Charge transport in organic molecular materials from fragment orbital-based non-adiabatic molecular dynamics simulation

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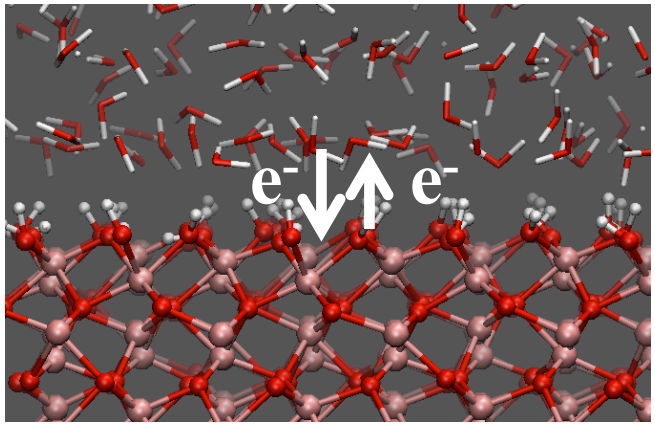
Department of Physics and Astronomy

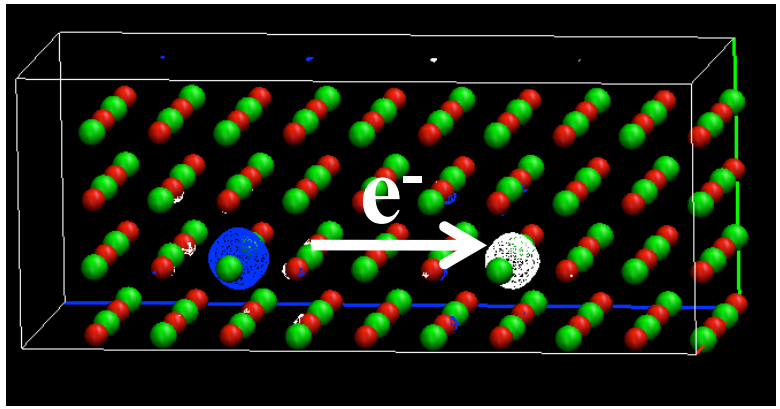
Workshop on spectroscopy and dynamics of photoinduced electronic excitations

Trieste, 10.05.2017

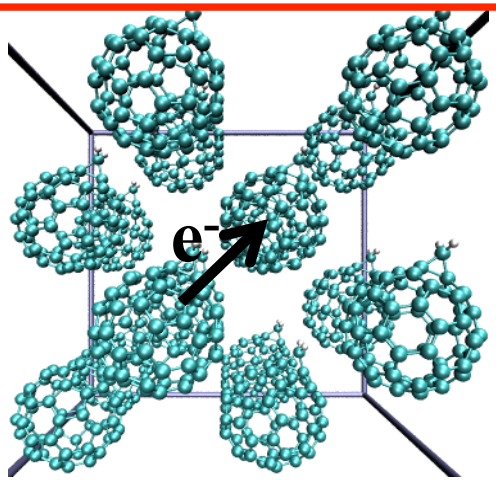
Electron transfer/transport in material science and biology



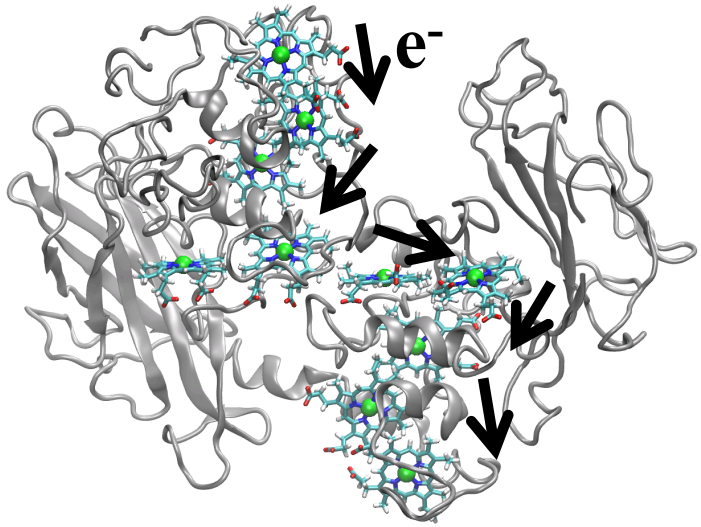
ET at photo-electrode/water interface



ET between defects in oxide materials



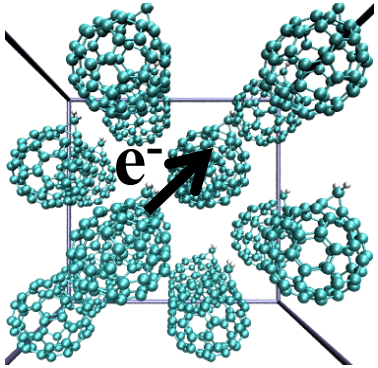
ET in organic materials



ET in bacterial `wire' protein

Overview

- A challenge for theory:
  Charge transport in organic materials

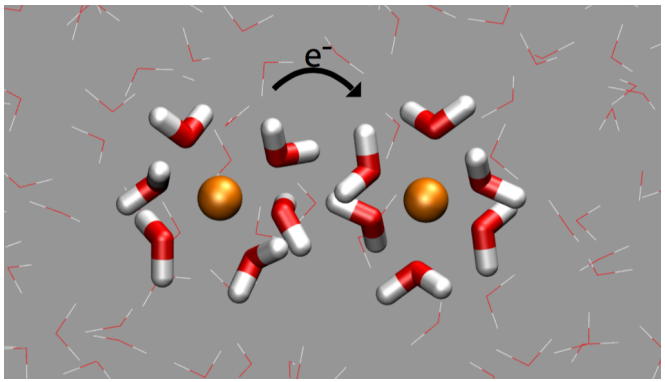


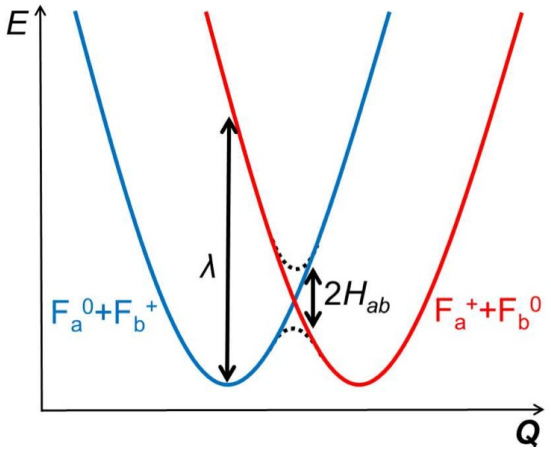
- Novel methodology:
  Fragment orbital-based surface hopping (FOB-SH)

- Application of FOB-SH:
  Hole mobilities in 1D chains of ethylene, rubrene

Marcus theory of electron transfer (high dielectric)

Ions, proteins in water: ε_s **= LARGE** H_{ab} / λ **= SMALL**

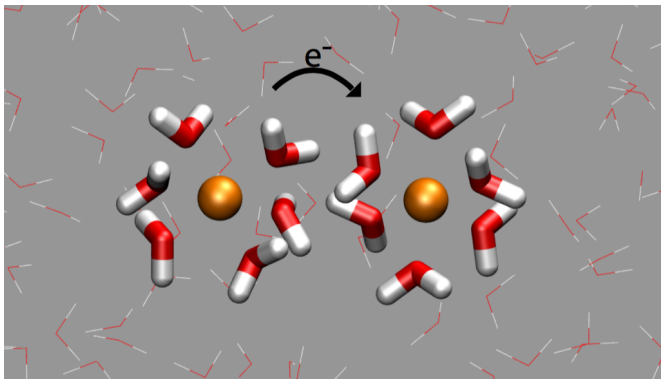


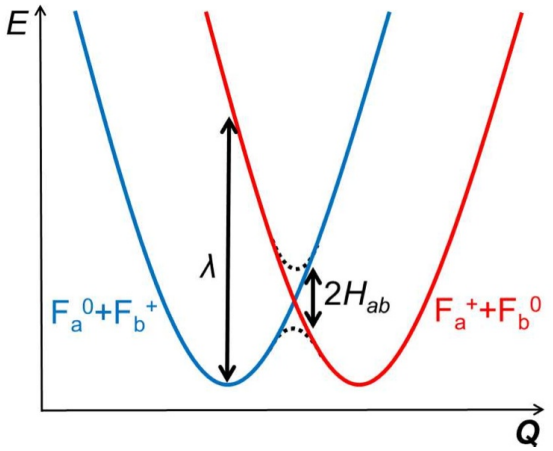


→ in Marcus regime

Charge transfer in organic materials (low dielectric)

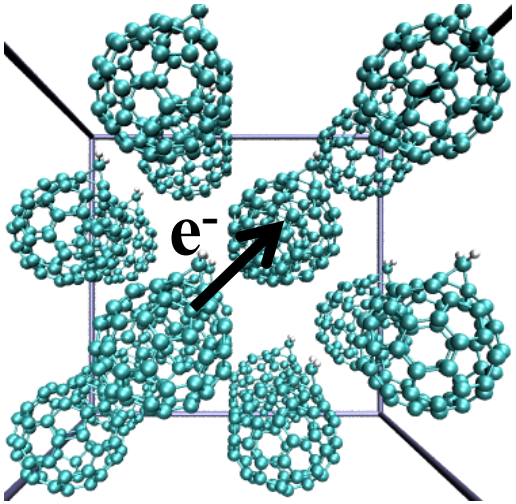
Ions, proteins in water: ε_s = LARGE H_{ab} / λ = SMALL





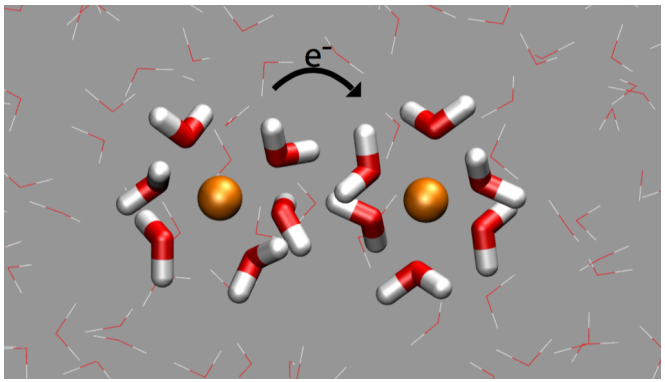
→ in Marcus regime

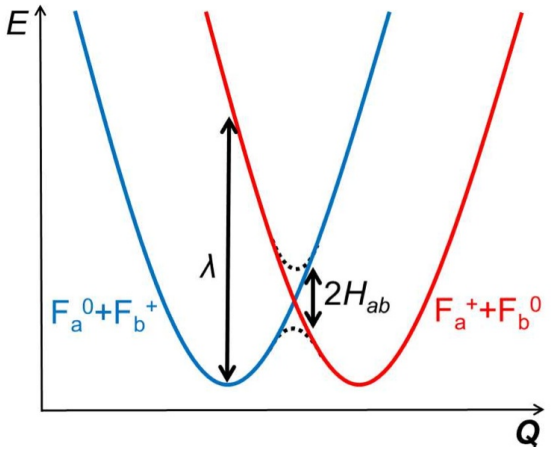
Organic semiconductors: ε_s = SMALL H_{ab} / λ = LARGE



Charge transfer in organics: outside Marcus regime

Ions, proteins in water: ε_s = LARGE H_{ab} / λ = SMALL





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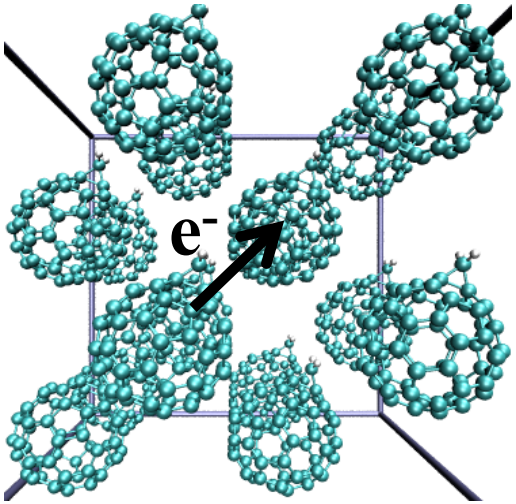
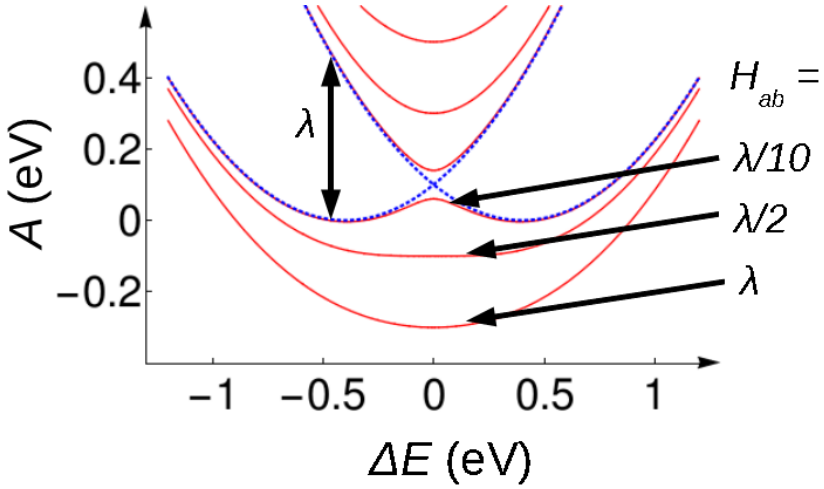
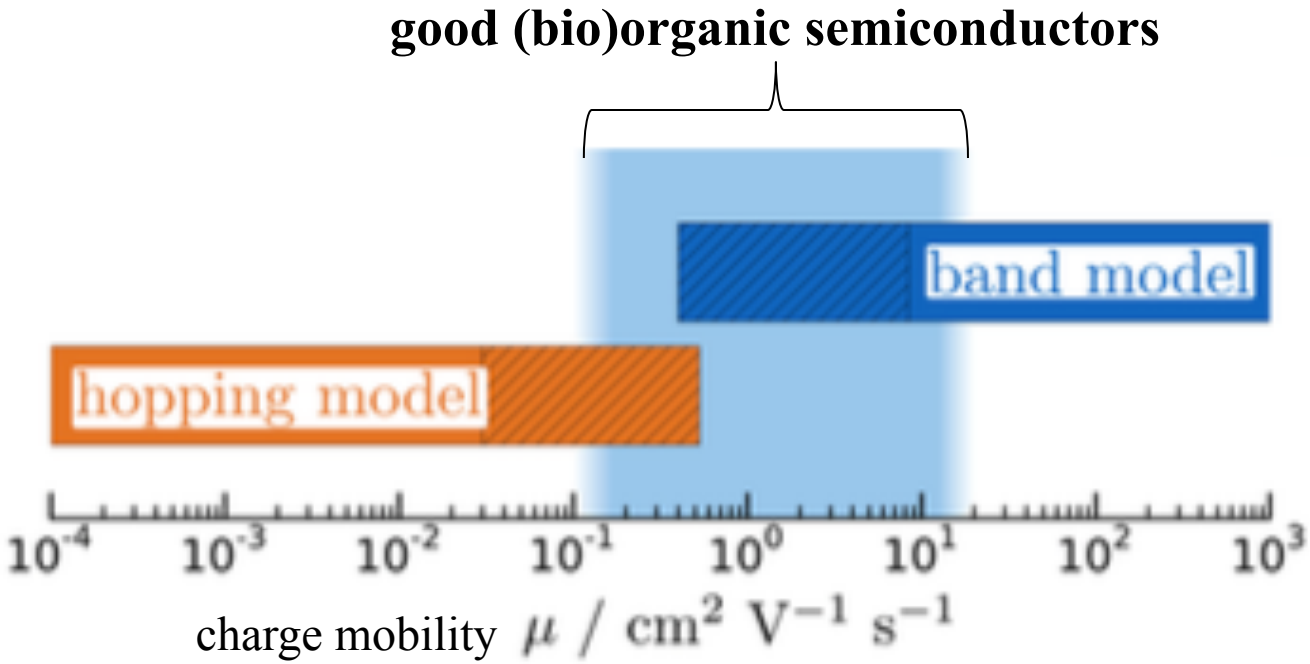




→ outside Marcus regime

Speed limits for charge hopping and band transport



$$\mu_{hop} \leq \frac{2\pi c \tilde{\delta} d_{ab}}{k_B T} = \mu_{hop}^{\max}$$

$$\mu_{band} \geq \frac{q d_{ab}}{v_g m^*} = \mu_{band}^{\min}$$

ET rate << vibrational relaxation time

carrier mean free path > lattice spacing

Troisi, Org. Electron. 12, 1988 (2011)

→ Charge transfer too fast for rate theories to apply

→ Coupling charge transfer & nuclear dynamics too large for band theory to apply

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→ Solve coupled electron-nuclear dynamics directly (non-adiabatic dynamics)

Non-adiabatic dynamics methods

Ehrenfest molecular Dynamics

Fewest switches surface hopping (Tully)

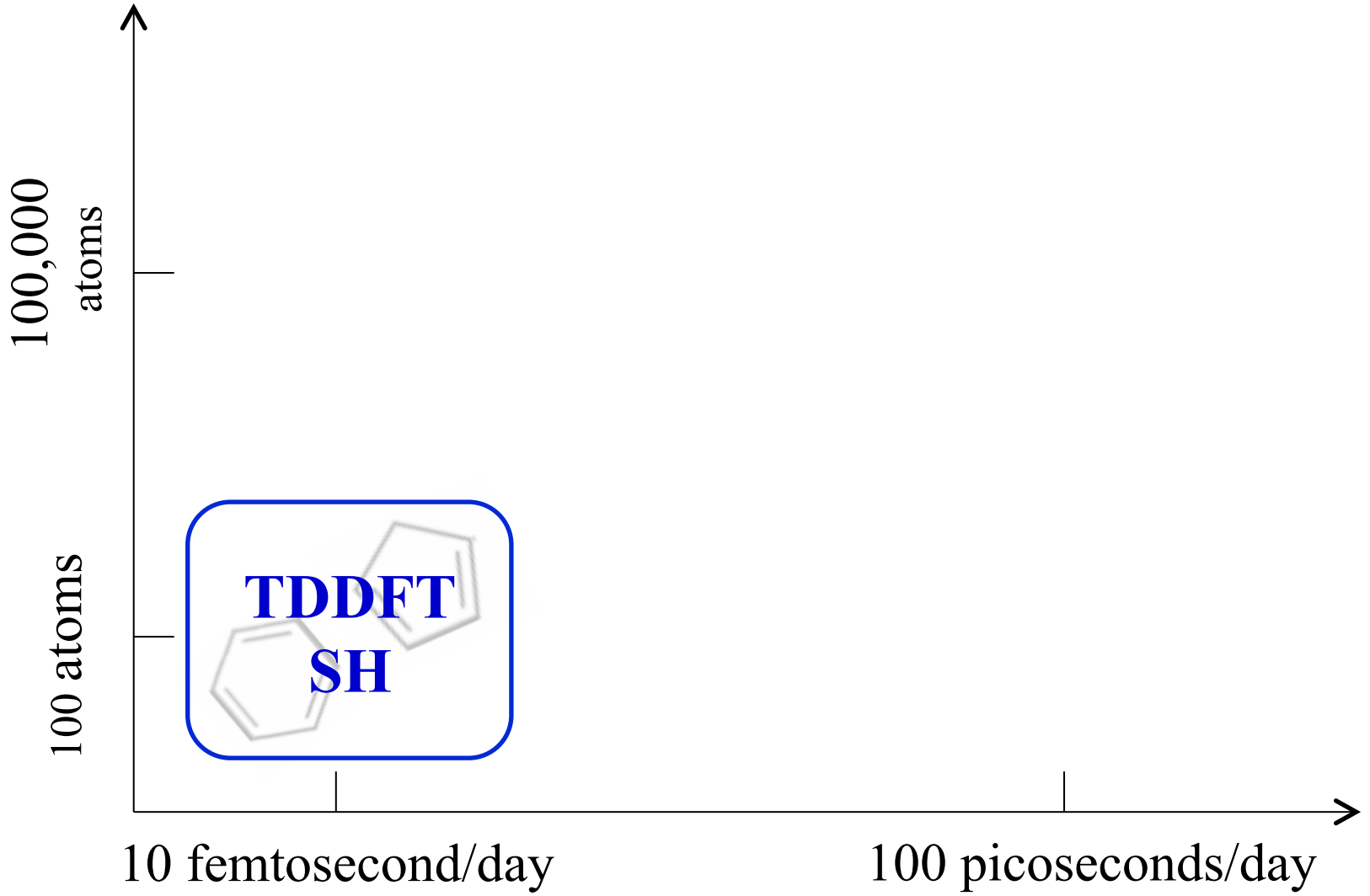
Ab-initio multiple spawning (Martinez)

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

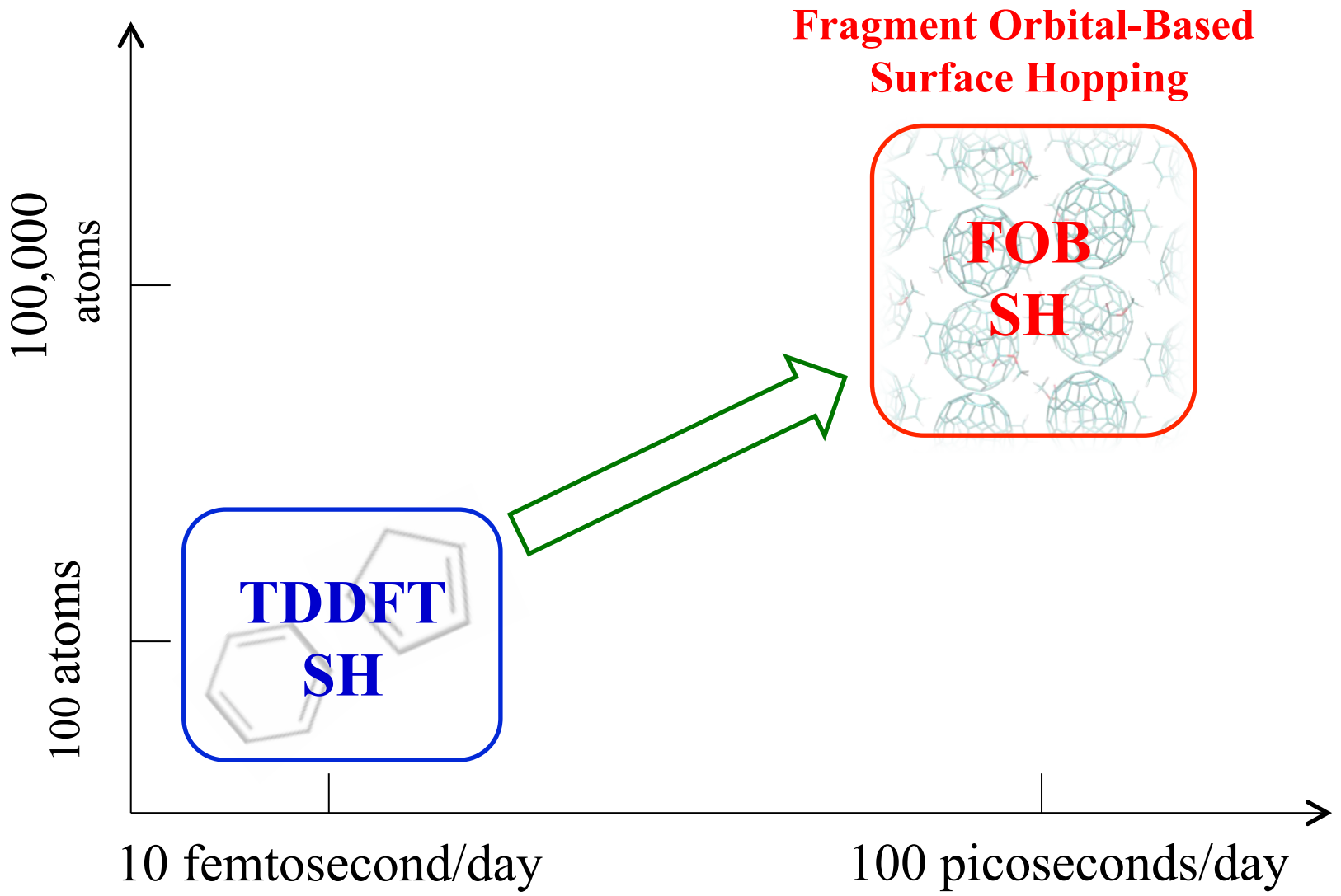
Multiconfigurational time-dependent Hartree (Worth, Burghardt,…)

Exact factorisation of molecular wavefunction (Gross et al)

TDDFT-SH: VERY high computational cost



Use cheap (but reasonably accurate) electronic Hamiltonians



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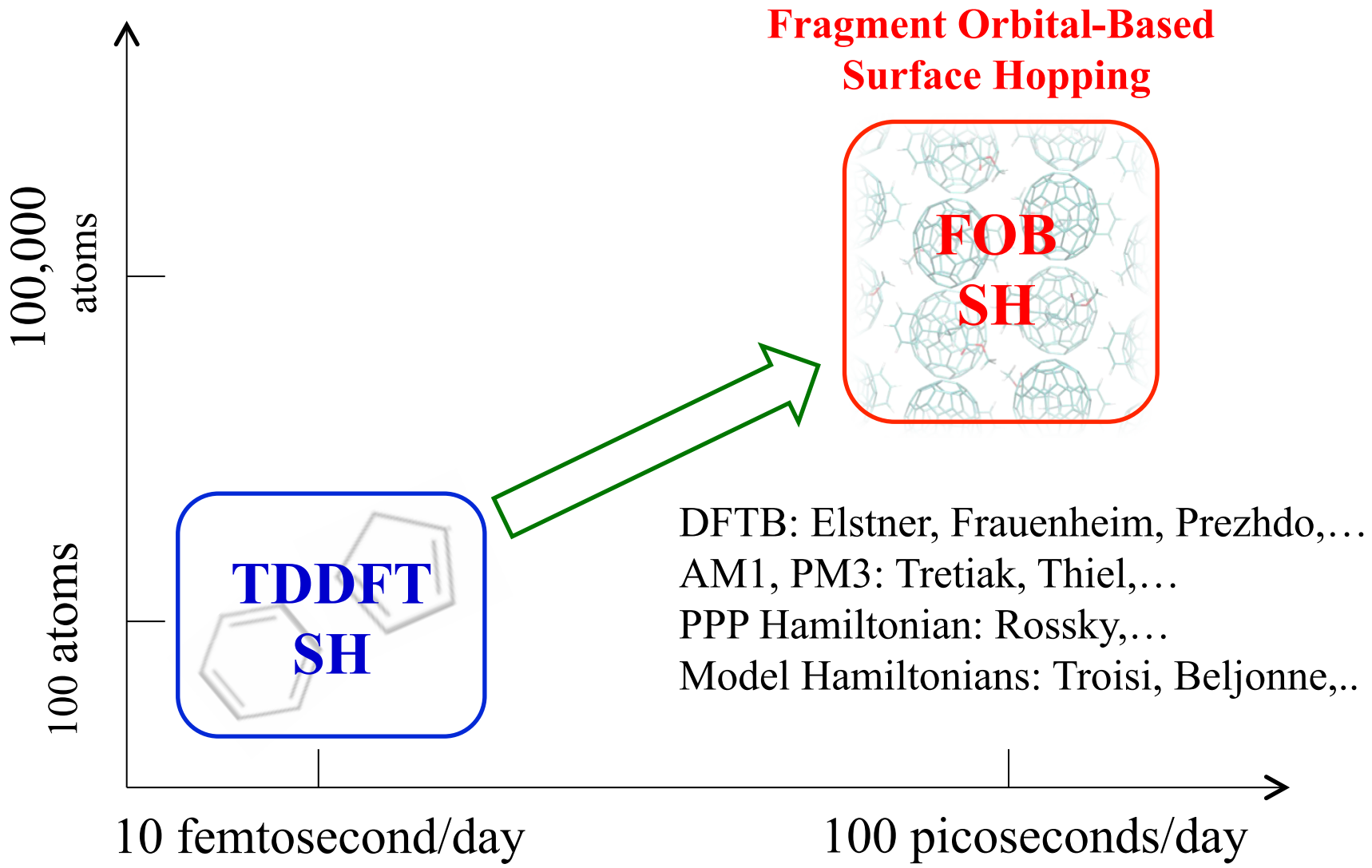

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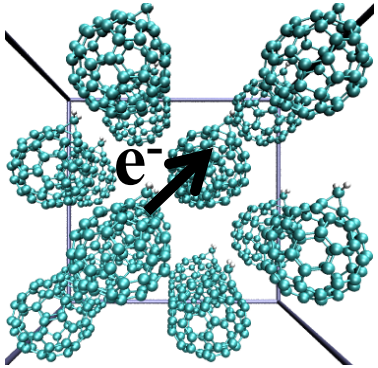

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Strategy: Minimalistic model that gives the right physical behaviour
Being rigorous within that model

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2 major approximations:

1. Exact electron-nuclear quantum dynamics replaced by
   mixed quantum-classical dynamics (here, surface hopping)

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

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1. Exact electron-nuclear quantum dynamics replaced by
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   a 1-particle wavefunction describing the excess electron or hole

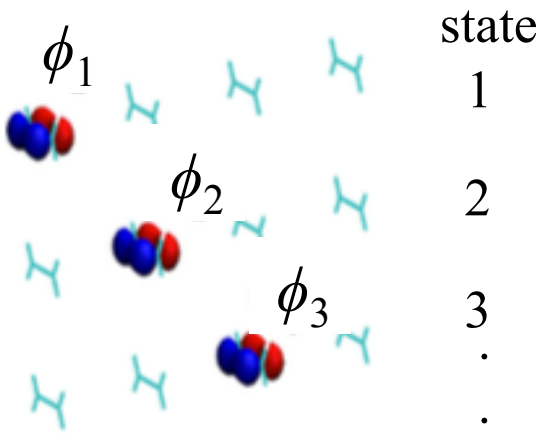
→ **NO explicit core and valence electrons.**
Implicitly included by parametrization of electronic Hamiltonian.

FOB-SH: electronic equation of motion

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

electron hole

State basis of SOMO orbitals



state
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Electron hole wavefunction:

$$\psi(\boldsymbol{r},t) = \sum_k u_k(t)\phi_k(\boldsymbol{r},\boldsymbol{R}_I(t))$$

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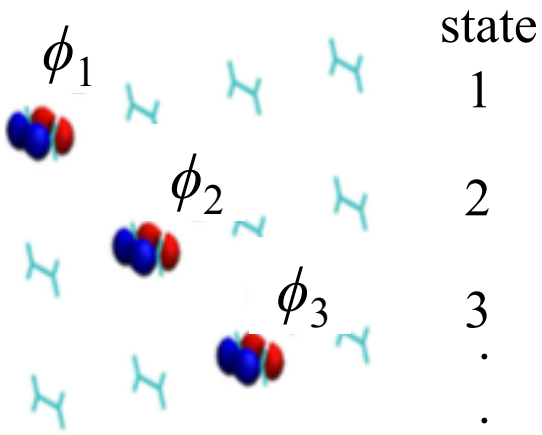

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$$i\hbar\dot{u}_k = \sum_l u_l\left(H_{kl} - i\hbar\left\langle\phi_k\middle|\dot{\phi}_l\right\rangle\right)$$

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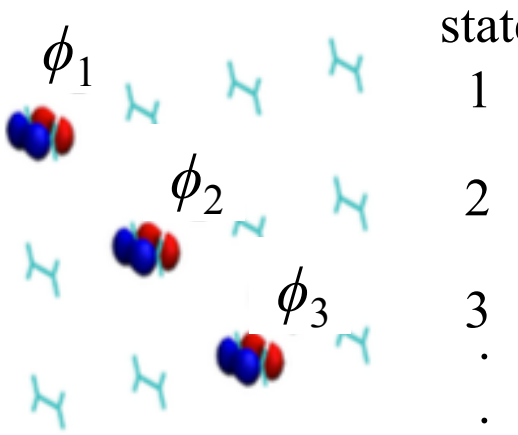

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nuclei

Classical nuclear dynamics

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

*i*th adiabatic electronic state

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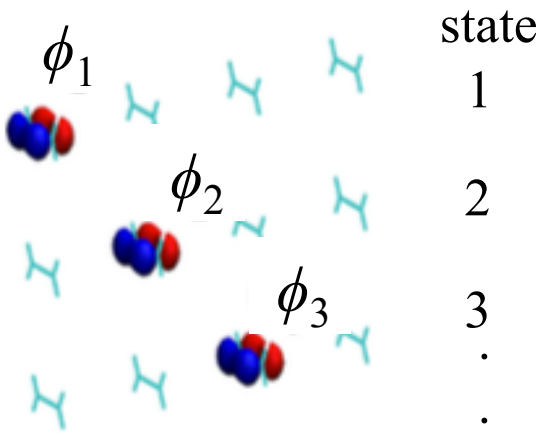

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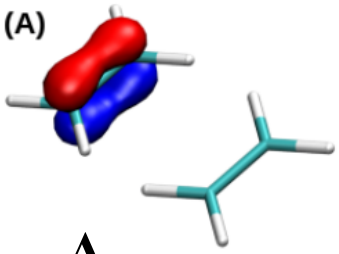
Stochastic hopping from surface $E_i \rightarrow E_j$ with probability

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

Illustration: hole transfer in ethylene dimer

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



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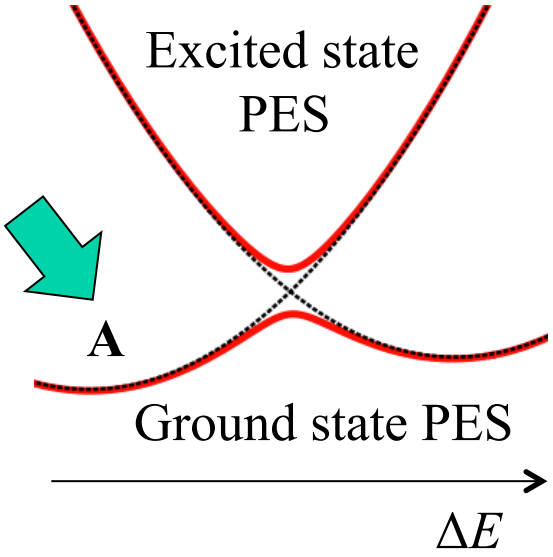

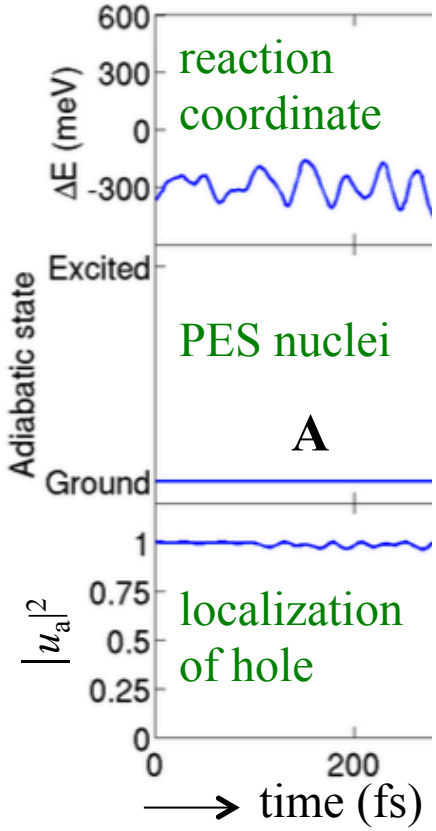

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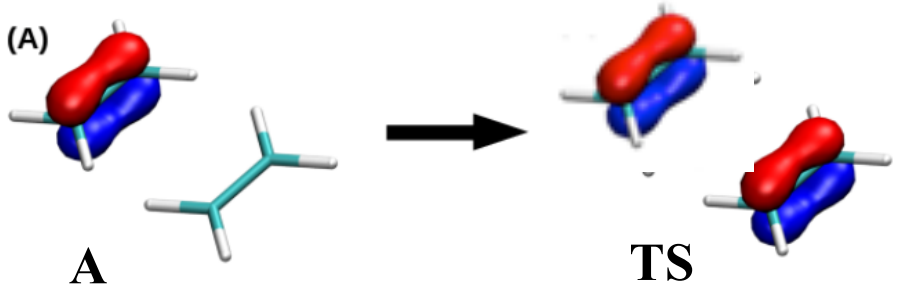

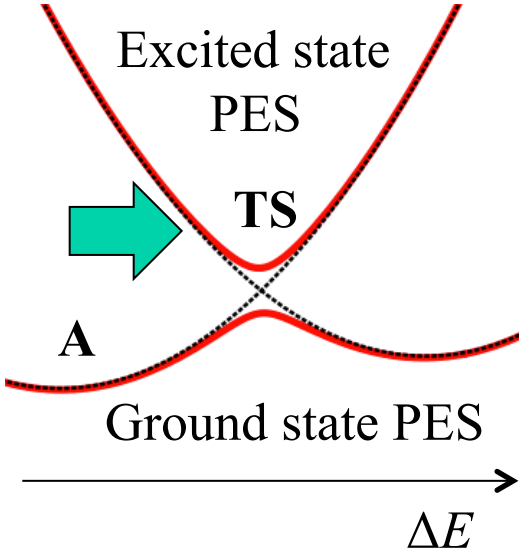

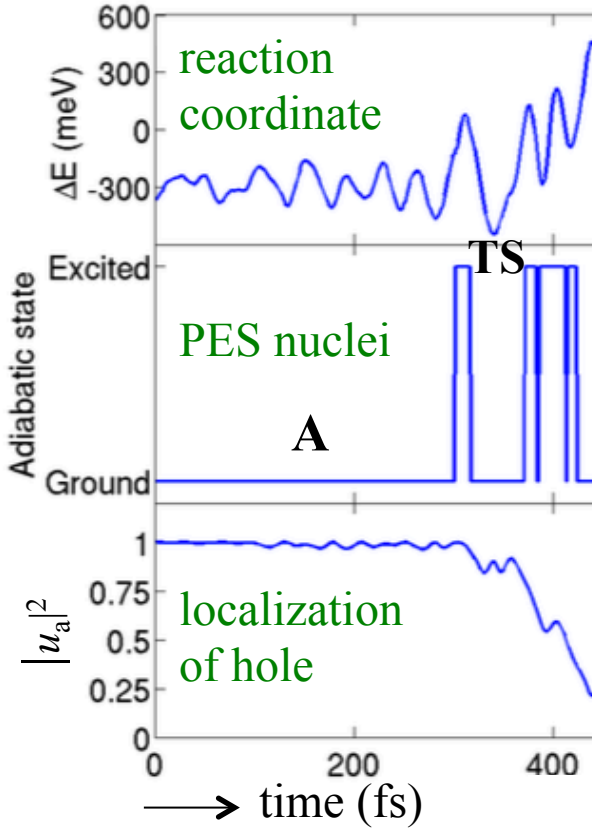

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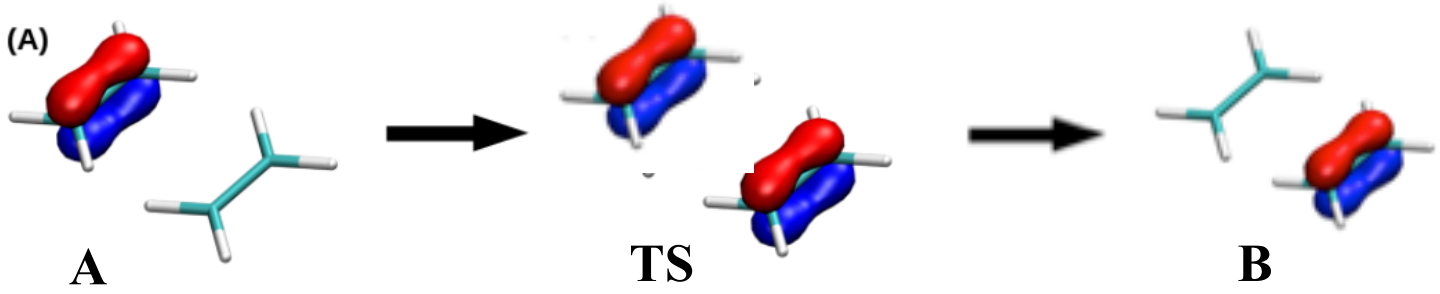
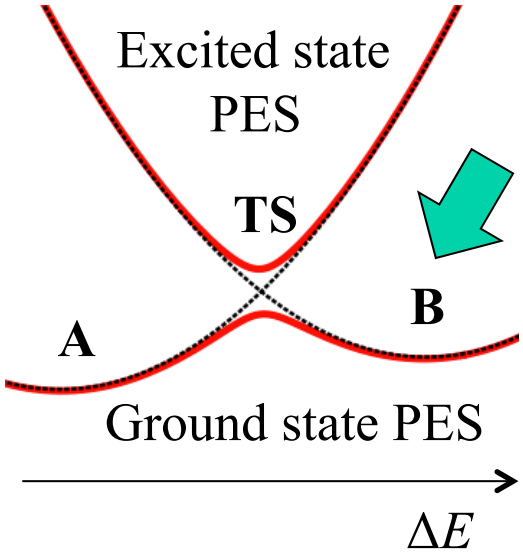
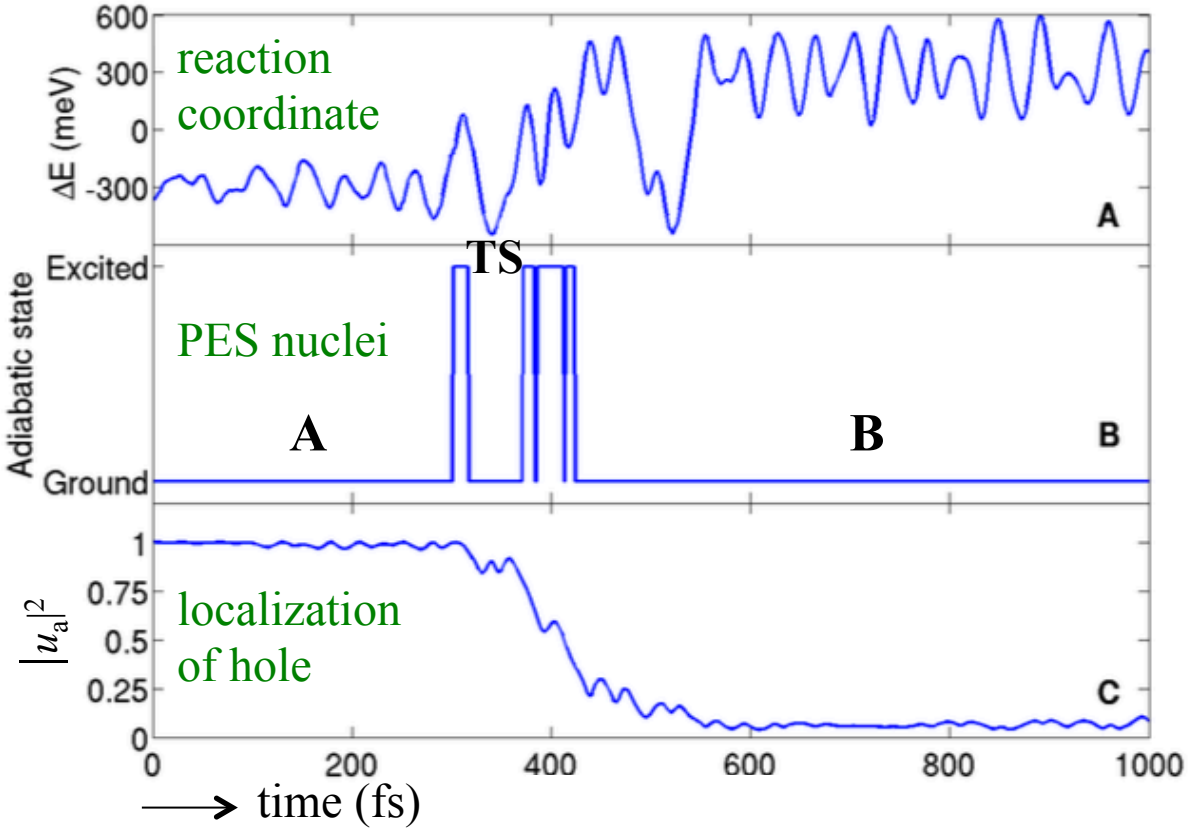
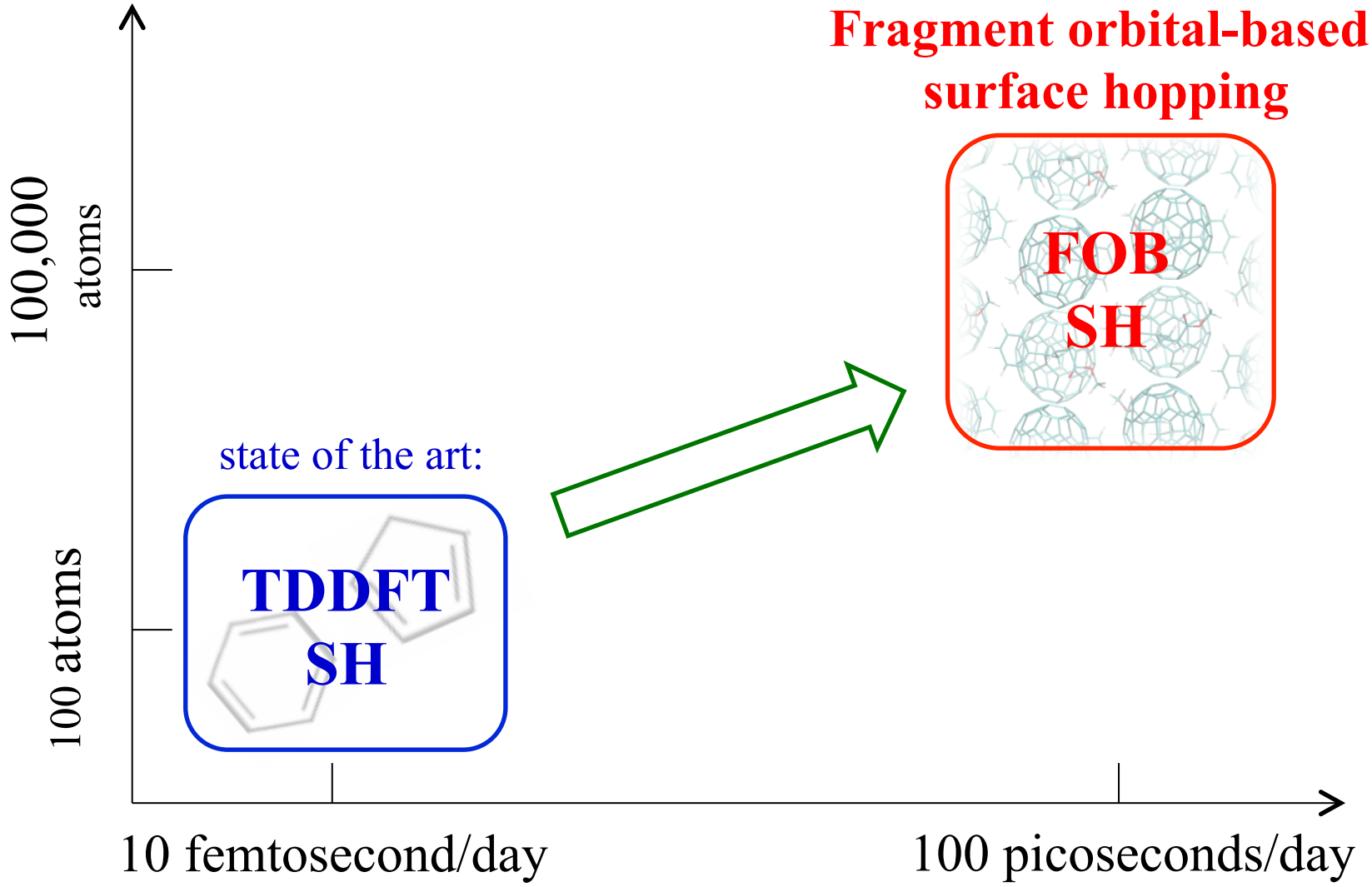






Faster, Bigger

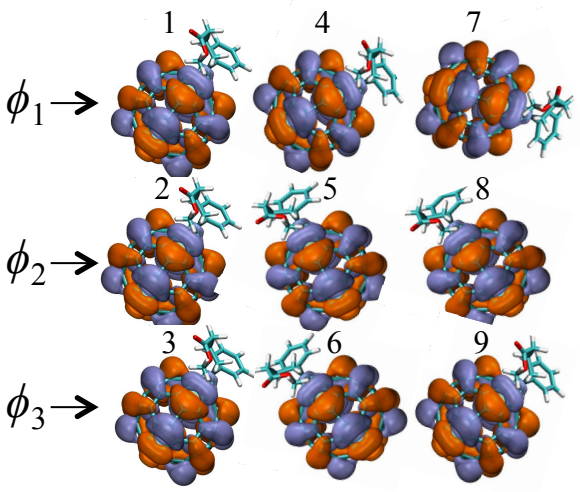


1. Fast calculation of electronic Hamiltonian

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

Electronic Hamiltonian:

$$H_{kl} = \langle \phi_k | H | \phi_l \rangle$$



force field

Analytic overlap method (AOM)

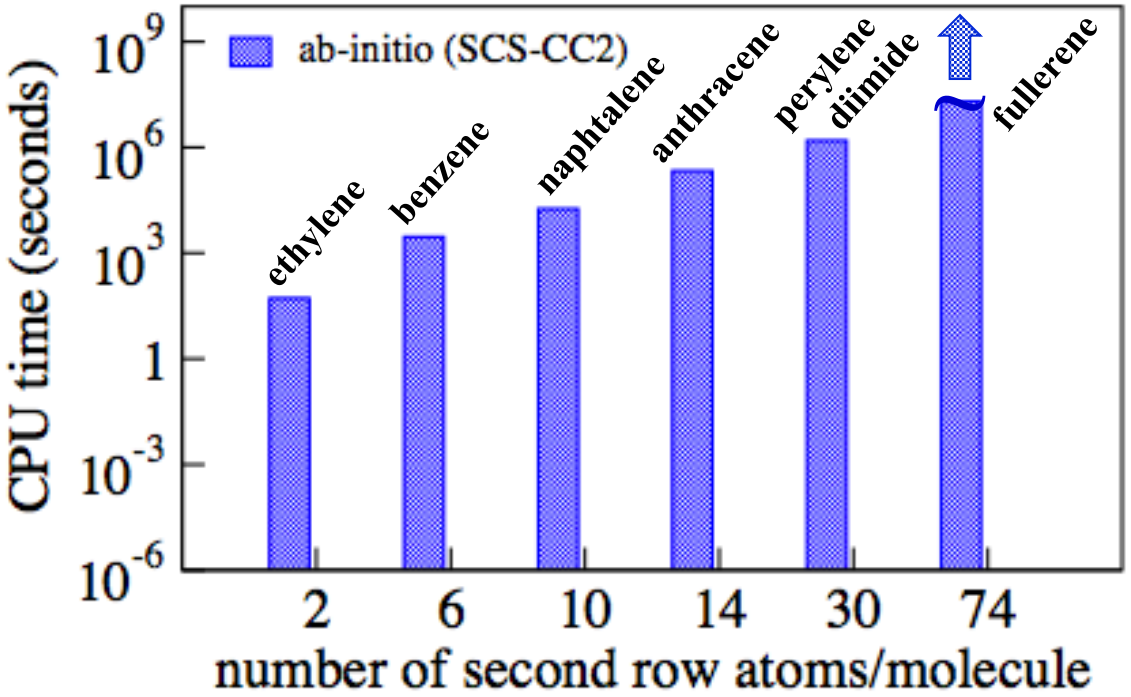
$$H_{kl} = \bar{C}\,\bar{S}_{kl}$$

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

Reference ab-initio (SCS-CC2) calculation of H_{kl}

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

$$H_{ab} = \langle \; | \hat{H} | \; \rangle$$



AOM: Speed-up

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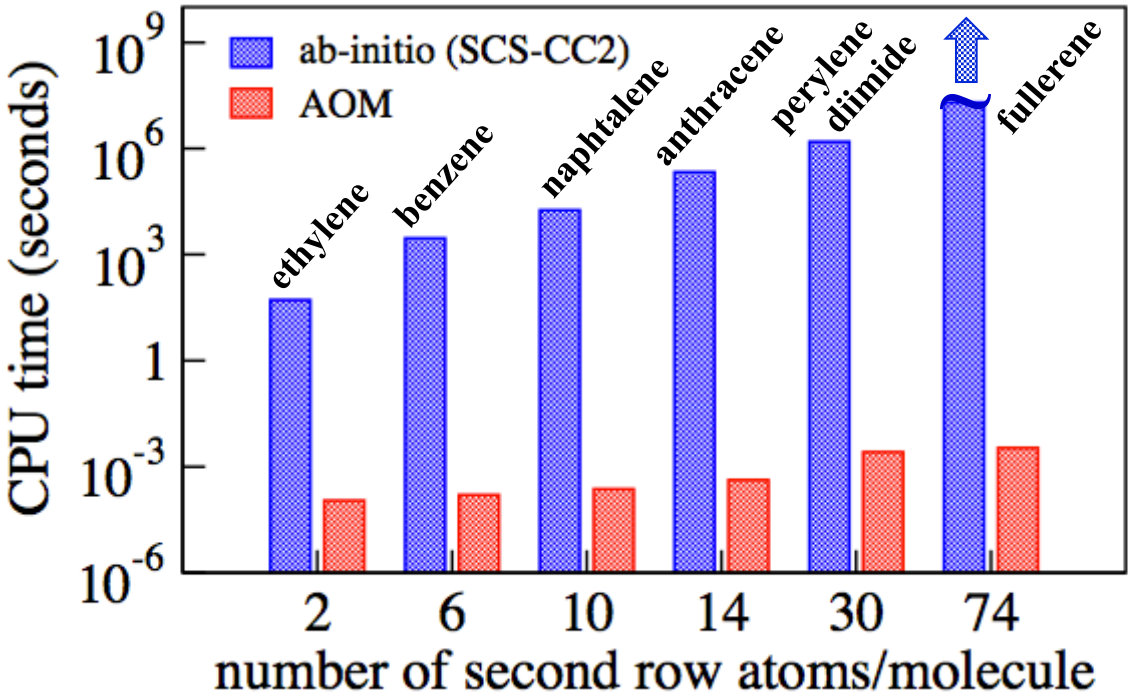

→ speed-up of 9 (6) orders of magnitude wrt ab-initio (DFT)

→ reaches relevant system sizes (30-100 atoms/molecule)

Accuracy

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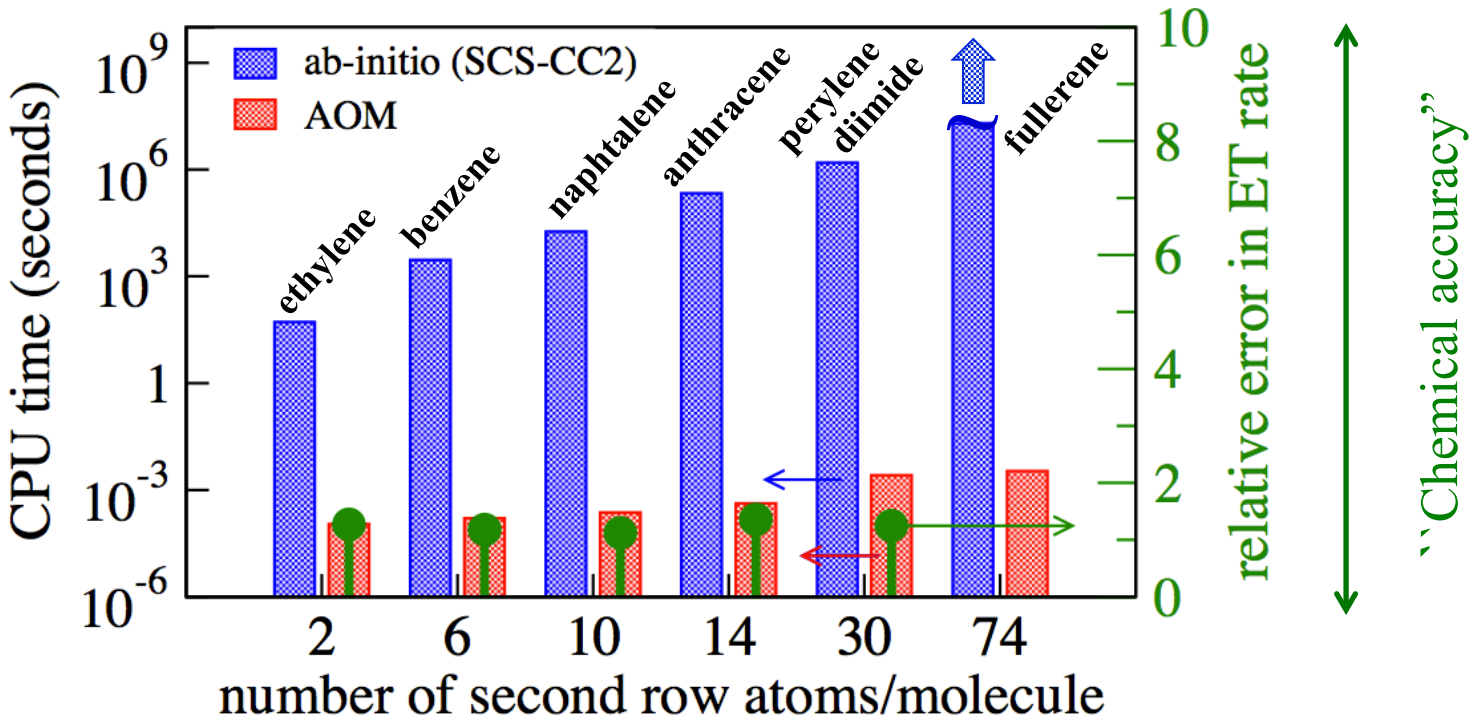


→ speed-up of 9 (6) orders of magnitude wrt ab-initio (DFT)

→ reaches relevant system sizes (30-100 atoms/molecule)

→ Error in ET rate $i \leftarrow j$ < factor of 2 → AOM chemically accurate

2. Fast calculation of nuclear gradients

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

$$\boldsymbol{F}_{I,i} = -\sum_{kl} U^{T*}_{ik} \nabla_I H_{kl} U_{li}$$

nuclear force on adiabatic electronic surface *i*

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

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

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

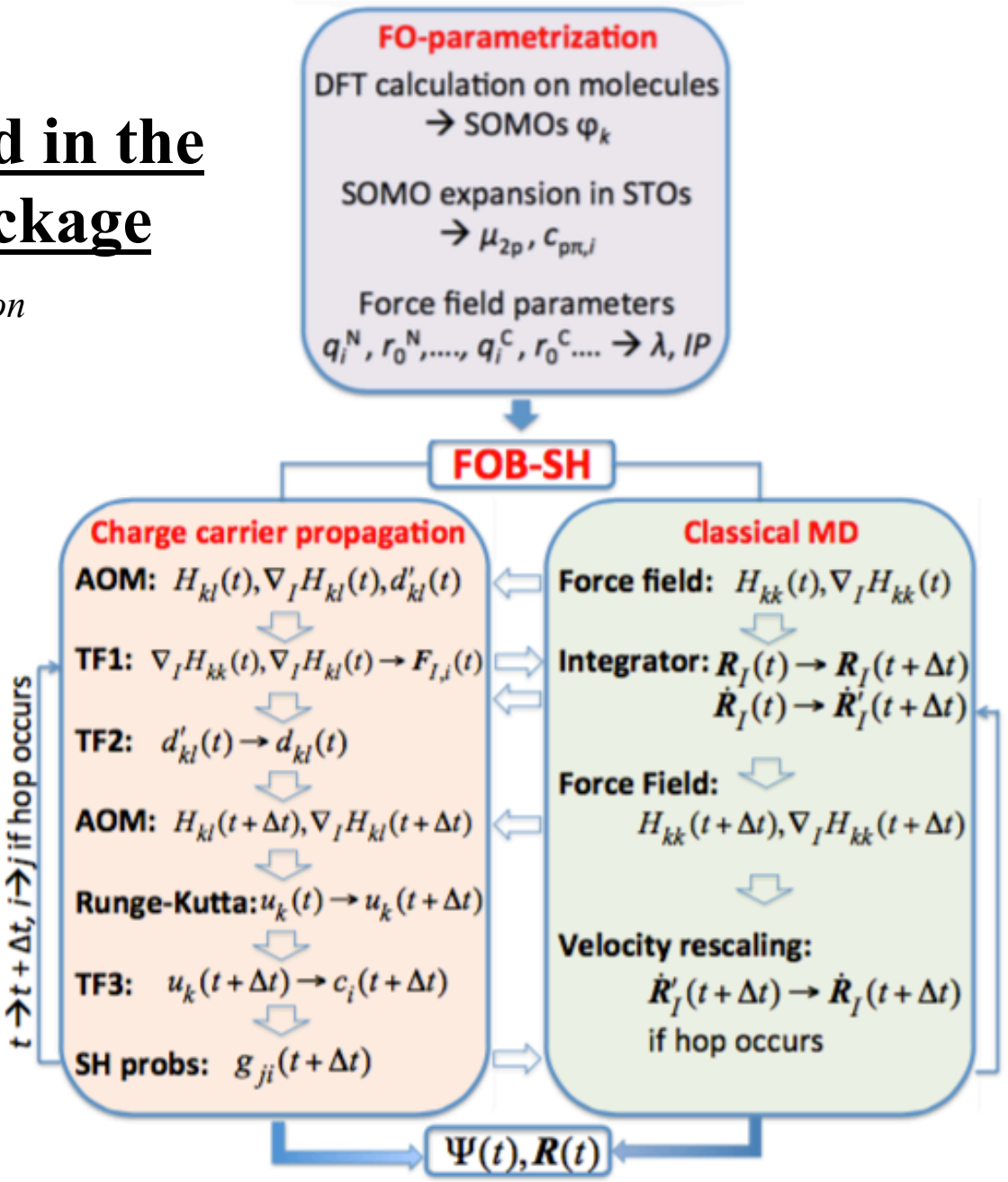
overlap gradients in SOMO basis

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

NACV in SOMO basis
(finite difference)

FOB-SH implemented in the CP2K program package

A. Carof, JB, *in preparation*



Issues to consider in surface hopping simulations

- Electronic wavefunction remains overly coherent after surface crossing

  Decoherence correction: (i) instant collapse of wf to active electronic state
  (ii) exponential damping of inactive electronic states

- Total energy conservation after hop

  Rescaling of nuclear velocity (i) using total velocity vector
  (ii) velocity component parallel to NACV

- After unsuccessful (frustrated) hops: should velocity be reversed? yes

- How to detect trivial surface crossings: (i) flexible SH
  (ii) Self-consistent FSSH (Prezhdo *et al*)

Validation of FOB-SH approach

- **Total energy conservation**

$$\frac{\mathrm{d}E_{tot}}{\mathrm{d}t} = 0 \quad (NVE \text{ ensemble})$$

- **Detailed balance (DB)**

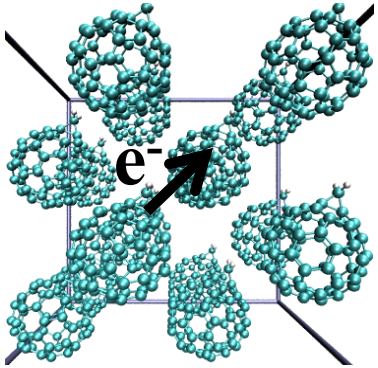
$$\text{Probability of adiabat } i = \frac{\exp(-\beta A_i)}{\sum_j \exp(-\beta A_j)} \qquad A_i \text{ the free energy of adiabat } i$$

- **Internal consistency (IC)**

$$\mathrm{IC}(t,i) = \frac{\text{fraction of trajectories on adiabat } i \text{ at time } t}{\text{average electronic population of adiabat } i \text{ at time } t} = 1 \quad \text{for all } t,i$$

Overview

- A challenge for theory:
  Charge transport in organics materials



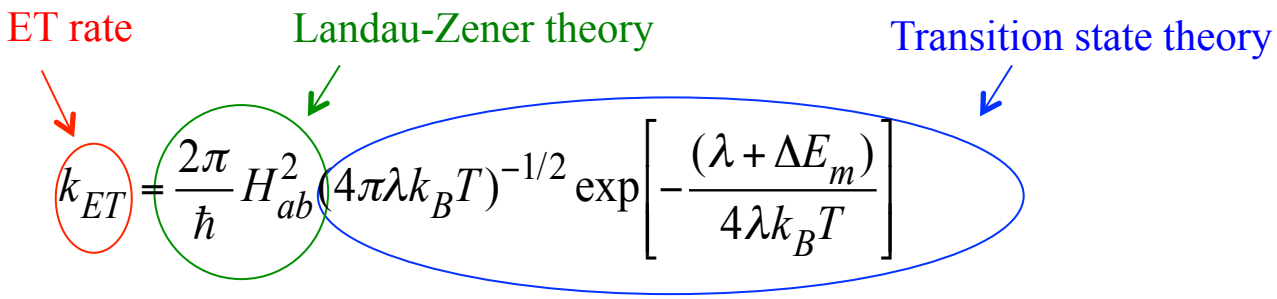
- Novel methodology:
  Fragment orbital-based surface hopping (FOB-SH)

- Application of FOB-SH:
  Hole mobilities in 1D chains of ethylene, rubrene

Questions

J. Spencer, L. Scalfi, A. Carof, JB, *Faraday Disc* 2016.

- *Can FOB-SH recover Marcus Theory ET rates in the regime where Marcus Theory is valid?*

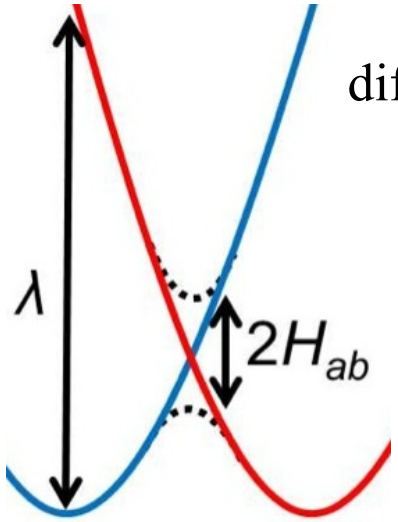


- *What happens beyond that regime?*

Rate k_{ET} vs electronic coupling H_{ab}

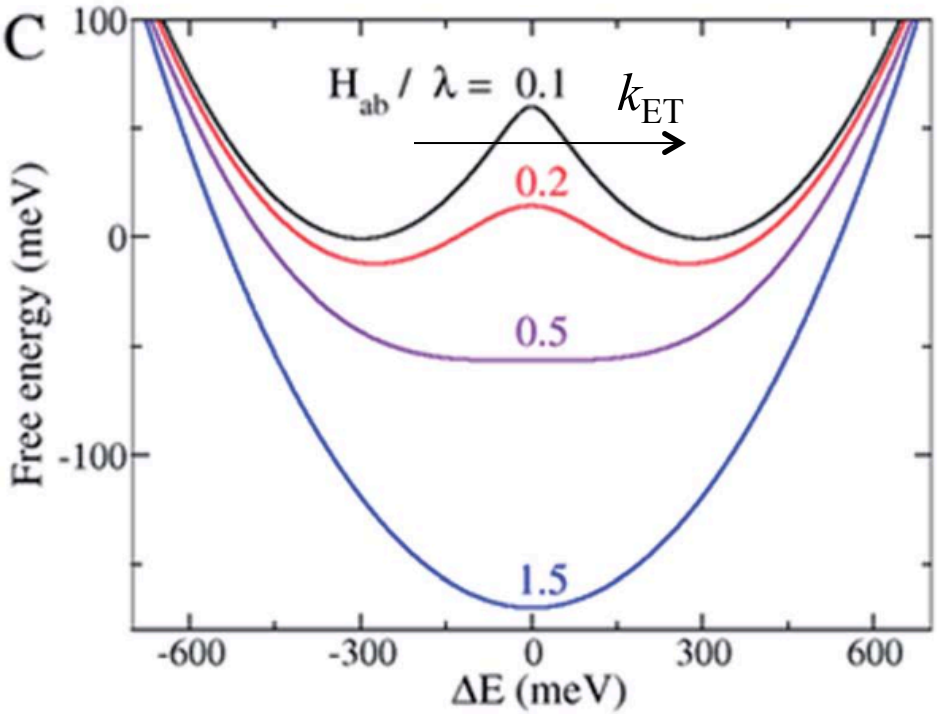
J. Spencer, L. Scalfi, A. Carof, JB, *Faraday Disc* 2016.

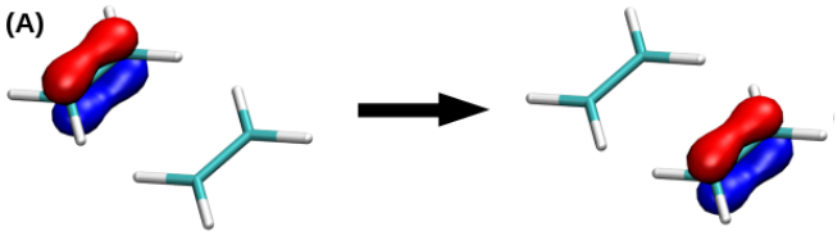
diabatic states



different coupling strengths H_{ab}

adiabatic ground states

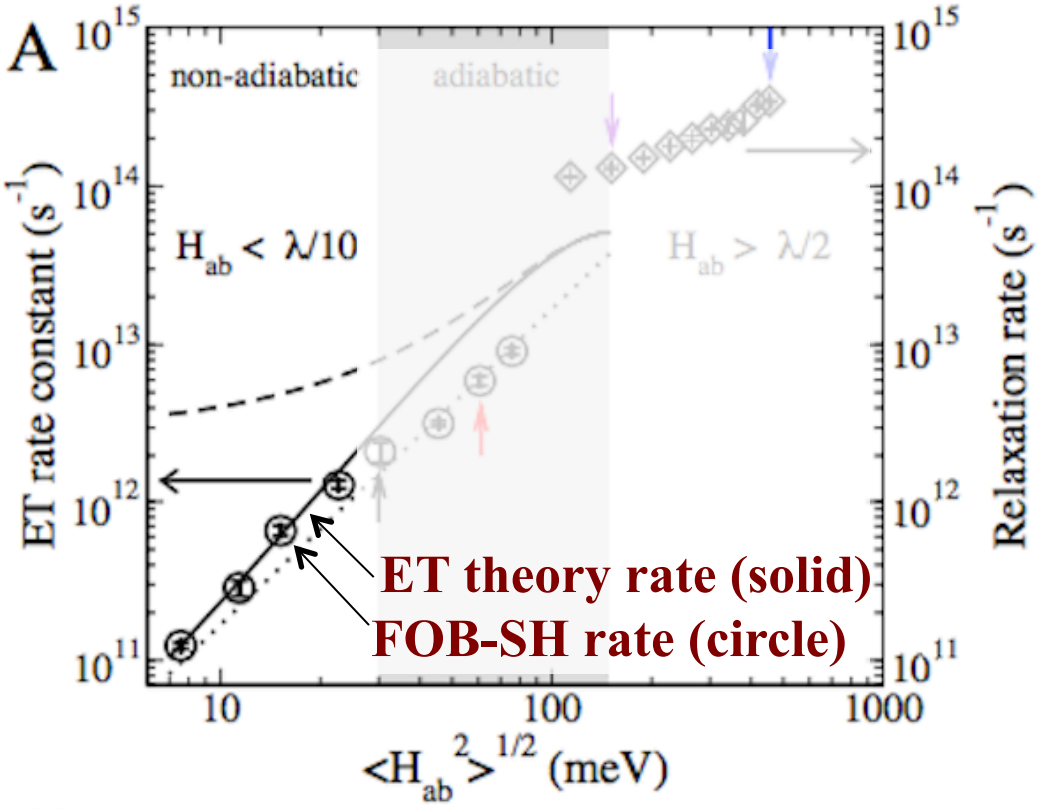


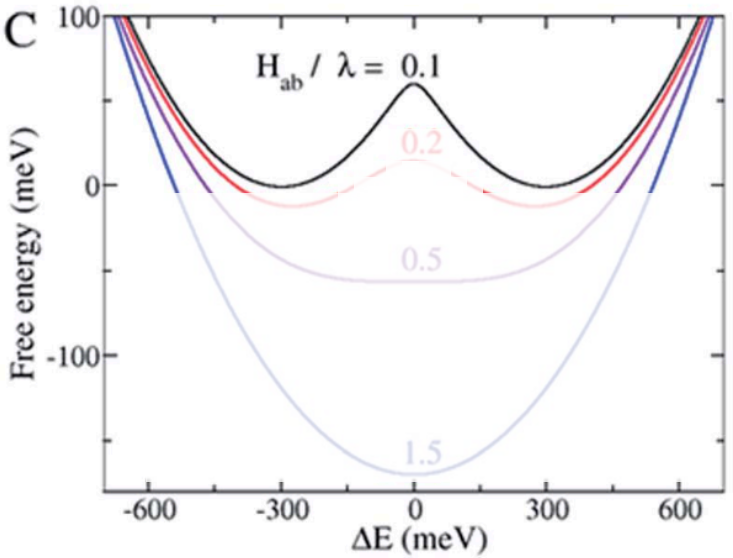


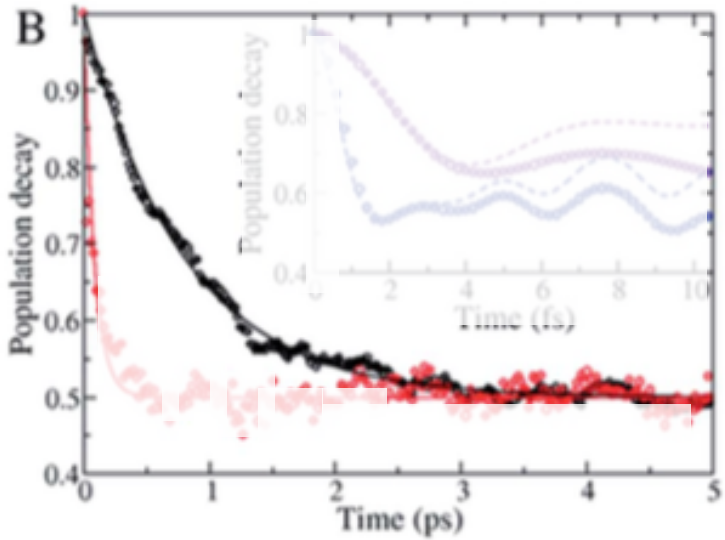
Can FOB-SH recover theory?
What happens for very large H_{ab}?

Rate k_{ET} vs electronic coupling H_{ab}

J. Spencer, L. Scalfi, A. Carof, JB, *Faraday Disc* 2016.







ET theory: $\ln k_{ET} \propto 2 \ln H_{ab}$ small H_{ab}

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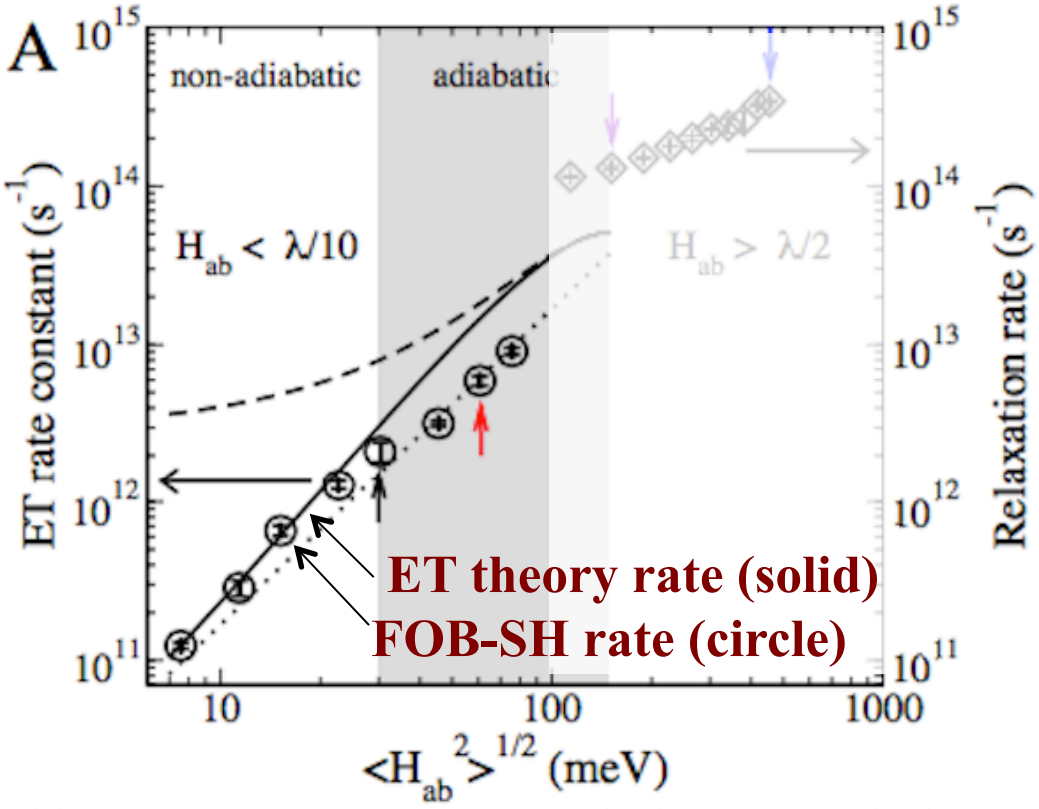

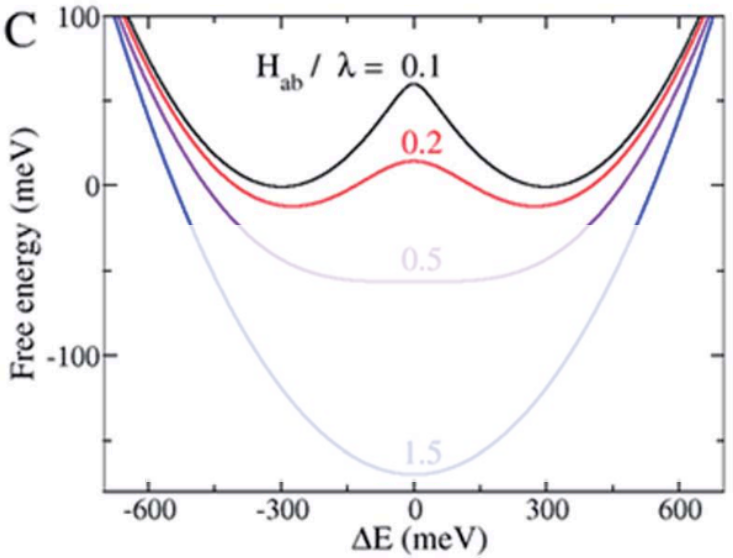

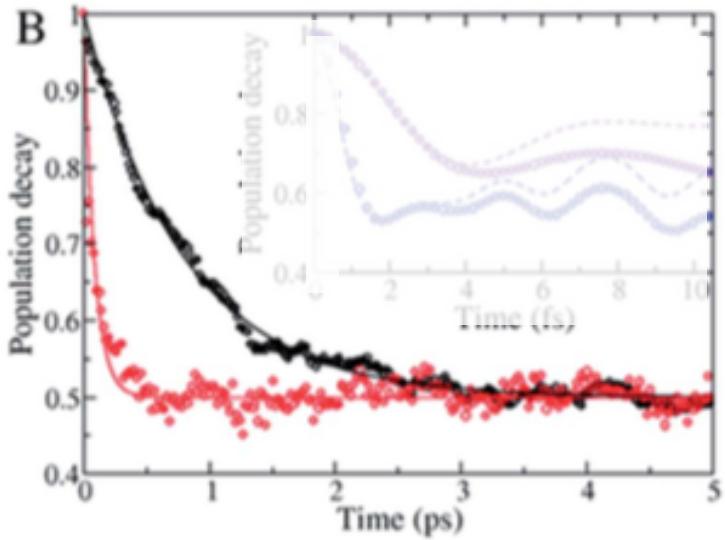

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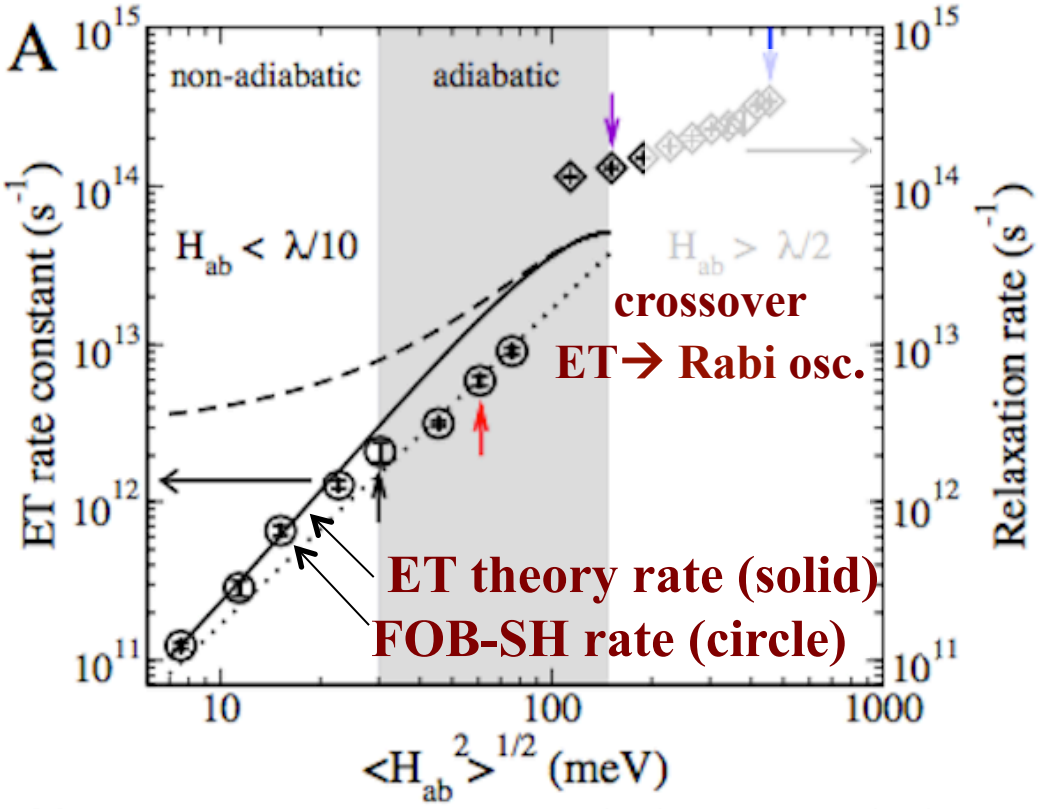

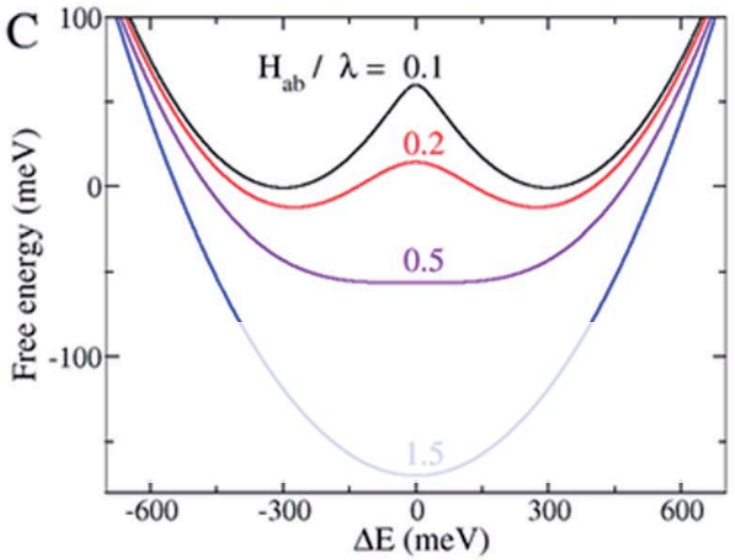

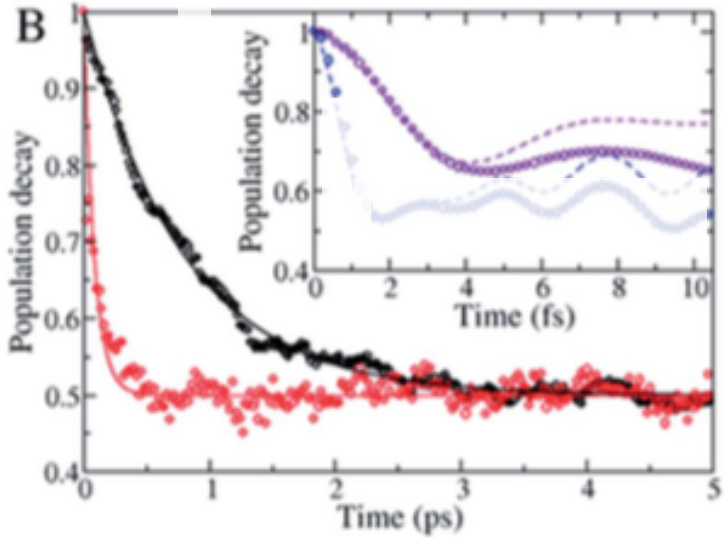

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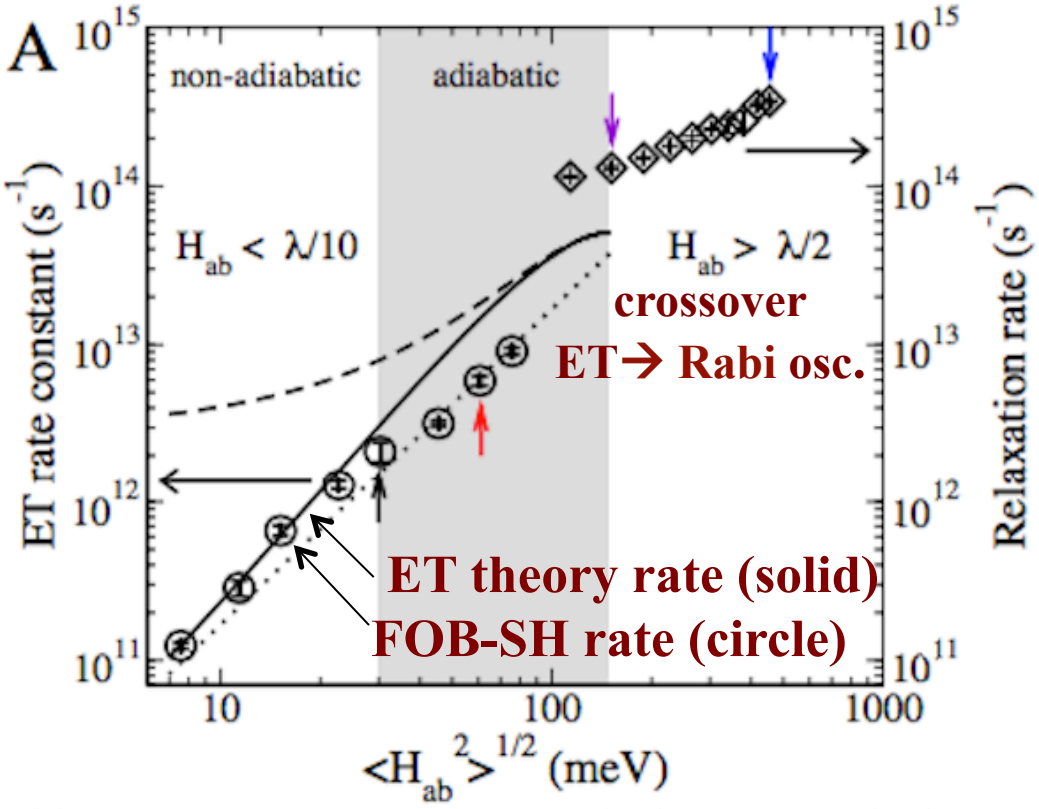

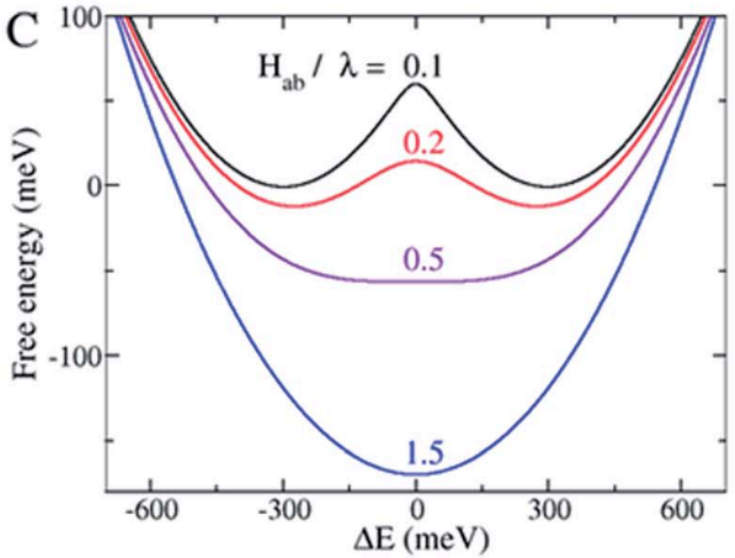

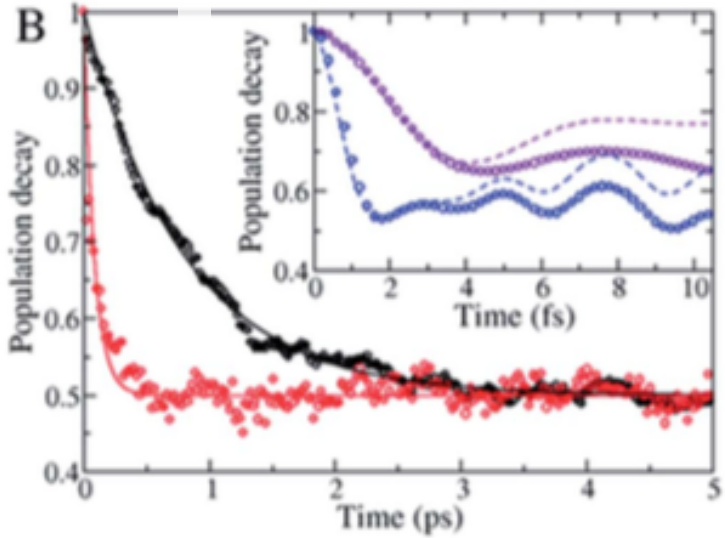

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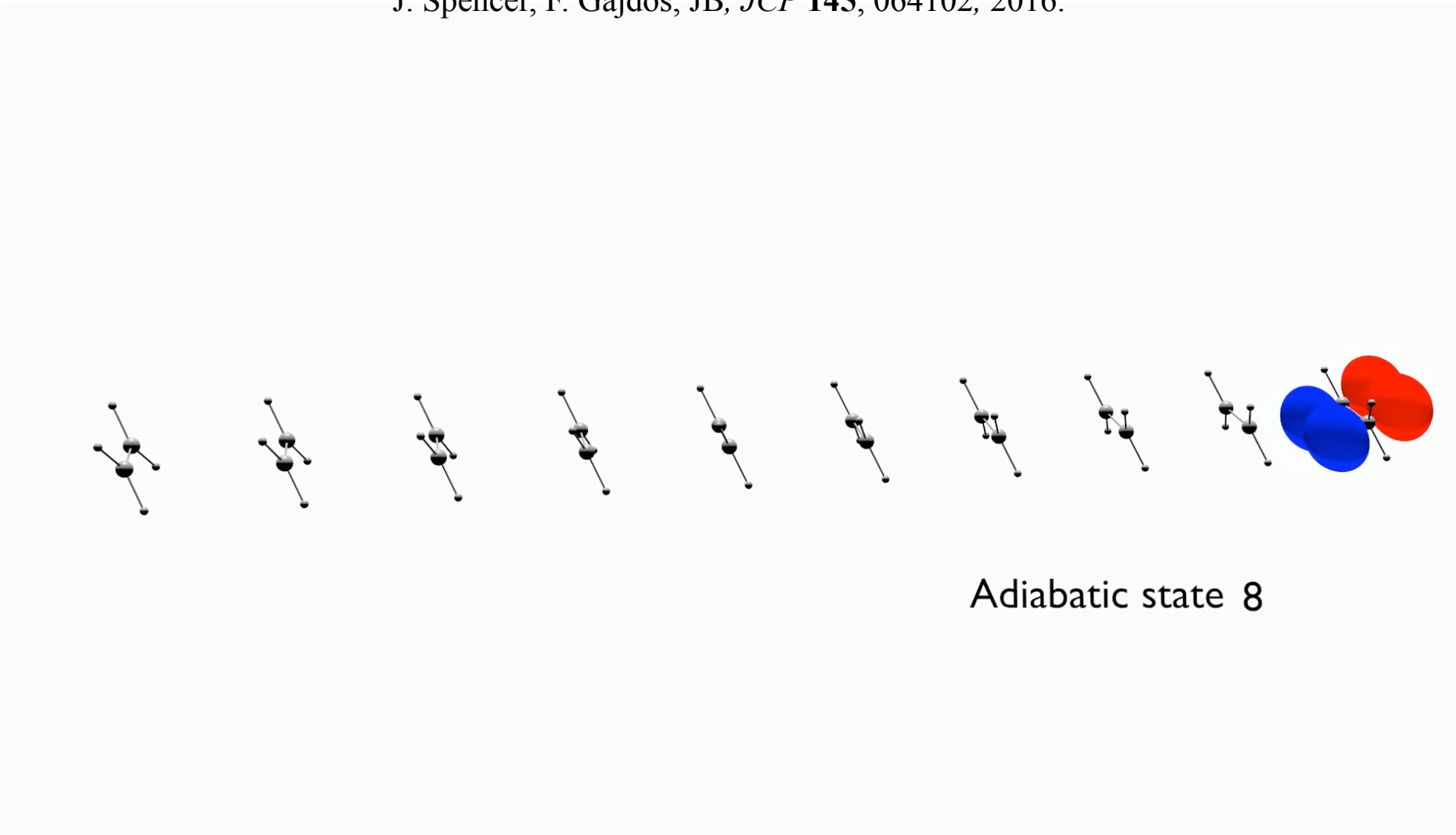
Hole transport along ethylene chain from FOB-SH

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



Hole mobilities from FOB-SH

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

- ~1000 trajectories
- hole mobility

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

$$D = \frac{1}{2}\frac{d}{dt}\left\langle \left\langle \psi_n(t)\middle| x \middle|\psi_n(t)\right\rangle_x^2 \right\rangle_n$$

for T = 100-1000 K

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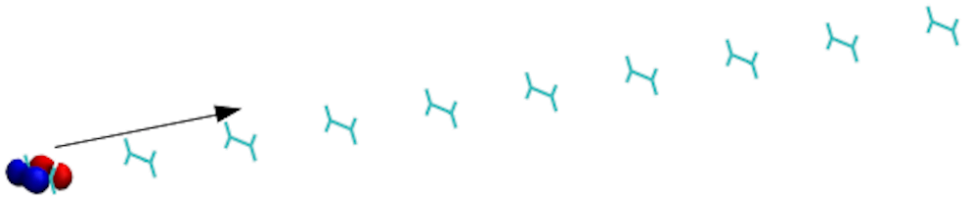

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- 3 electronic couplings

small (2 meV)
medium (20 meV)
large (140 meV)

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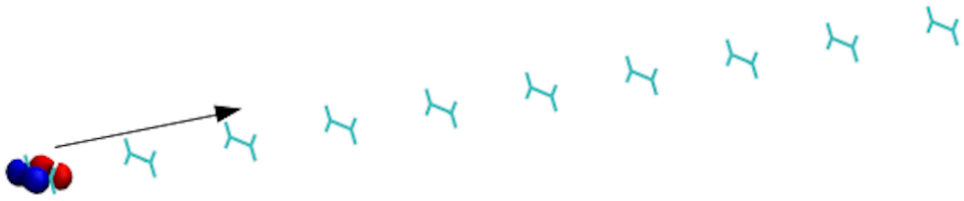

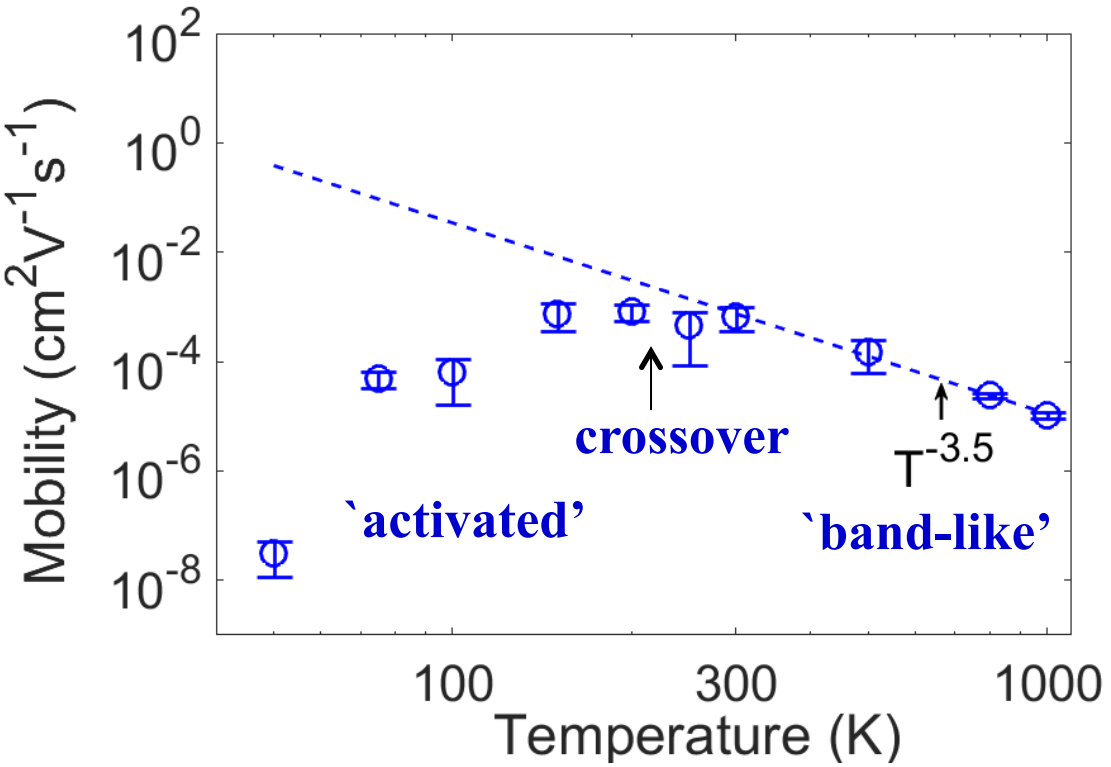

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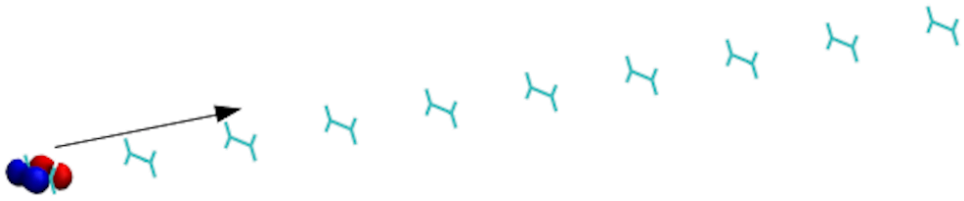

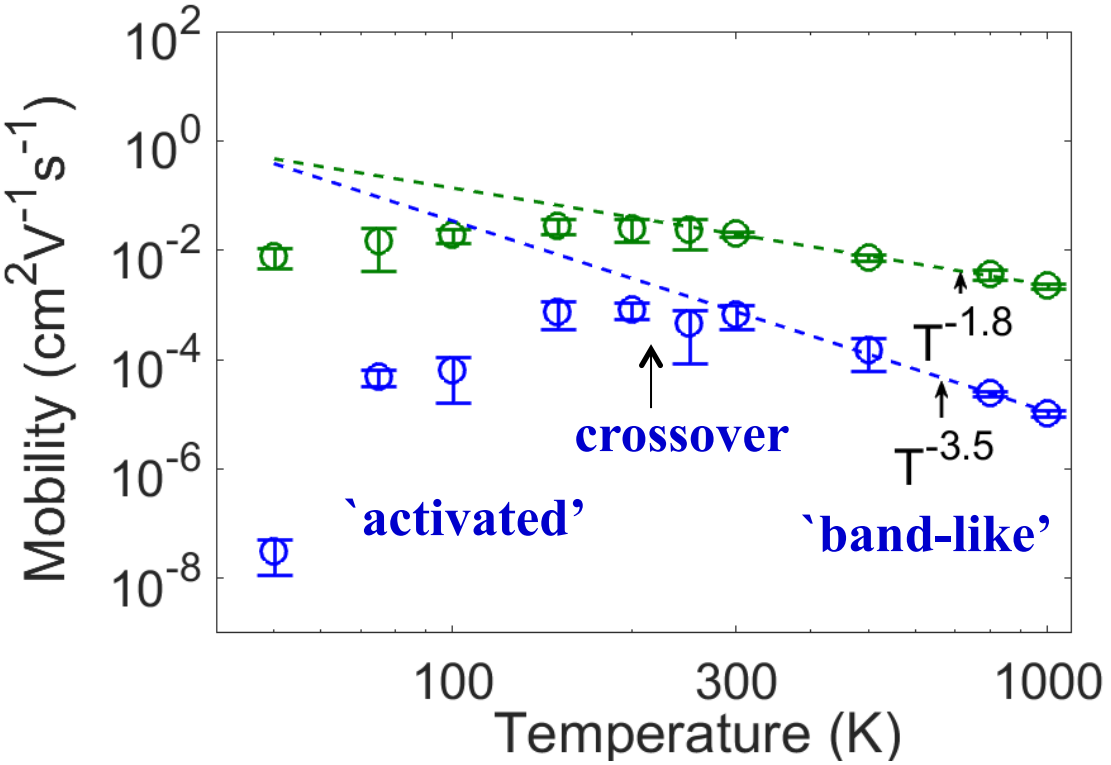

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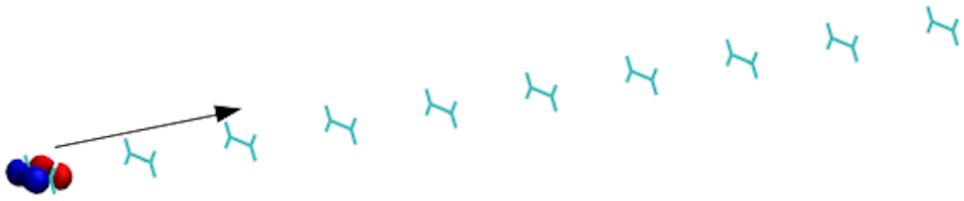

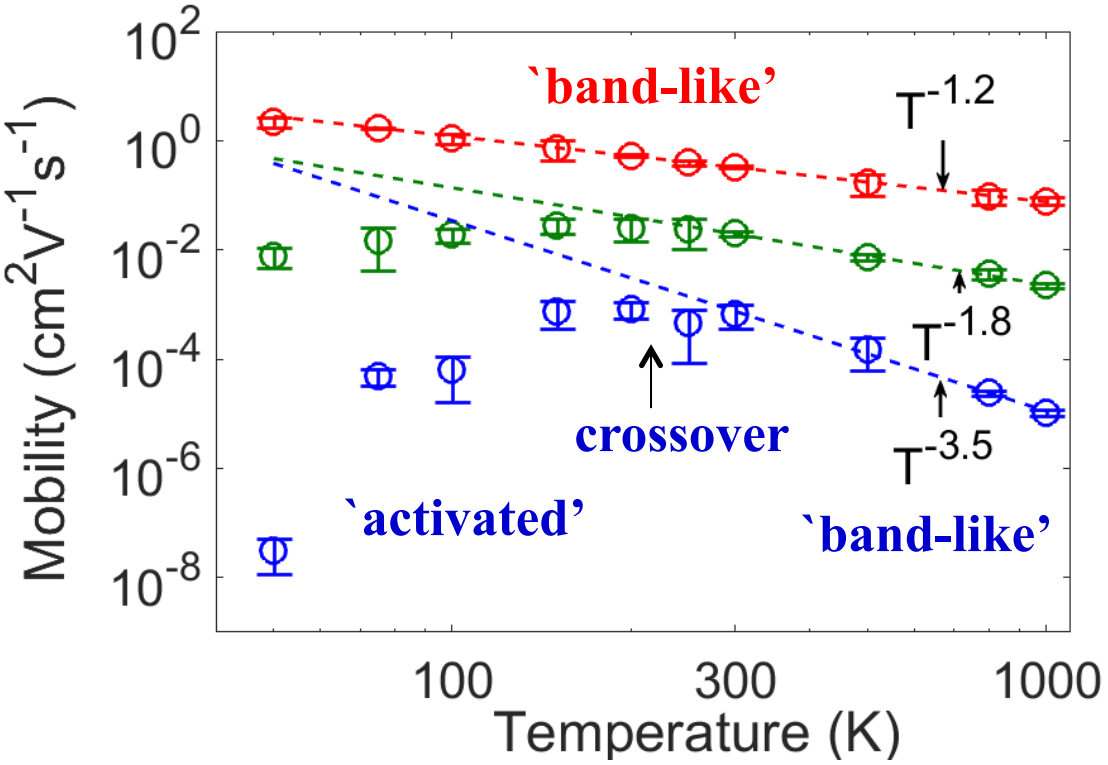

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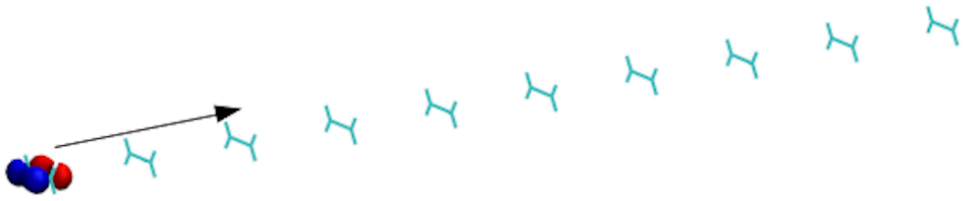
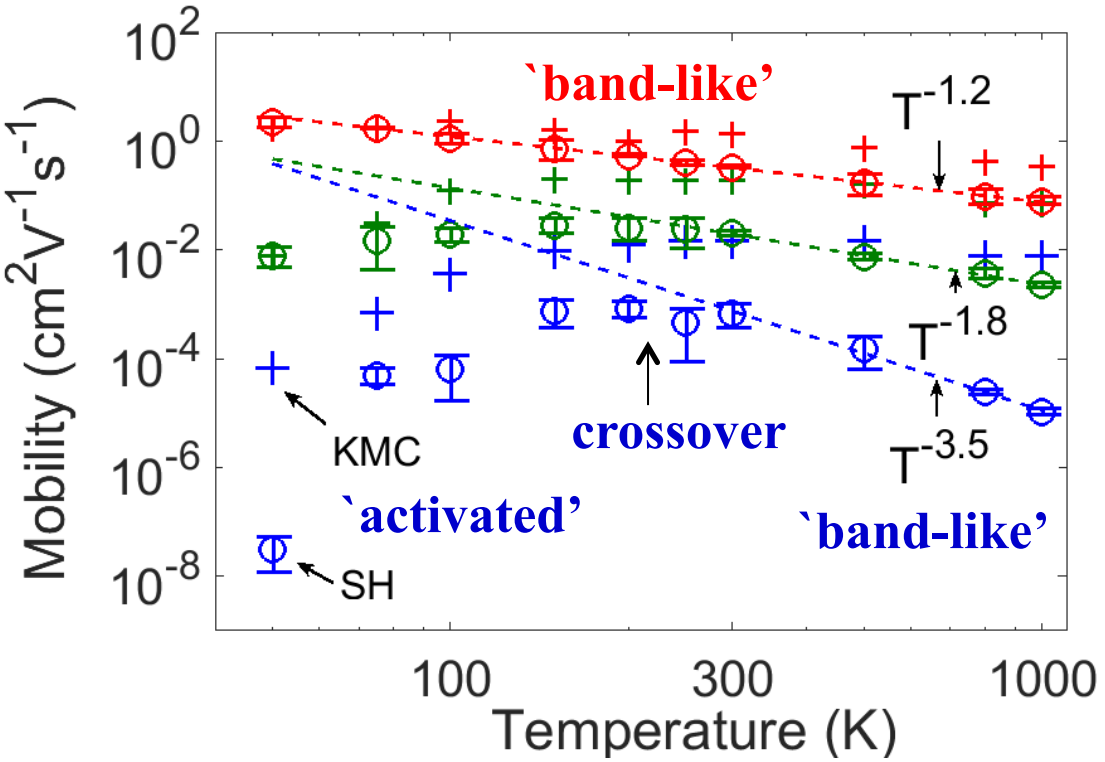
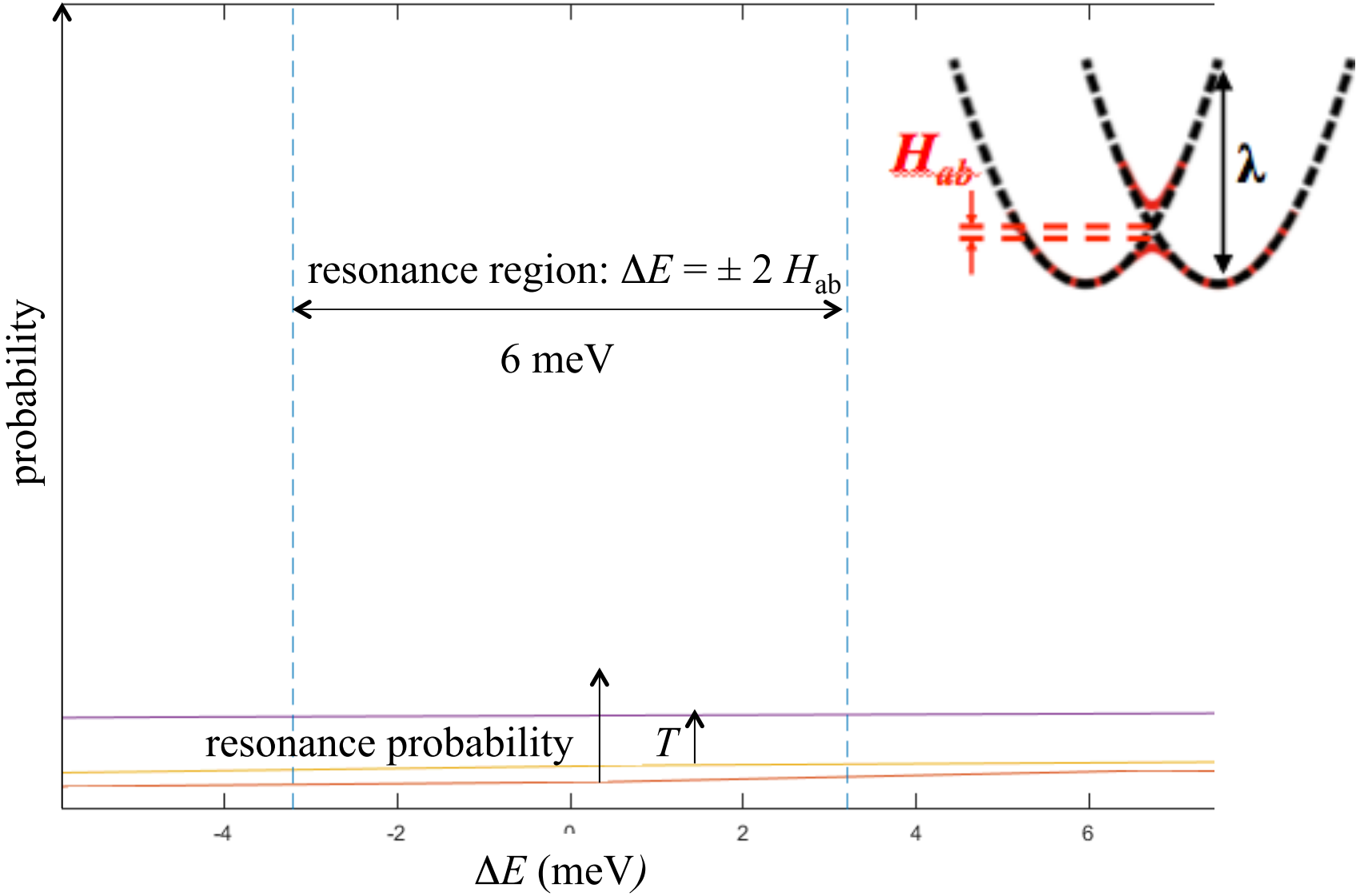




Activated transport (low H_{ab}): resonance probability

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



Band-like transport (high H_{ab}): resonance probability

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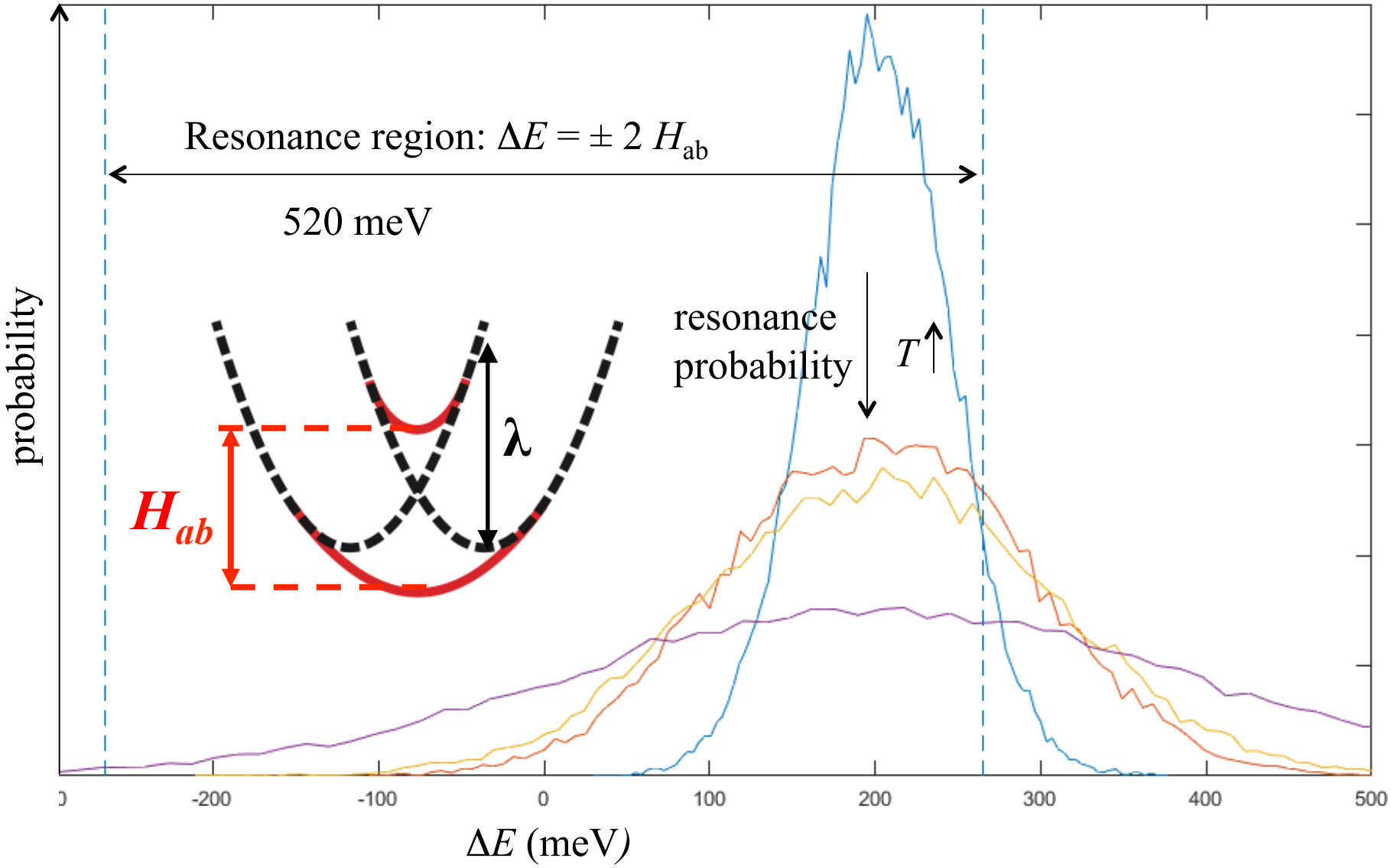


Summary

- Organic semiconductors: No small parameters: $H_{ab} \sim \lambda/2 \sim k_B T$
  → band theory and small polaron model inadequate.

- Fragment-orbital based surface hopping (FOB-SH)
  → a fast quantum-classical MD method for propagation of excess charge carrier at approx the cost of classical MD simulation.

- Reproduces Marcus ET rates in regime where rate theory is valid. Crossover to Rabi oscillations when barrier disappears (high couplings).

- Hole transfer in ethylene chain:
  → crossover from ``activated" to "band-like" at low electronic coupling
  → ~ temperature independent mobility at medium electronic couplings
  → ``band-like" power-law decay of mobility at high electronic coupling

- First application to real material (rubrene):
  → experimental *T*-dependence well reproduced

Acknowledgment

Antoine Carof (UCL)

Samuele Giannini (UCL)

Peter Cooke (UCL)

Hui Yang (UCL)

Jacob Spencer (UCL)

Fruzsina Gajdos (UCL)

Laura Scalfi (ENS Paris)

European Research Council

IAS TUM Institute for Advanced Study

European Commission

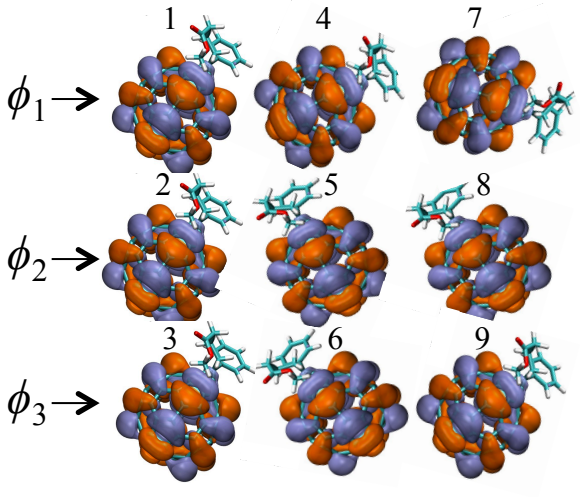
UCL

Implementation of FOB-SH method

J. Spencer, F. Gajdos., JB *in preparation*

1.) Expand 1-particle wavefunction of charge carrier in DFT SOMO site basis

$$\psi(r,R,t) = \sum_j c_j(t)\phi_j(r,R)$$



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

sparse

2.) Ultrafast estimation of Hamiltonian matrix elements

(i) H_{kl} from Analytic Overlap Method (AOM) (ii) H_{kk} from polarizable force field

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

3.) Ultrafast calculation of nuclear derivatives

(i) $\nabla_R H_{kl}, NACVs$ from AOM (ii) $\nabla_R H_{kk}$ from force field

4.) Transformation of nuclear forces from site to adiabatic basis $F_{I,i} = \left(U^{-1}\nabla_I H U\right)_{ii}$

Implementation of fast NAMD method (condinued)

J. Spencer, F. Gajdos., JB *in preparation*

5.) Solving electronic Schrodinger equation for the orbital expansion coefficients

$$i\hbar\dot{c}_k = \sum_j c_j \left(H_{kj} - i\hbar \left\langle \phi_k \middle| \frac{d\phi_j}{dt} \right\rangle\right)$$

Runge-Kutta
δt = 0.01-0.1 fs

6.) Calculation of hopping probabilities between adiabatic electronic states

$$p_{j\leftarrow i} = \frac{-2\,\mathrm{Re}\left(c_j^* c_i d_{ji}\right)\Delta t}{\left|c_i\right|^2}$$

7.) Propagate nuclei on current adiabatic surface *i*

$$F_I = -\frac{\partial}{\partial R_I} E_i$$

Velocity-Verlet
Δt = 0.5 fs

8.) Apply decoherence correction if system passed through an avoided crossing

9.) Calculate electronic Hamiltonian at new nuclear positions and repeat steps 3-8.

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

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

1.) Projection of DFT SOMOs of sites k, l in minimum Slater type orbital (STO) basis

$$c_{p\pi,i} = \left\langle \sum_{n\in k}^{atoms} S_{ni}^{-1} p_{\pi,n} \middle| \phi_k^{N'} \right\rangle$$

p_π-STO SOMO site k from DFT

2.) Analytic calculation of SOMO overlap in terms of STOs (very fast!)

$$\bar{S}_{kl} = \sum_{i\in k}^{atoms} \sum_{j\in l}^{atoms} c_{p\pi,i}^{*} c_{p\pi,j} \left\langle p_{\pi,i} \middle| p_{\pi,j} \right\rangle$$

3.) Training of linear relation using large number of DFT/ab-initio H_{kl} values

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

electronic coupling between sites k and l

constant

SOMO(STO) overlap

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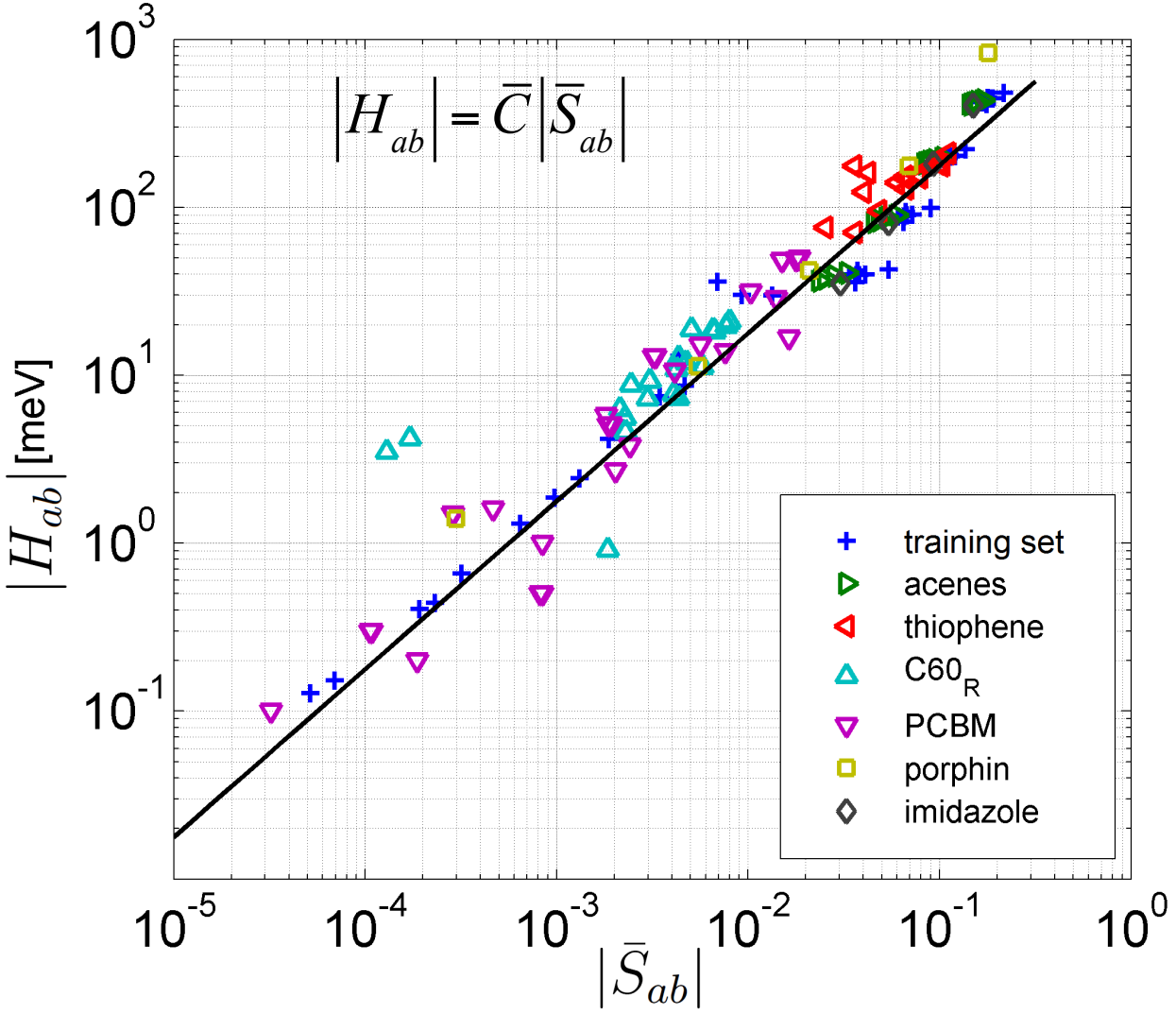

blue symbols
=
Training set

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

other symbols
=
Test sets

mean error = factor 1.9
over 5 decades!