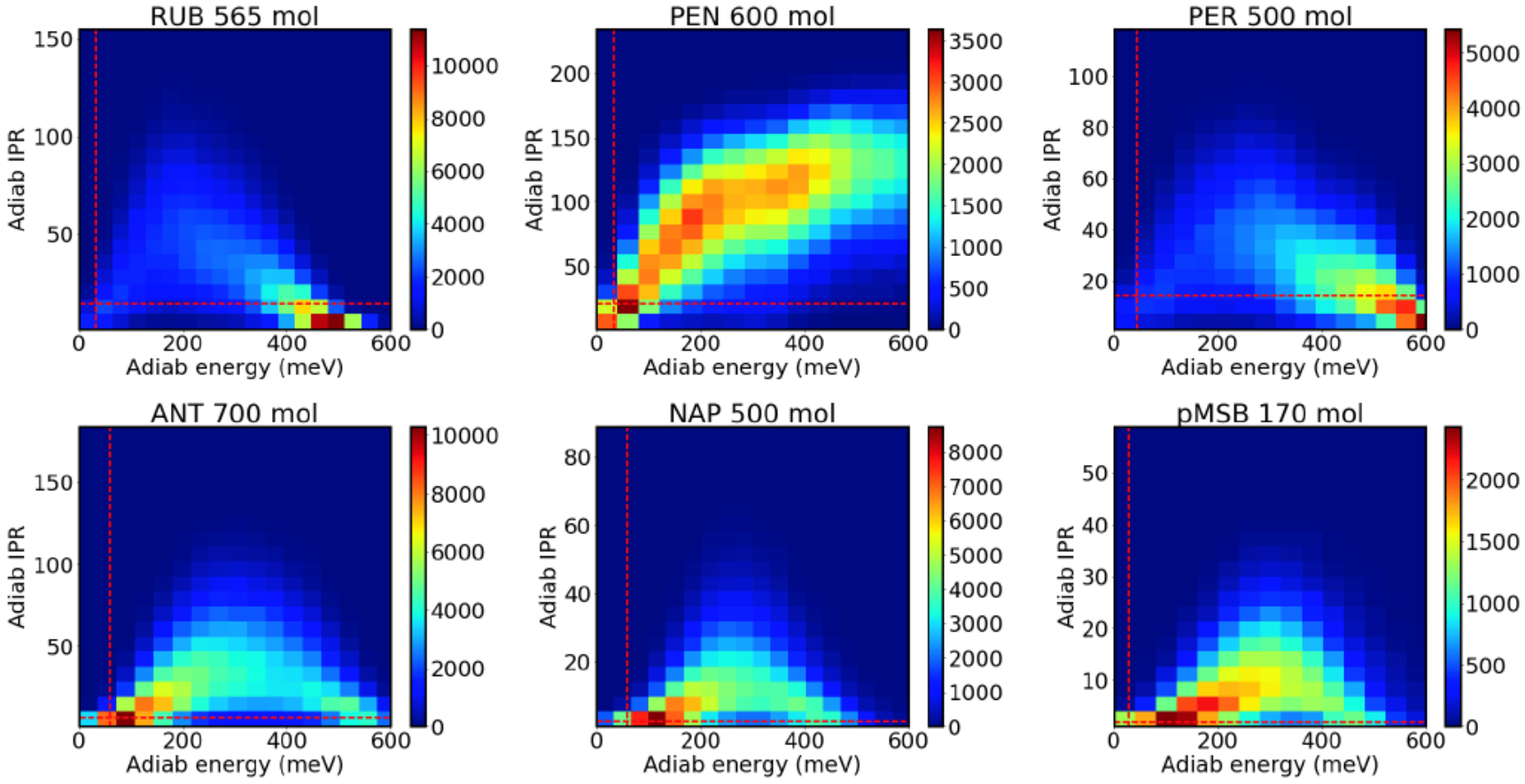
2. Time-dependent multi-determinantal electronic wavefunction replaced by
   a 1-particle wavefunction describing the excess electron or hole

→ **NO explicit core and valence electrons.**
Implicitly included by parametrization of electronic Hamiltonian.

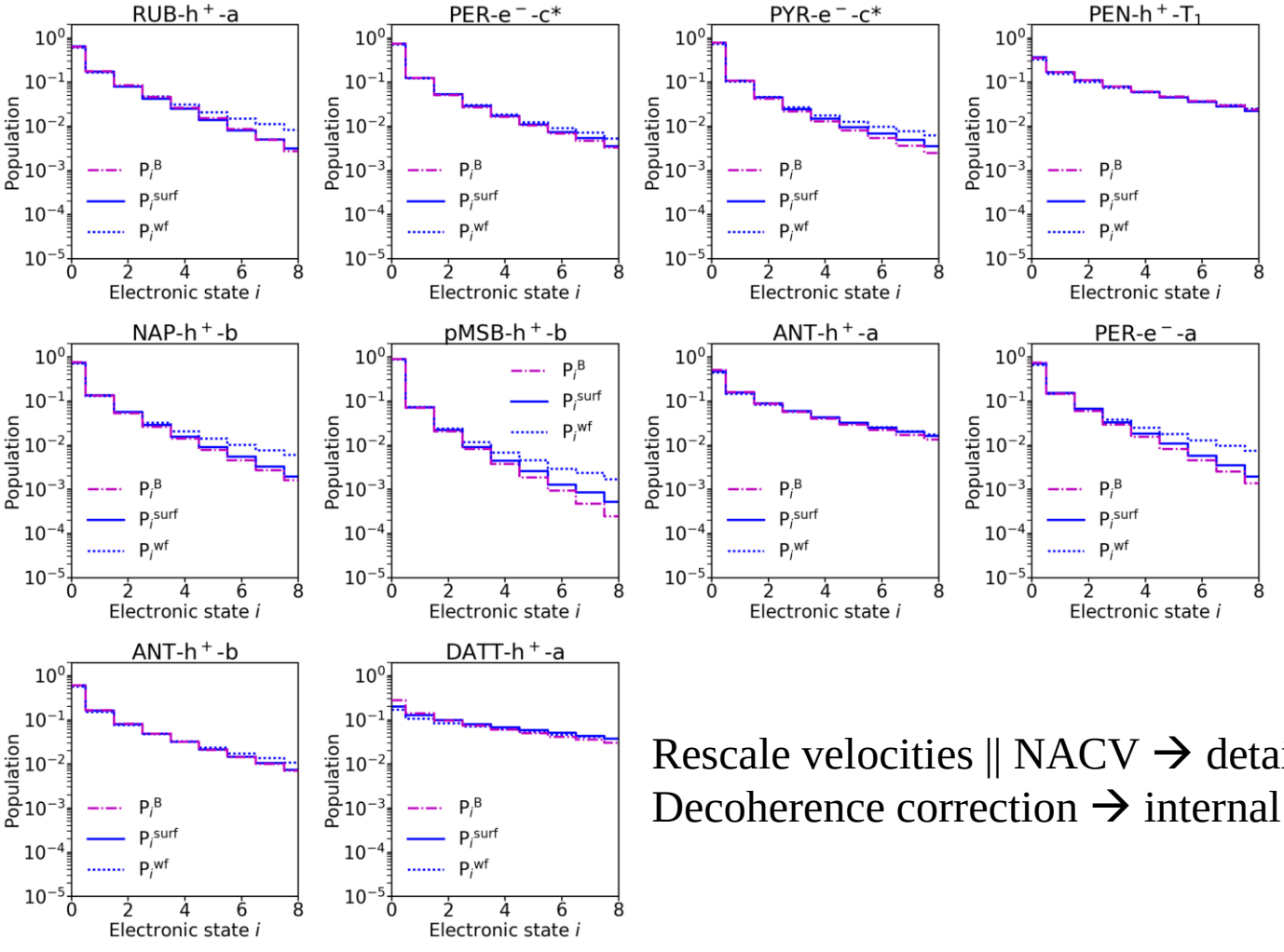
Analytic Overlap Method (AOM) for electronic couplings H_{kl} (as published)



Density of states and IPR (new data)



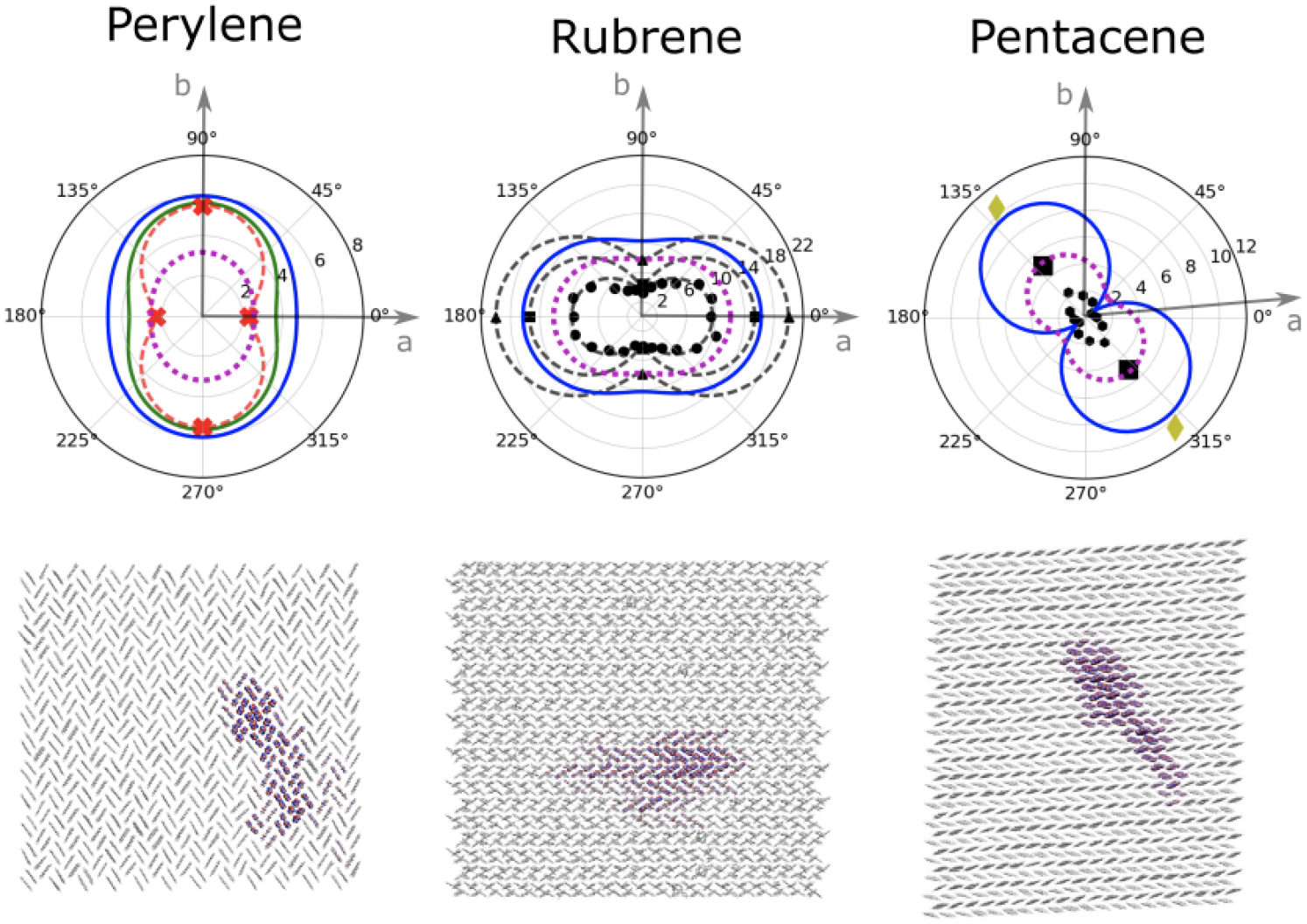
Detailed balance and internal consistency



Rescale velocities || NACV → detailed balance
Decoherence correction → internal consistency

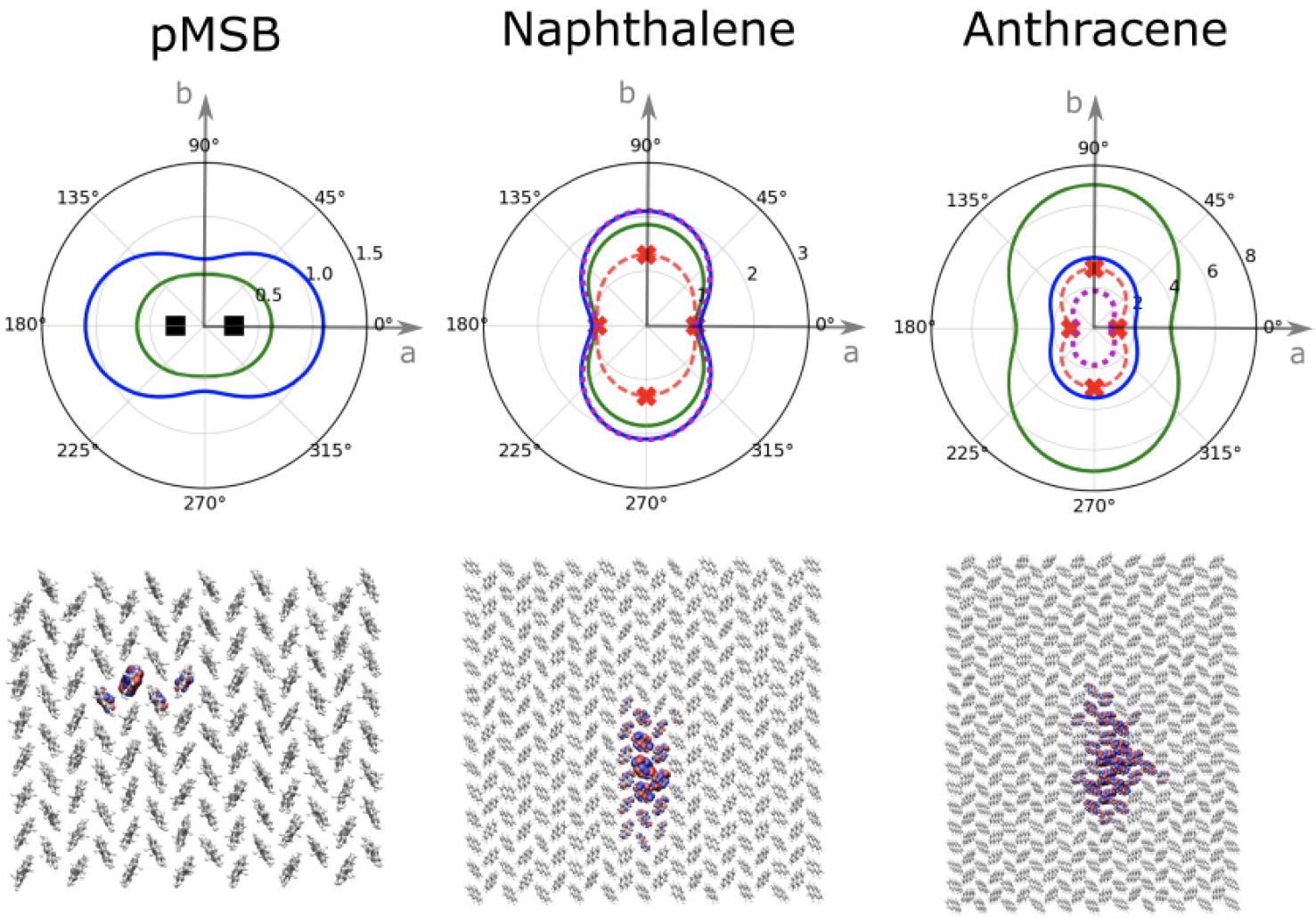
Summary: Nature of holes in OS crystals

Giannini *et al. Nature Comm.* **10**, 3843, 2019.

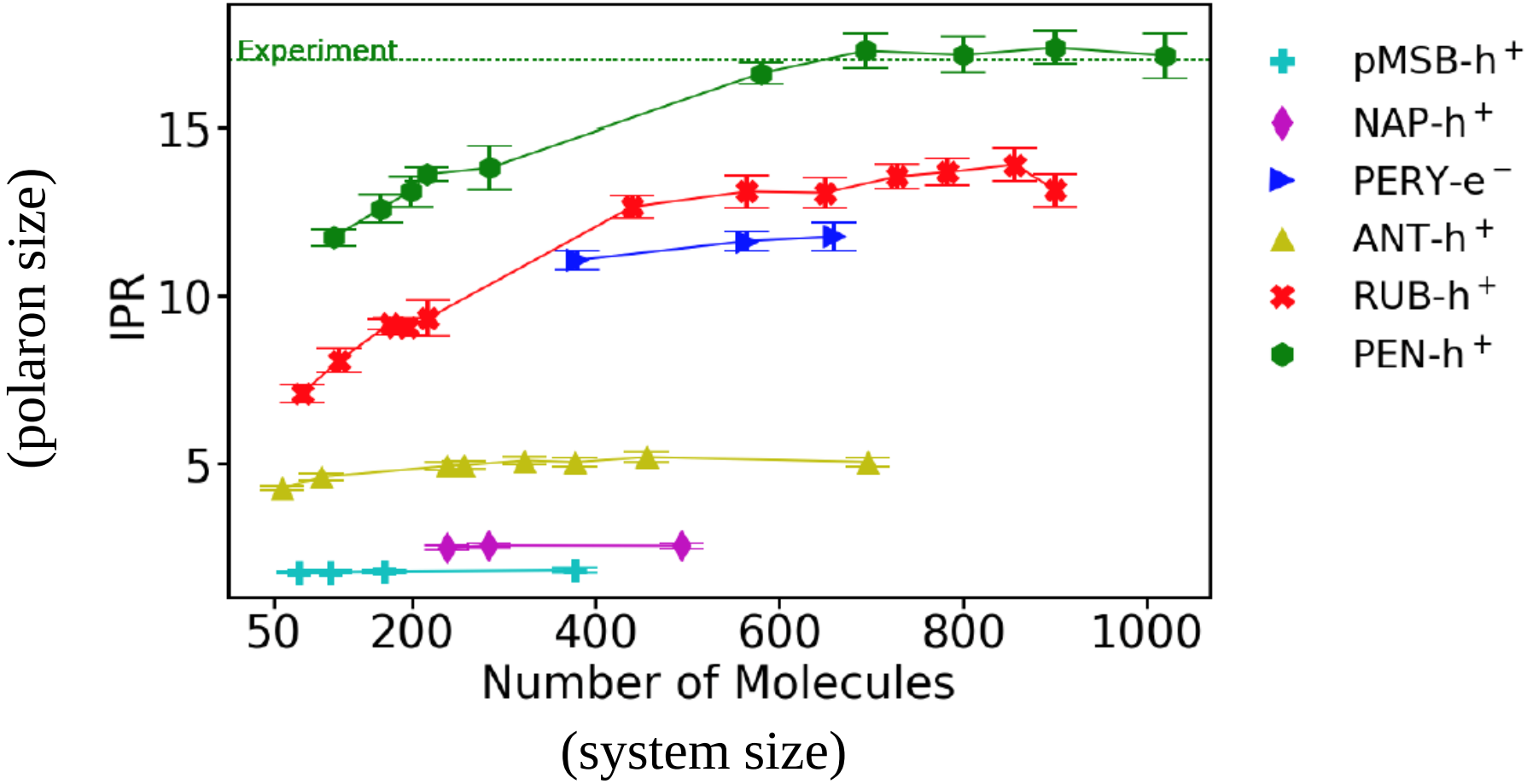


Summary: Nature of holes in OS crystals

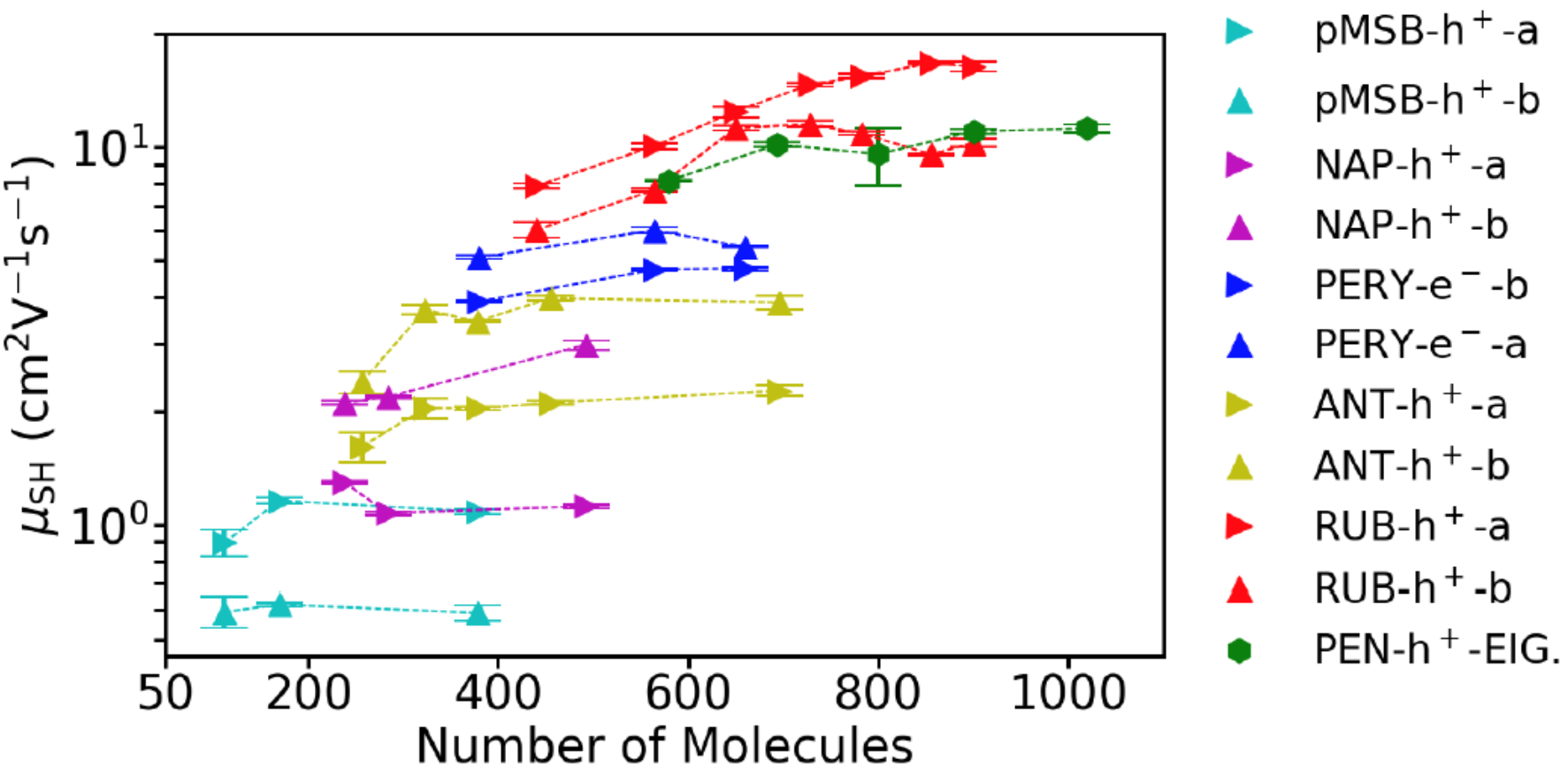
Giannini *et al. Nature Comm.* **10**, 3843, 2019.



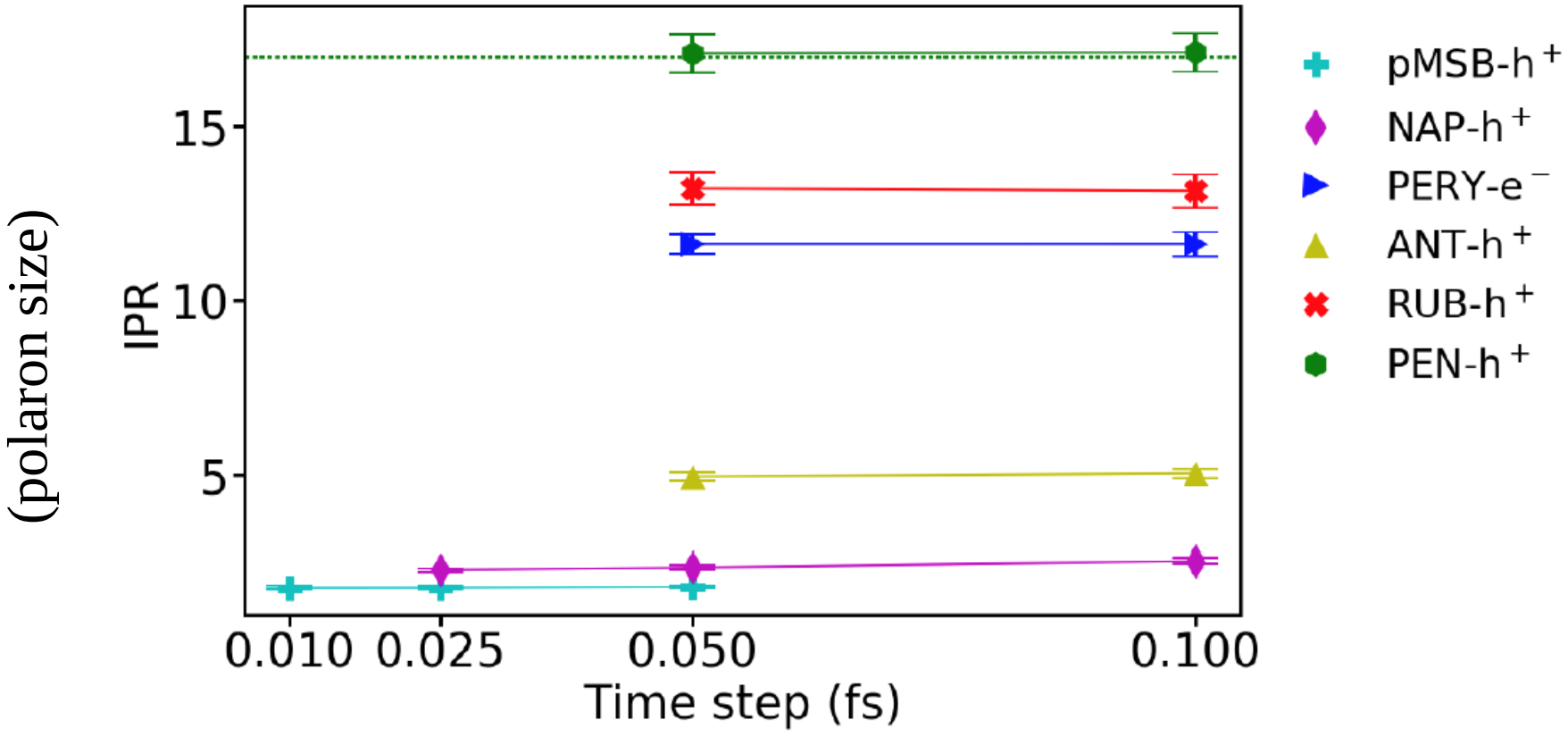
Convergence IPR wrt system size (new data)



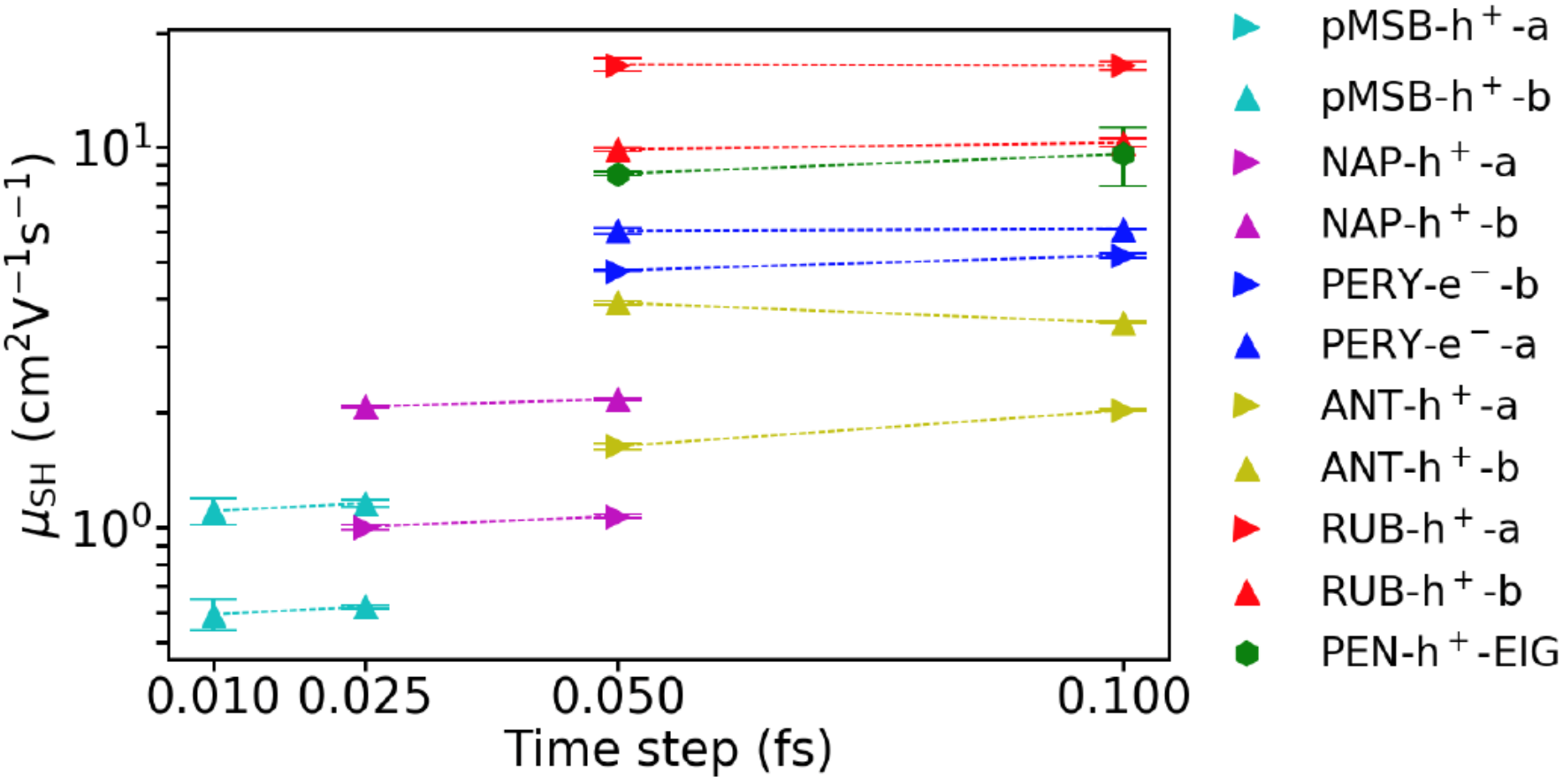
Convergence 2D mobility wrt system size



Convergence IPR wrt time step (new data)



Convergence 2D mobility wrt time step (new data)



Mobility correlates well with polaron size (as published)

Giannini *et al. Nature Comm.* **10**, 3843, 2019.