Multi-Scale Modeling of Spin Dynamics in Molecular Semi-Conductors

Erik R. McNellis

Research Team Leader
Johannes Gutenberg Universität Mainz

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ITN SEPOMO | NWE4 Mons, Belgium

INSPIRE group
INTERDISCIPLINARY SPINTRONICS RESEARCH

Alexander von Humboldt Stiftung/Foundation

erc European Research Council

SPICE SPIN PHENOMENA INTERDISCIPLINARY CENTER

Who We Are - ERC Synergy Grant

- ERC Synergy Grant focused on **organic spintronics**
- Interdisciplinary, joining theory / experiment / physics / chemistry / materials science

European Research Council

- PIs
  - H. Sirringhaus, Cambridge
  - J. Sinova, JGU Mainz
  - I. McCulloch, Imperial College
  - J. Wunderlich, Hitachi Cambridge

- Outside Synergy Grant, groups of
  - D. Andrienko, MPIP Mainz
  - D. Beljonne, University of Mons

Who We Are - Theory Team

INSP/RE group
INTERDISCIPLINARY SPINTRONICS RESEARCH

Prof. Sergei A. Egorov

Dr. Reza Mahani

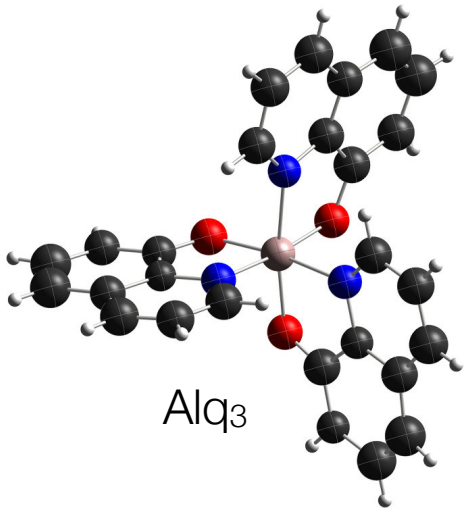
M. Sc. Uday Chopra

M. Sc. Sebastian Müller

https://www.sinova-group.physik.uni-mainz.de/research/organic-spintronics/

SP/CE

Why First-Principles, Multi-Scale Modeling?



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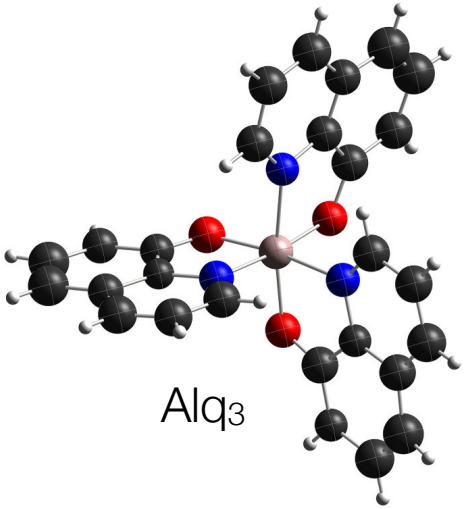
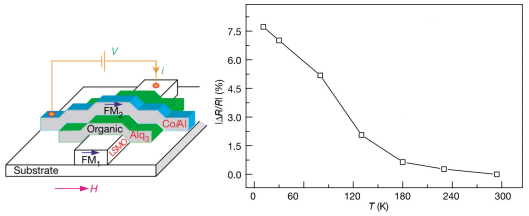
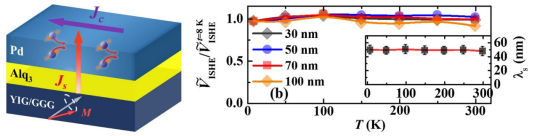
- 'Fruit-fly' example: characteristic Alq_3 spin dynamics **varies hugely** depending on e.g.
  - morphology
  - temperature
  - spin (charge) density



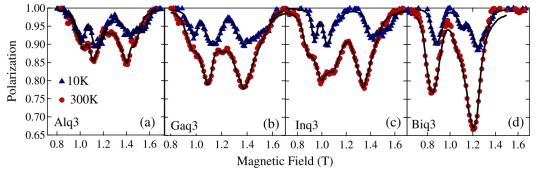
Alq_3



Charge hopping[1]



Spin exchange[2]



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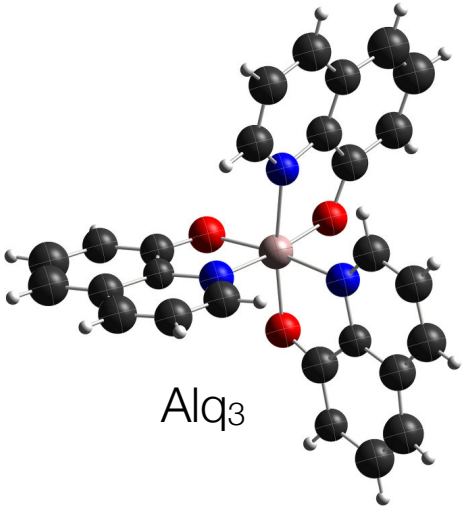

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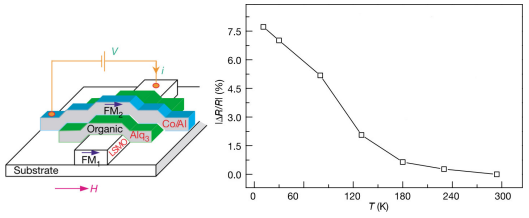

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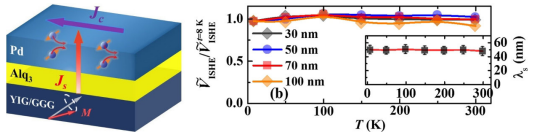
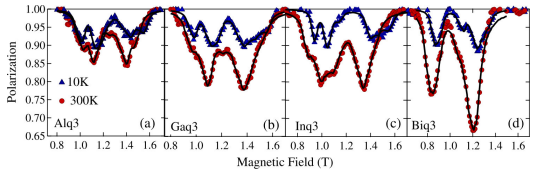


Spin exchange[2]

- Need modeling **consistently accurate** across spintronic device designs / operating regimes
- Phenomenological models struggle



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Molecular Spin Relaxation Mechanisms

- Molecular / organic semi-conductors characterized by
  - lower order / crystallinity, charge mobility (/ hopping frequency?)
  - weaker local fields, spin-orbit coupling (more ‘orbits’ relevant, ‘SOCs'?)
  - larger morphological variation / anisotropy

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- For hopping charge transport, no inter-system crossings
  five spin relaxation mechanisms

1. Spin dipole:
   - orients spins (anti-) parallel for (perpendicular) parallel separation vector **R**
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} Ideally, model from **first-principles**

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Least explored in this context

First-Principles Modeling in a Nutshell

"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to **equations much too complicated to be soluble***. It therefore becomes desirable that* **approximate practical methods** *of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems* **without too much computation.**"

1. P. A. M. Dirac, Proc. R. Soc. Lond. A 123, 714 (1929)

First-Principles Modeling in a Nutshell

- A quantum wave function contains a **lot of information**. Ideally, we
  - ✓ want **all necessary** information (accuracy)
  - ✓ do **not** want to **filter** for specific information (transferability)
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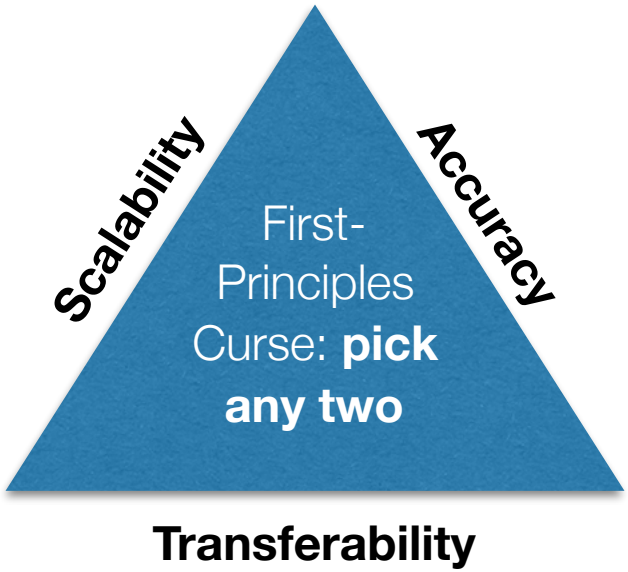

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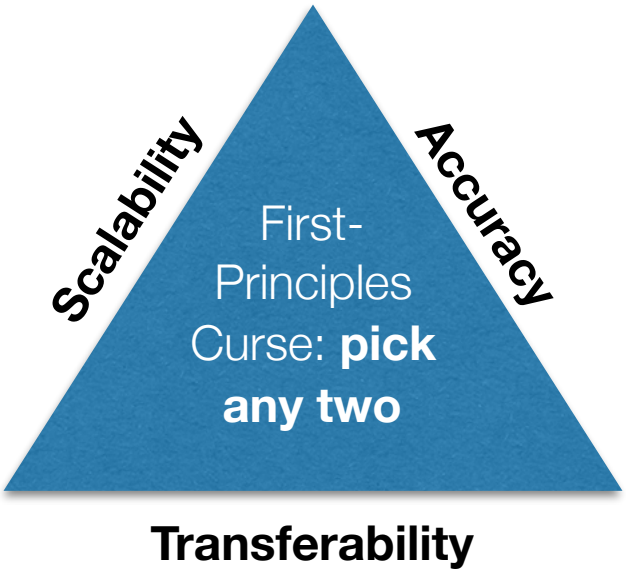

- Density Functional Theory (DFT): correction potential for classical mean-field
- Strikes good **balance** between all three - popular method

Multi-Scale Modeling of Materials

- **Perfect** theoretical material model:
  - ✓ From atomic- to material-relevant scale
  - ✓ No empiricism
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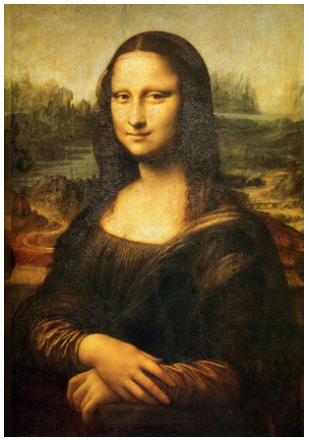
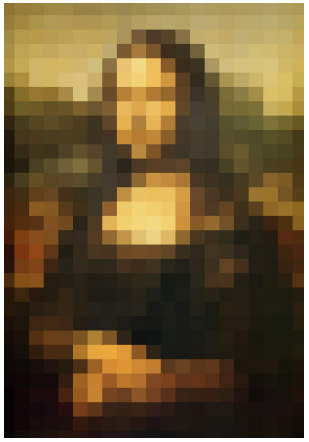
  - coarse-grained model at large scale
  - most important first-principles, atomistic information ideally retained
  - *balance* of accuracy and computational cost



Coarse graining



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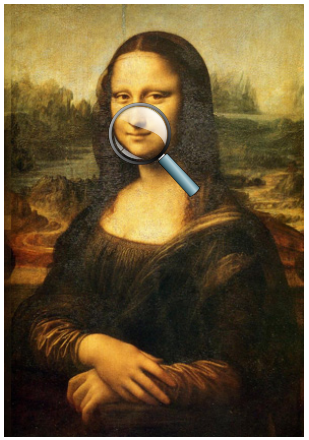

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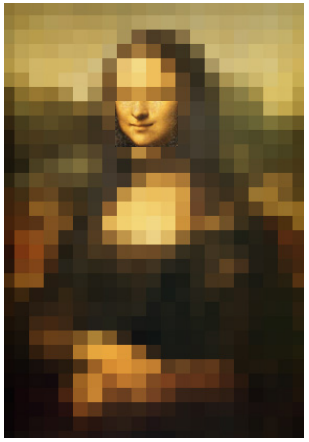
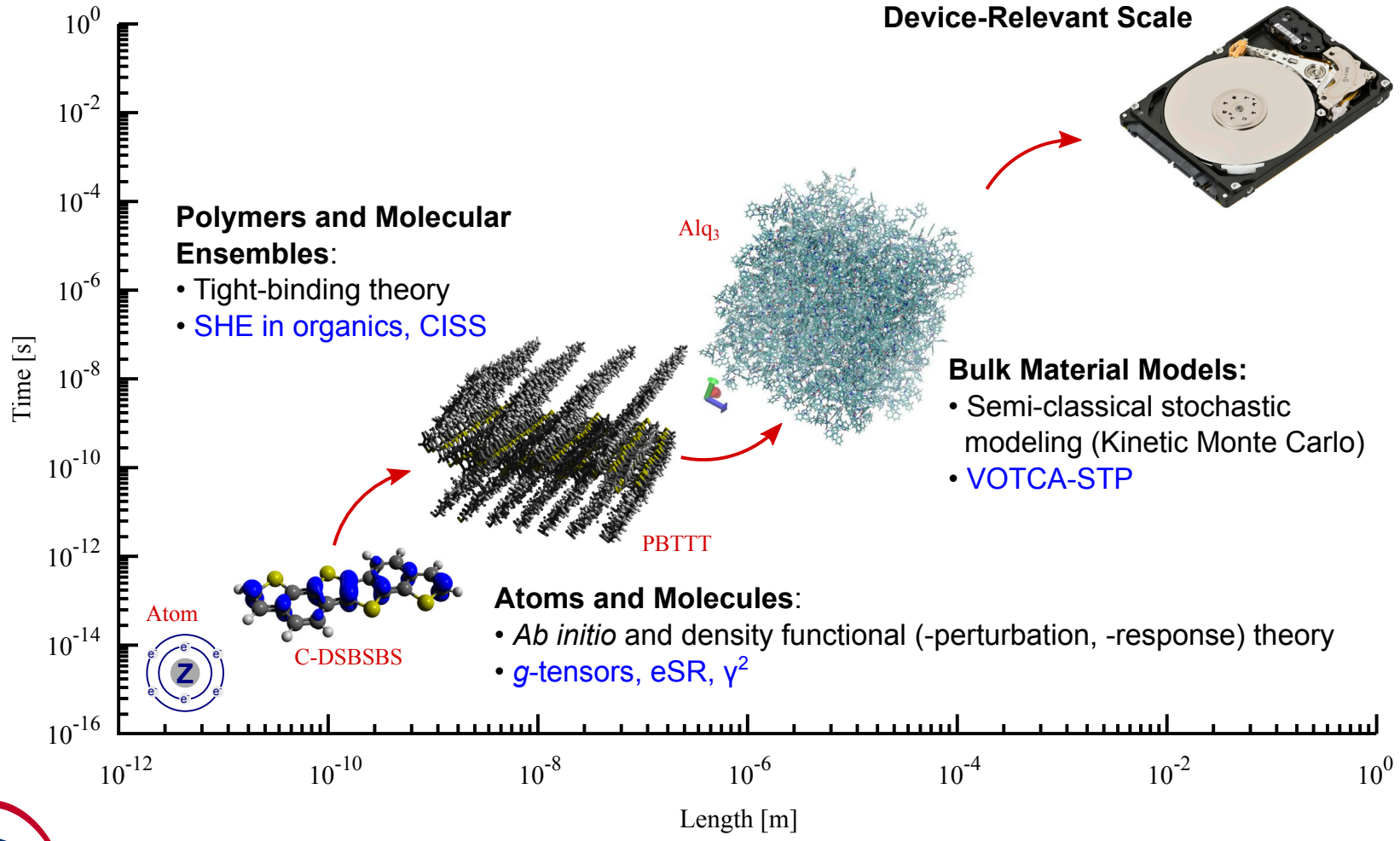


Multi-Scale Strategy: Single Molecules

INSP/RE group
INTERDISCIPLINARY SPINTRONICS RESEARCH

Target: 1st-principles spin dynamics in **realistic molecular semi-conductor** models



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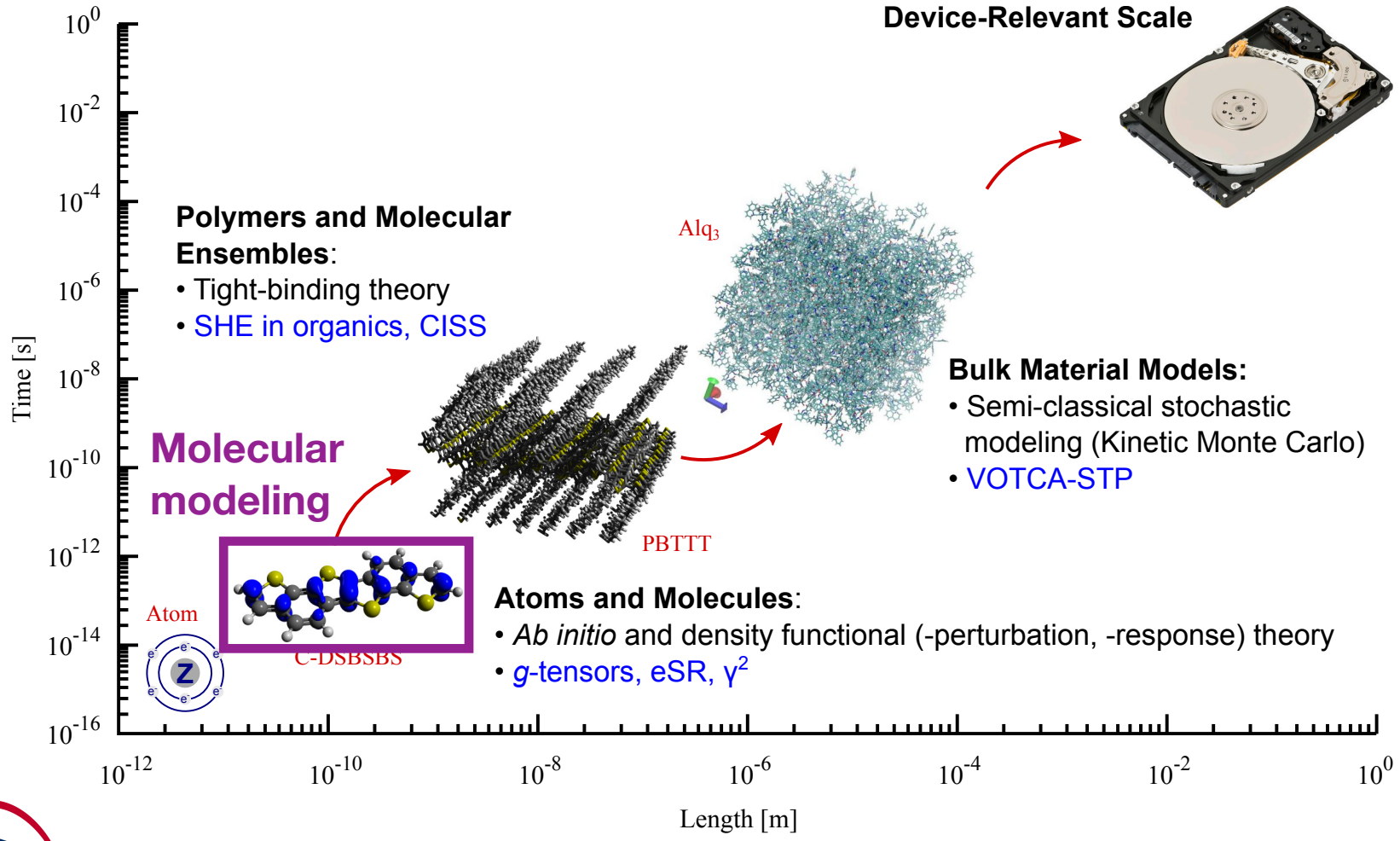
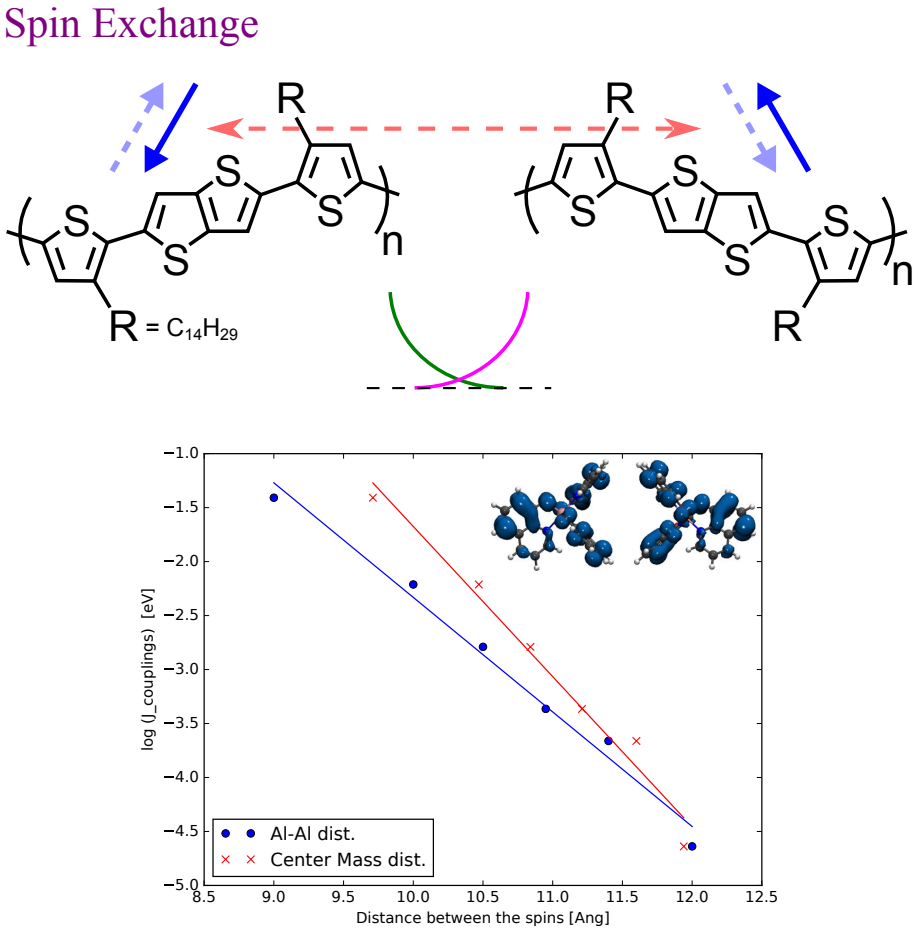


Spin Exchange

- *Exchange:* neighboring spin inversion, unchanged charge state
- Molecular wavefunction decays rapidly, exponentially in interstitial region - coupling also
- Two-body coupling $J_{ij} = \dfrac{E_{\uparrow\downarrow} - E_{\uparrow\uparrow}}{4\langle S_i \rangle \langle S_j \rangle}$
- $E_{\uparrow\downarrow}$, $E_{\uparrow\uparrow}$, $\langle S \rangle$ from constrained DFT[1]
- Coupling as function of polaron separation fitted to exponential function[2]

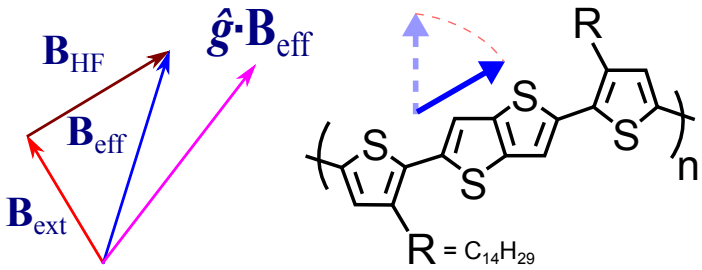


1. I. Rudra, Q. Wu and T. Van Voorhis, J. Chem. Phys. 124, 24103 (2006)
2. A. R. O'Dea, A. F. Curtis, N. J. B. Green, C. R. Tinunel and P. J. Hore, J. Phys. Chem. A 109, 869 (2005)

Hyperfine Field (HFI) / *g*-Tensor

- *Hyperfine coupling* (HFC): electronic, nuclear spin interaction
  - vanishes for ‘closed-shell’ molecules
  - organic elements often nuclear spin free
- **hydrogens, ionic** molecules main source

(External + Local Hyperfine Field) · *g*-tensor



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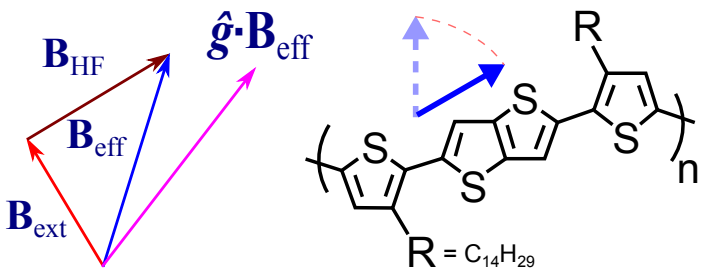
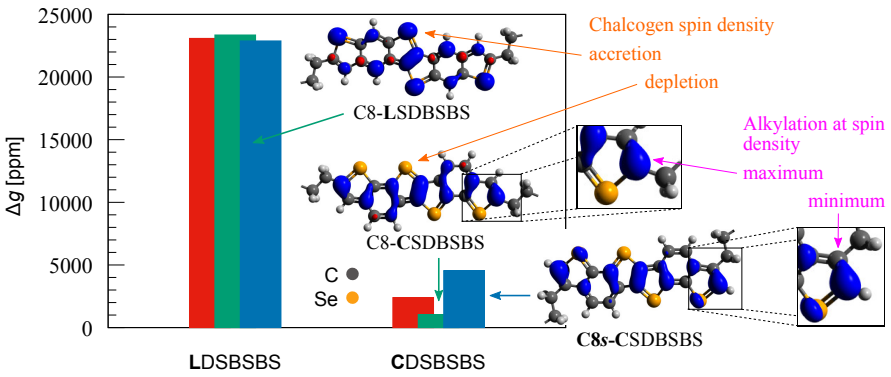


- Gyromagnetic coupling ("*g*-") tensor shift: deviation from free electron value
- Depends on spin-orbit coupling (SOC)
- Modeling, experiments:[1,2] overlap of electronic spin density with
  - nuclear spin → HFI
  - orbital angular momentum → *g*-tensor
- Spin density tuned via **push-pull chemistry**



g-tensor tuning[2]

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Spin-Mixing ('Hop-Flip') in Semi-Conductors

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- **Spin admixture parameter** γ

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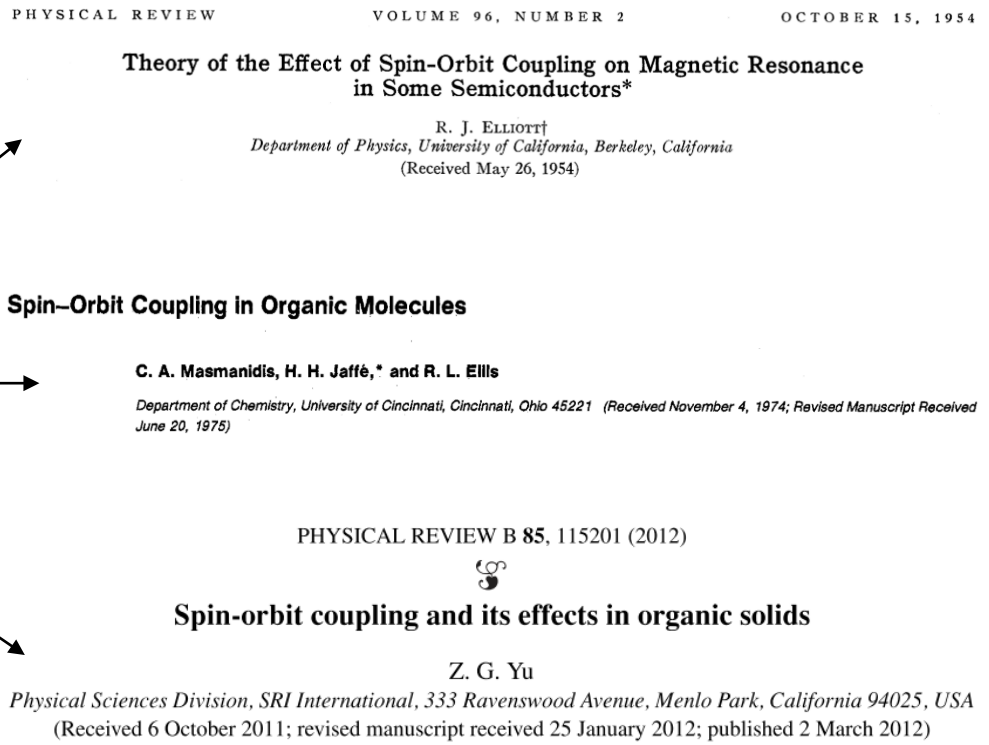
  - ✓ molecules[3]
  - ✓ molecular electronic structure from first-principles theory[4]



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Spin-orbit coupling and its effects in organic solids

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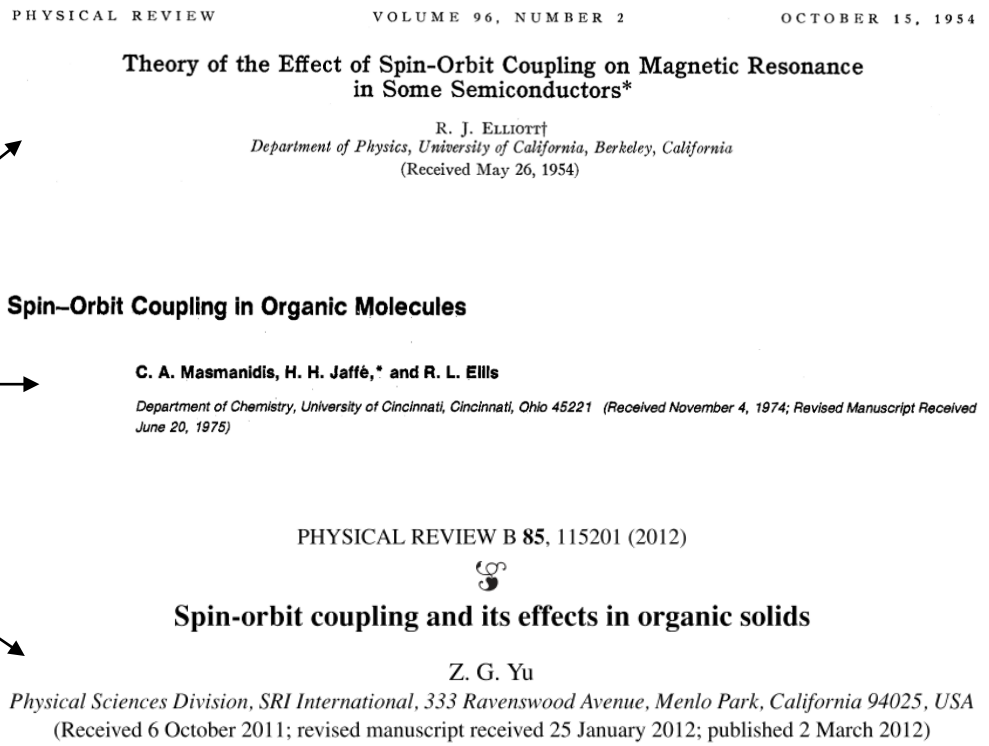

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A Complete Generalization of γ

- γ is change in norm of *spin-mixed, perturbed* molecular states
- Spin relaxation $\propto$ hopping frequency $\cdot\ \gamma^2$

$$\langle \psi_0 + | \psi_0 + \rangle = 1 + \gamma^2 = 1 + \gamma_{\uparrow\uparrow}^2 + \gamma_{\uparrow\downarrow}^2$$

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✗ Restricted wavefunction
✗ Empirical SO constants → minimal basis set ≤ **p**-functions → only light molecules, poorly
✗ No understanding of xc-approximation influence

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- Our generalization:[2]

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✓ Any basis set
✓ Any molecule
✓ Any single-determinant level of theory, (e.g., DFT)

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✓ Unrestricted wavefunction
✓ Any basis set
✓ Any molecule
✓ Any single-determinant level of theory, (e.g., DFT)

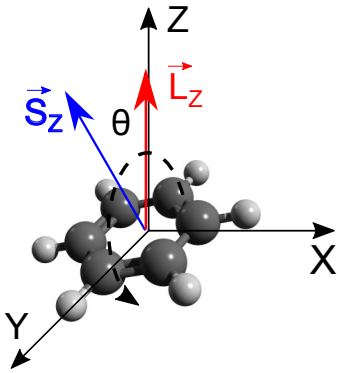
- We have reformulated γ with increased
  - accuracy
  - transferability
- … while maintaining scalability?

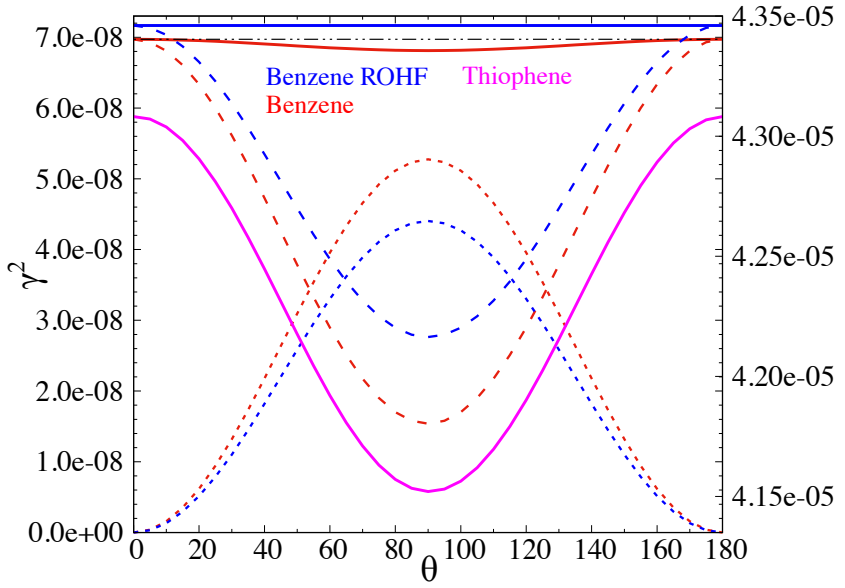
1. Z. G. Yu, Phys. Rev. B 85, 115201 (2012)
2. U. Chopra, S. Shambhawi, S. A. Egorov, J. Sinova, and ERM, Adv. Func. Mater. (submitted)

SP/CE

Effects of Generalization: Model Systems

- New *cos*^{2} dip in γ^2 $\mathbf{S_z}$ rotation curve in benzene (cf. $(\mathbf{L} \cdot \mathbf{S})^2$)
- More pronounced for stronger SOC (thiophene)





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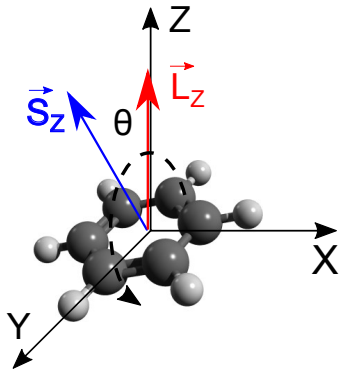

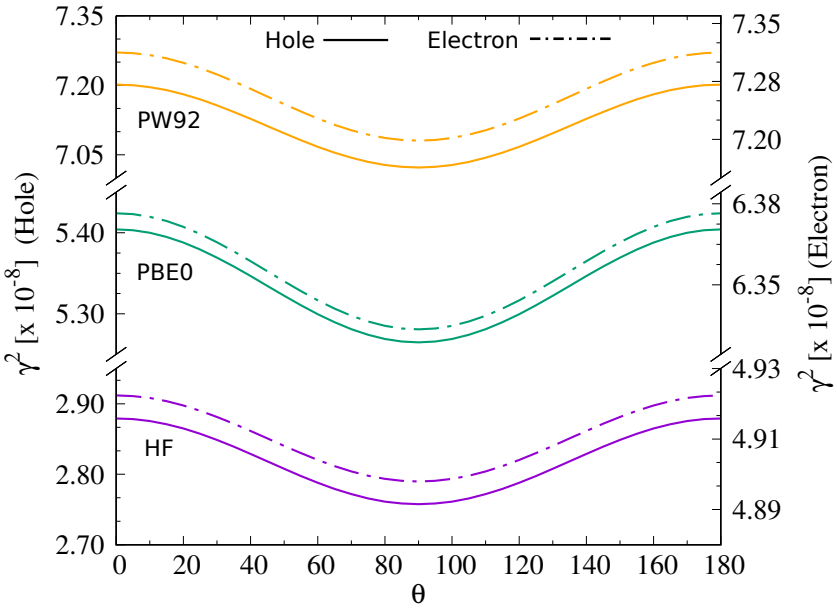

- Better DFT functionals = large quantitative corrections

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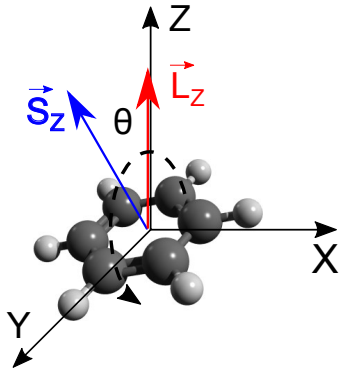
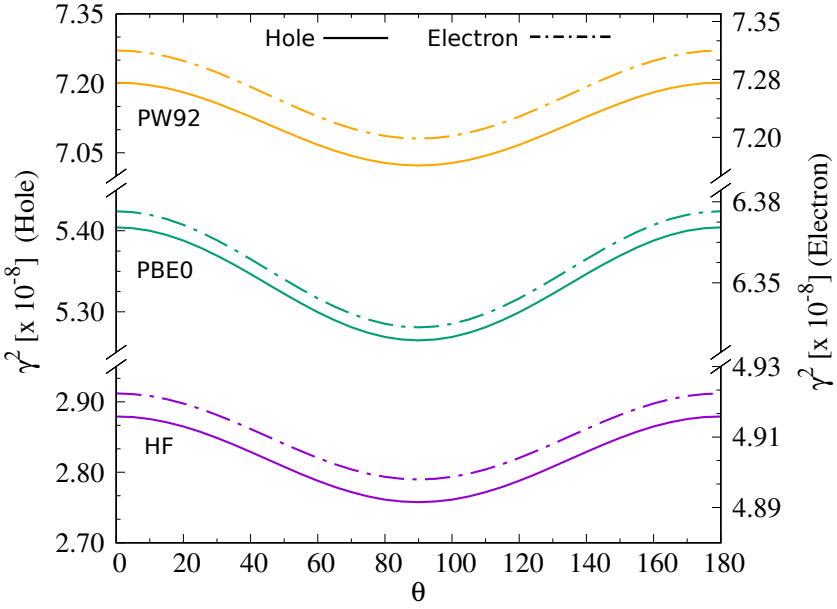
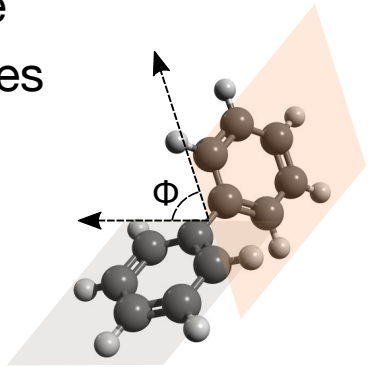
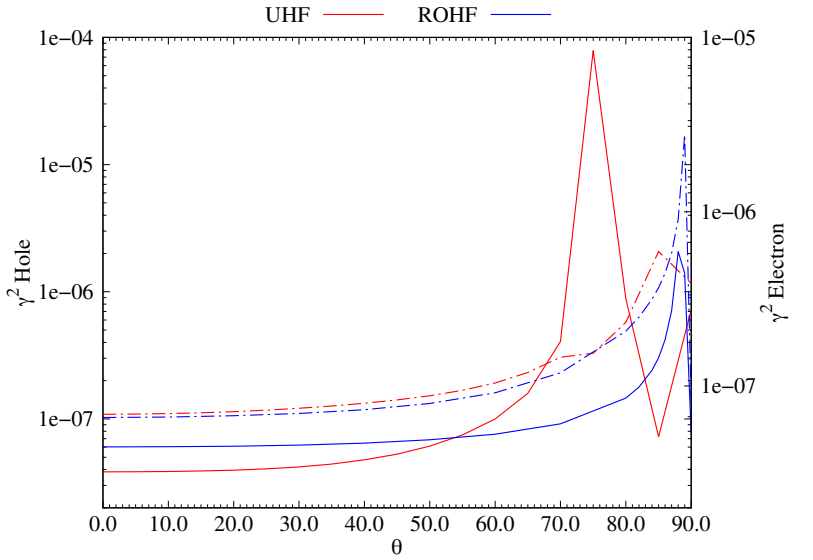




- Better DFT functionals = large quantitative corrections

- γ (SOC) depends on relative orientation of π-orbital planes
- Effect qualitatively and quantitatively improved for biphenyl twist

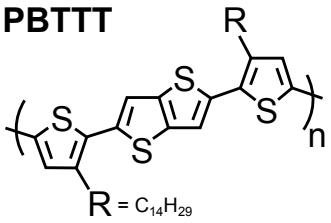




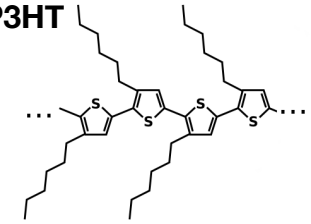
Accurate Spin Transport in Organic Polymers

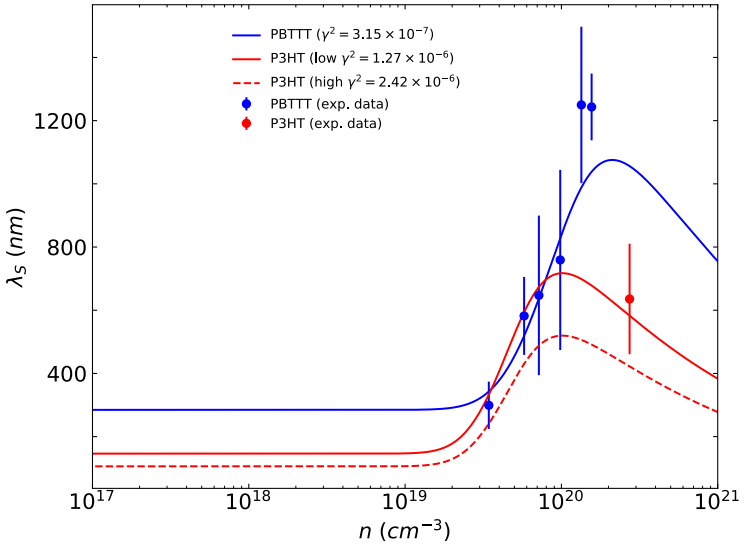
- Spin diffusion lengths L_s of ~ **1200, 600** (nm) in semi-crystalline PBTTT, P3HT polymers[1]
- Simple spin diffusion model[2], generalized γ predicts L_s within experimental errors

PBTTT



P3HT





1. Wang, Shu-Jen, …, R. Mahani, U. Chopra, ERM, et al, Nat. Electron. 2, 98 (2019)
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Accurate Spin Transport in Organic Polymers

INSP/RE group
INTERDISCIPLINARY SPINTRONICS RESEARCH

- Spin diffusion lengths L_s of ~ **1200, 600** (nm) in semi-crystalline PBTTT, P3HT polymers[1]
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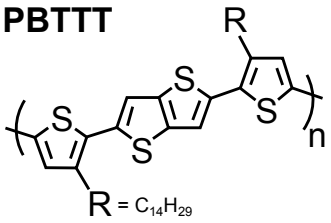

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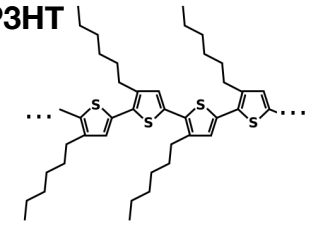
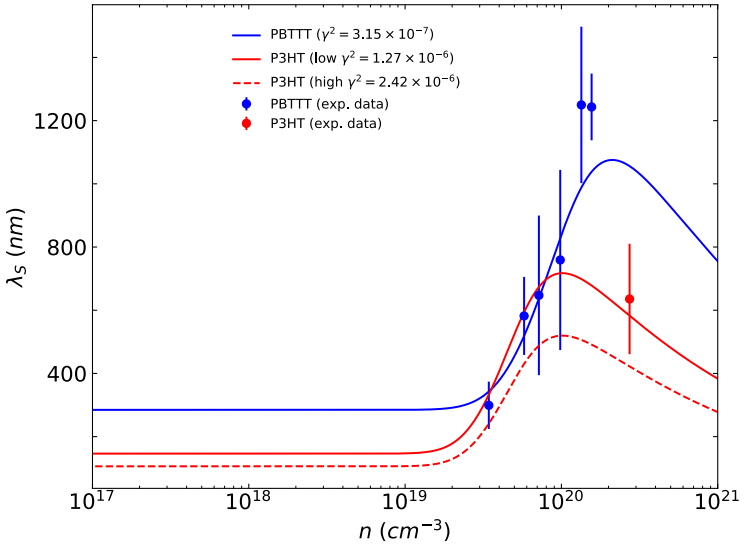
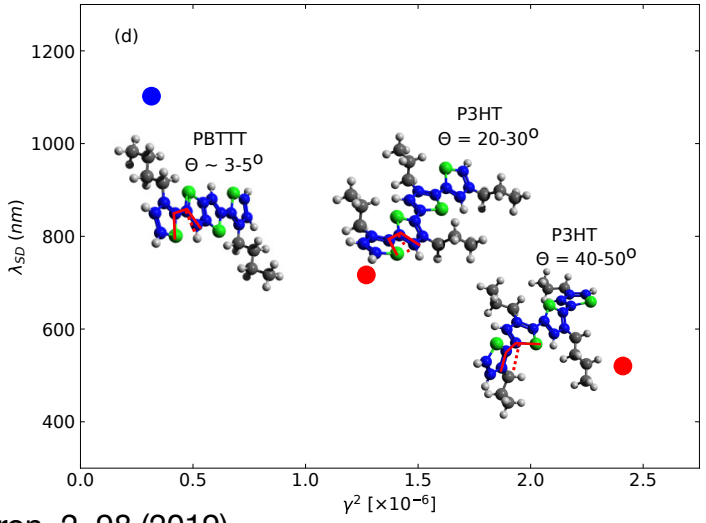




- Weak other mechanisms, locally high hopping rates → γ completely determines L_s
- Variation in γ, L_s because of **varying π-orbital planes** along chain

! Want long L_s? **Flatten** your π-conjugated polymer



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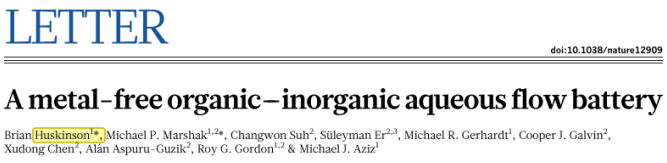
SP/CE

γ As a High-Throughput Computational Tool

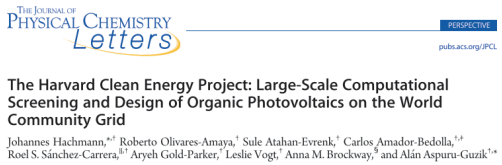
- **High-throughput**: characteristic property + robust modeling technique = huge scans of candidate molecules (e.g. batteries[1], photovoltaics[2])


LETTER

doi:10.1038/nature12909

A metal–free organic–inorganic aqueous flow battery

Brian Huskinson[1]*, Michael P. Marshak[1,2]*, Changwon Suh[2], Süleyman Er[2,3], Michael R. Gerhardt[1], Cooper J. Galvin[2], Xudong Chen[2], Alán Aspuru-Guzik[2], Roy G. Gordon[1,2] & Michael J. Aziz[1]


The Journal of Physical Chemistry Letters

PERSPECTIVE

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The Harvard Clean Energy Project: Large-Scale Computational Screening and Design of Organic Photovoltaics on the World Community Grid

Johannes Hachmann,*,† Roberto Olivares-Amaya,† Sule Atahan-Evrenk,† Carlos Amador-Bedolla,†,‡ Roel S. Sánchez-Carrera,‖,† Aryeh Gold-Parker,† Leslie Vogt,† Anna M. Brockway,§ and Alán Aspuru-Guzik†,*

1. B. Huskinson et al., Nature 505, 195 (2014)
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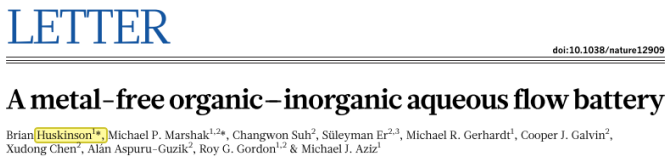
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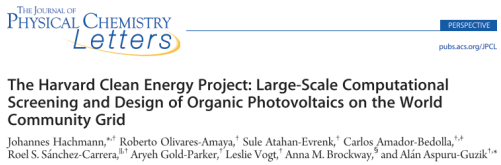
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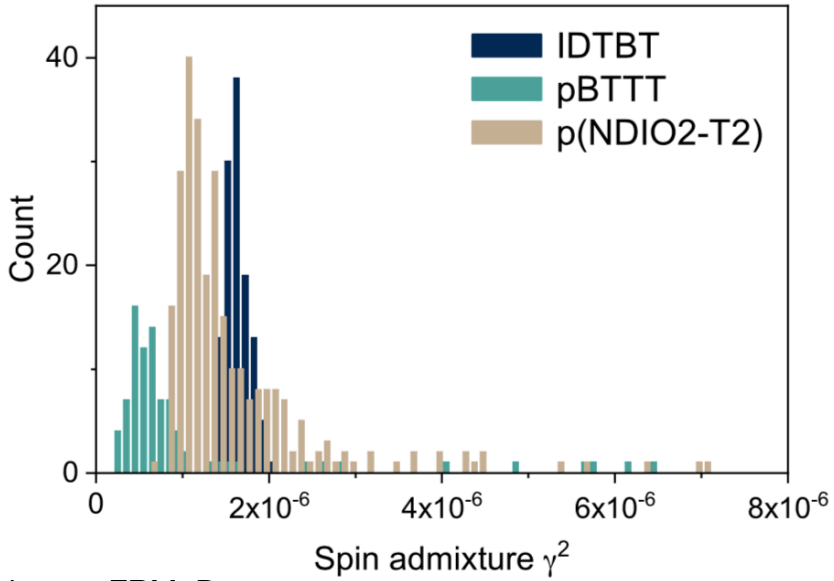
2. J. Hachmann et al., J. Phys. Chem. Lett. 2, 2241 (2011)

- Our γ calculation technique
  - ✓ relies on standard DFT
  - ✓ is highly task parallel
  - ✓ is highly automatable
- γ calculations of **every** state in polymer morphologies possible
- Statistical picture of polymer spin relaxation otherwise unattainable[1,2]



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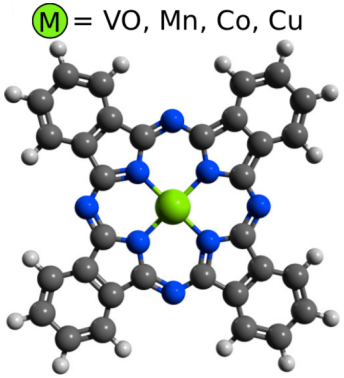
SP/CE

γ Transferable to Metal-Phthalocyanines (MPcs)

- Bader[1] et al. measure longitudinal spin relaxation times T_1 in dissolved MPcs
- MPcs too complex for old formulation



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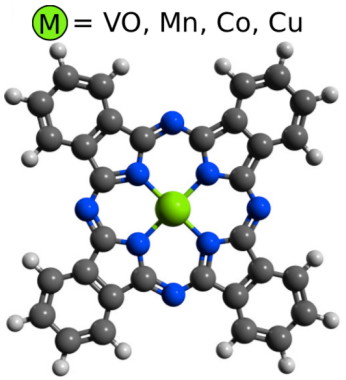
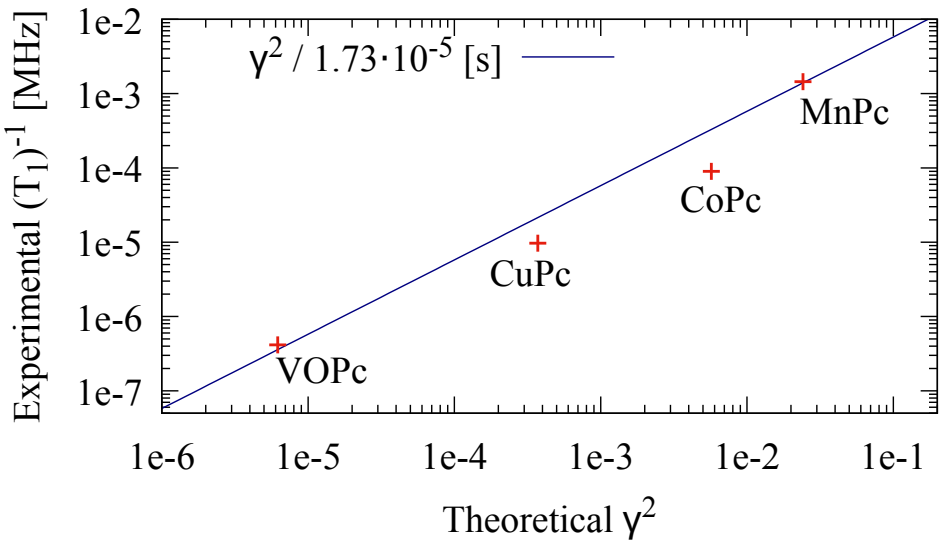


- If spin relaxes through charge hopping, $T_1 \propto \frac{1}{\gamma^2}$
- Fit of $T_1 \approx \kappa/\gamma^2$ predicts experiment to **~ 40 %** over **4 orders** of magnitude



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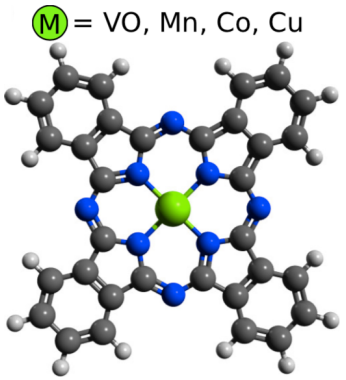

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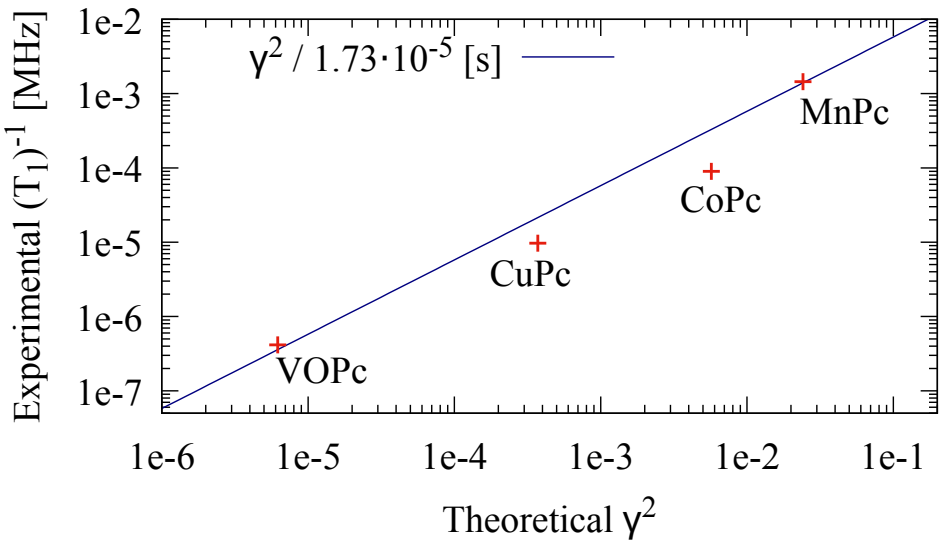
! Spin relaxation indistinguishable mix of (maybe) hopping and **thermal** effects

✓ Thermal (spin-phonon coupling) also $\propto \hat{H}^2_{SOC}$ - fit still works

✓ SOC highly accurate



- Can we do equally well with thermal effects with method to γ^2 standard?

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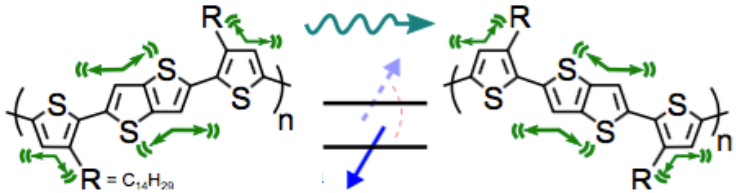
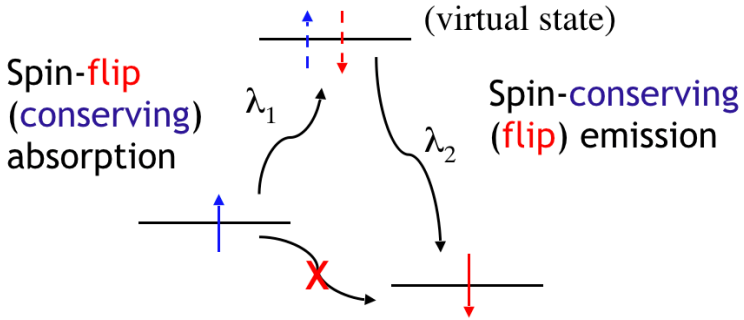
2. U. Chopra, S. Shambhawi, S. A. Egorov, J. Sinova, and ERM, Adv. Func. Mater. (submitted)

Spin-Phonon Coupling

- SOC coupling to a virtual state of opposite spin, resonant with zero-field Zeeman split via electron-phonon coupling
- Generally requires multiple phonons for resonance
- *Elastic*: spin relaxes on isolated, thermally excited molecule
- *Inelastic*: phonon absorption / emission



2nd order transitions



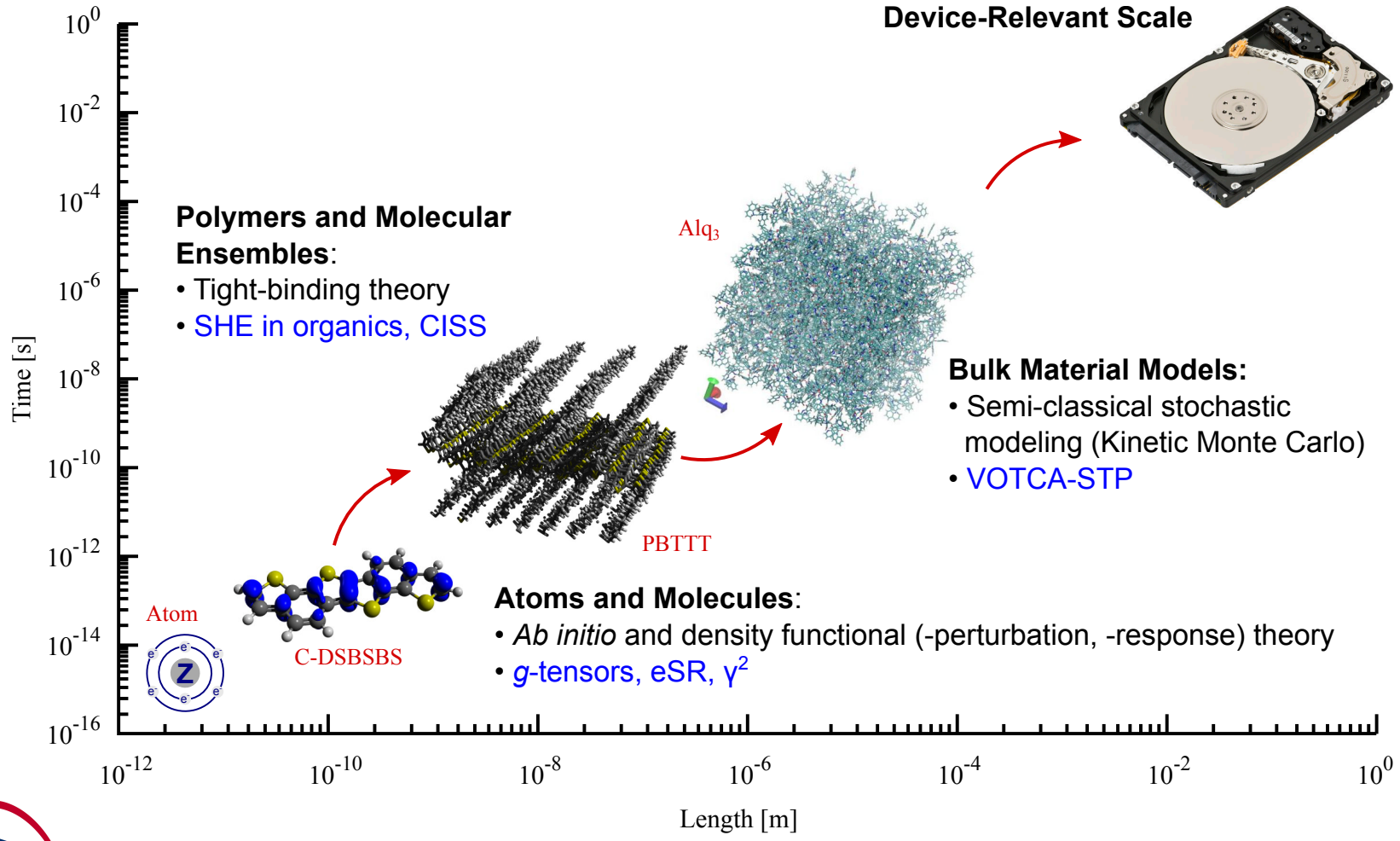
Absorption followed by emission (or vice versa) via virtual state

- Old method: DFT perturbation theory adapted from quantum dots[1], defects in solids[2]
- Updated: adapted from crystals[3], same SOC as γ

1. Y. G. Semenov and K. W. Kim, Phys. Rev. B 75, 195342 (2007)
2. S. A. Egorov and J. L. Skinner, J. Chem. Phys. 103, 1533 (1995)
3. S. Roychoudhari, S. Sanvito, PRB, 98, 125204 (2018)

Multi-Scale Strategy: Bulk Alq_3

Target: 1st-principles spin dynamics in **realistic molecular semi-conductor** models



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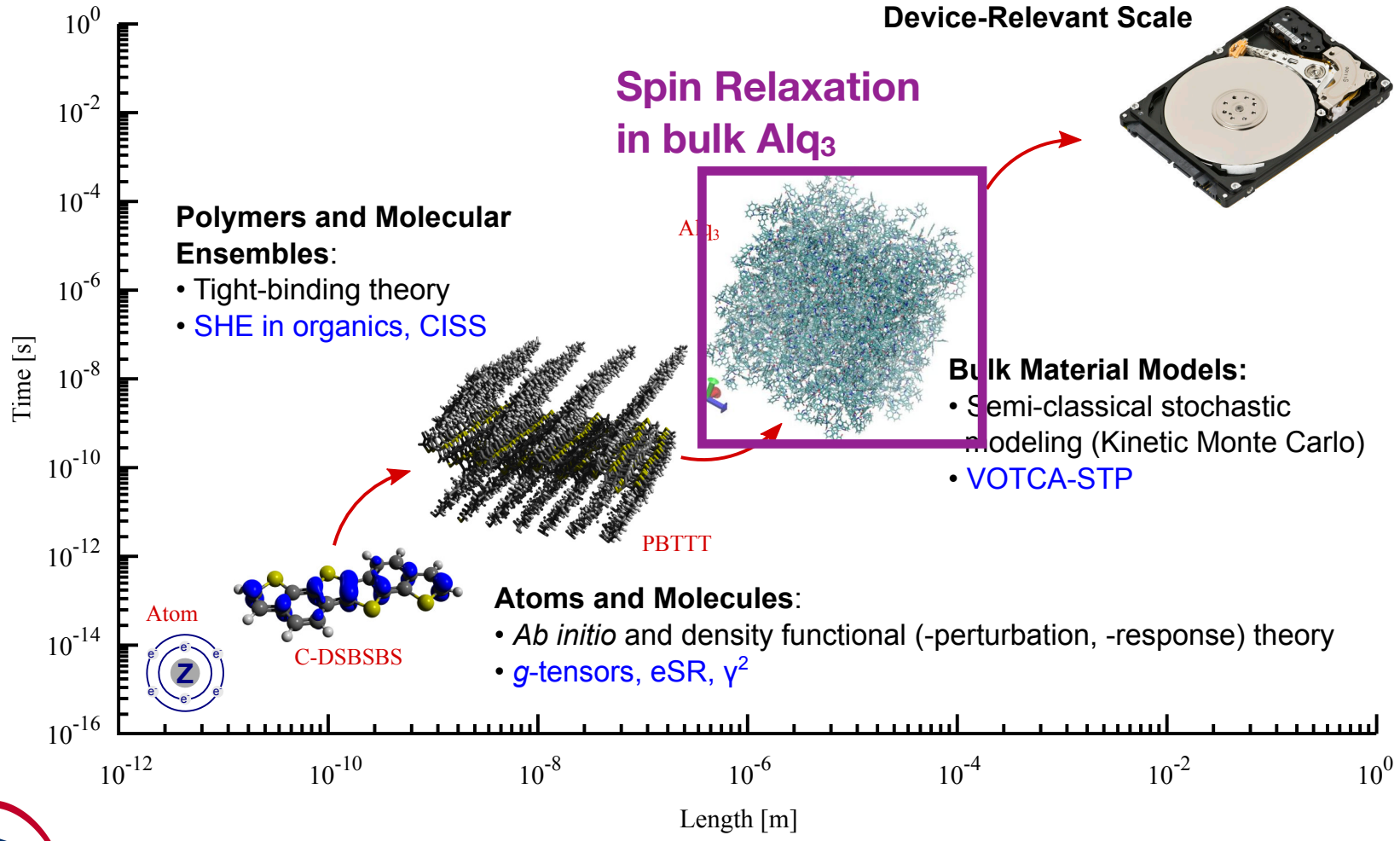
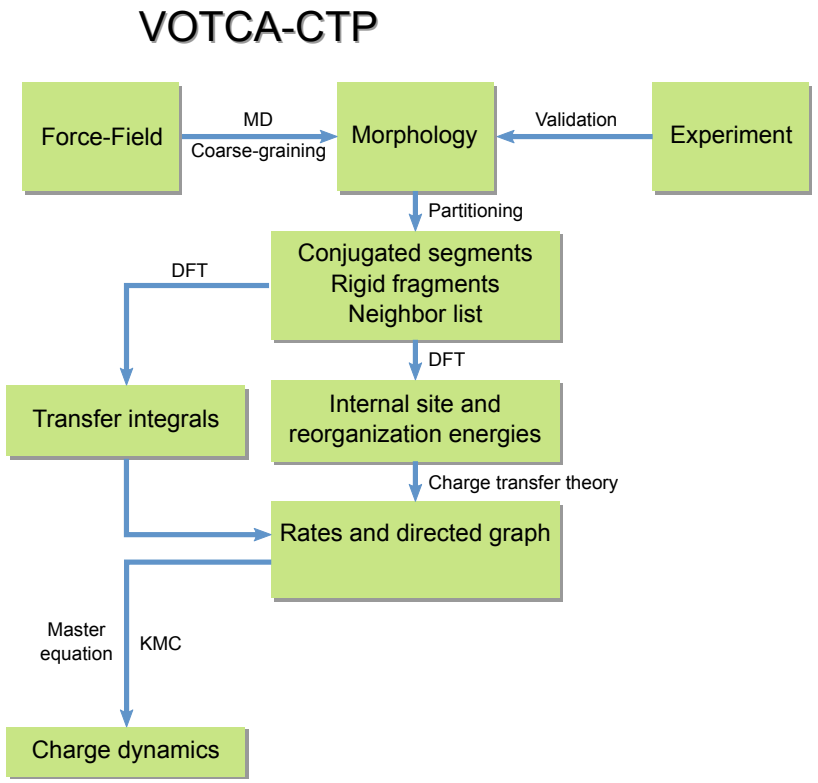


VOTCA-STP

- Our approach: spin-dynamics **on top** of multi-scale charge-dynamics

VOTCA-CTP[1]:

- Hopping charge transport in soft matter
- MD, Marcus theory → thermal effects



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VOTCA-CTP[1]:

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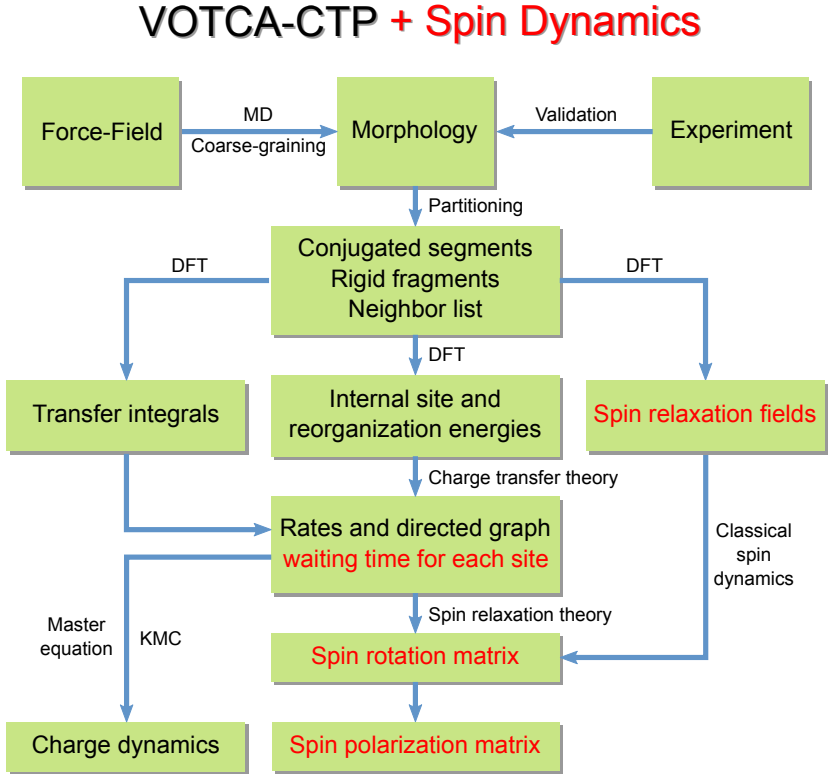
'VOTCA-**STP**':

- Separate spin dynamics KMC loop
- Single-site mechanisms:
  - hyperfine field[2] / *g*-tensor
  - thermal relaxation
- Two-site mechanisms:
  - spin-flip at hop (rate from γ[3])
  - spin exchange[4]
  - spin dipole



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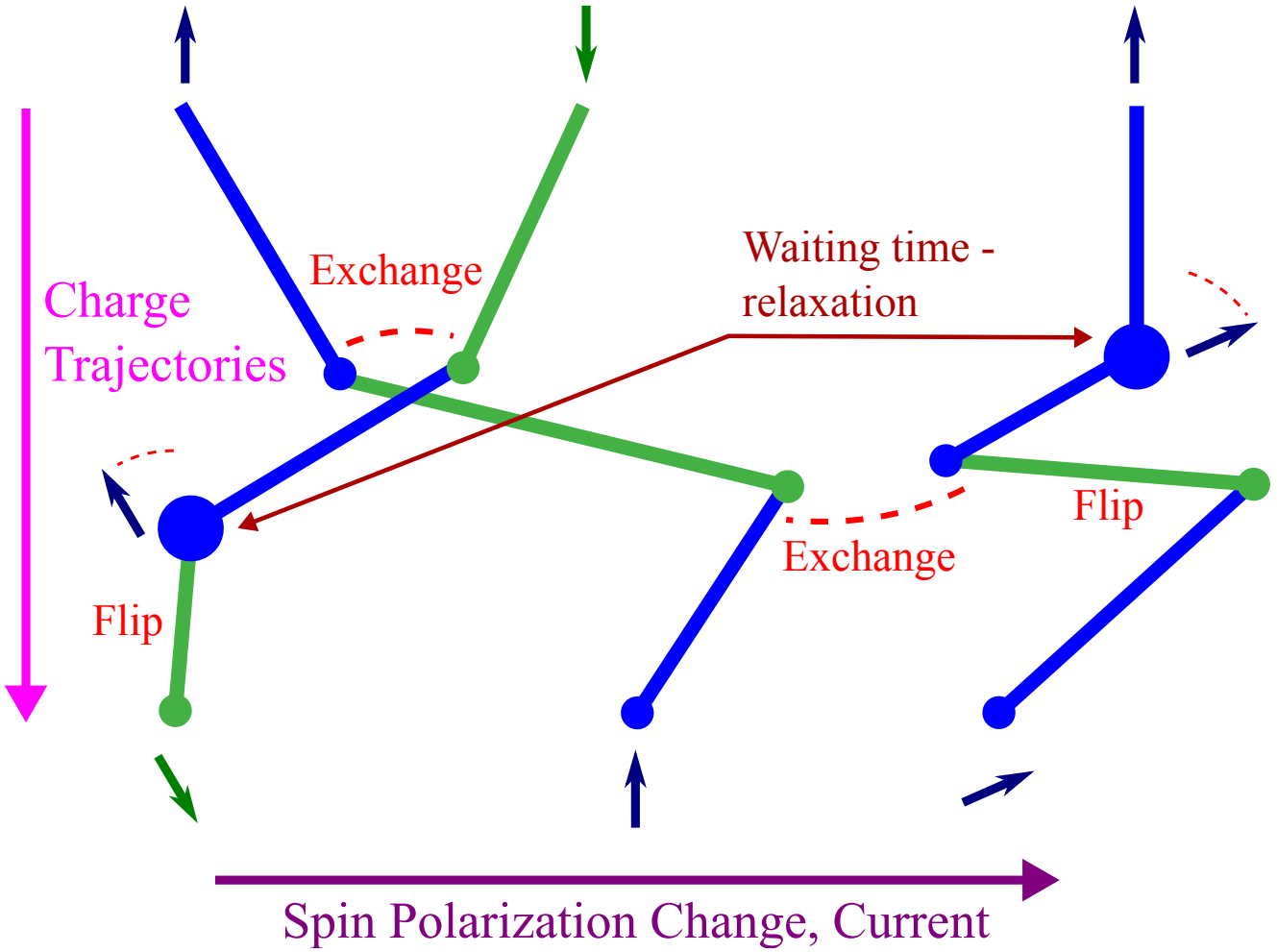
VOTCA-STP Spin Dynamics Concept

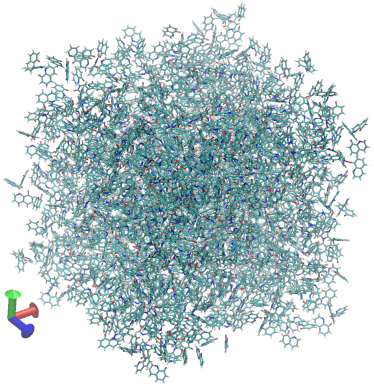
- Material model randomly seeded with charges
- Changes in spin polarization monitored as charges move

- **Explicit link** between charge- and spin-dynamics
- Allows for **unprecedented inference** of one from the other



T_1 Spin Relaxation Time in Bulk Alq_3

- Proof of concept: bulk Alq_3 longitudinal spin relaxation time
- Amorphous bulk model: 4096 molecule cell, periodic boundary conditions, monopolaronic transport approximation



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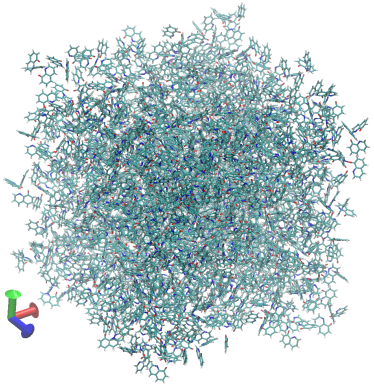

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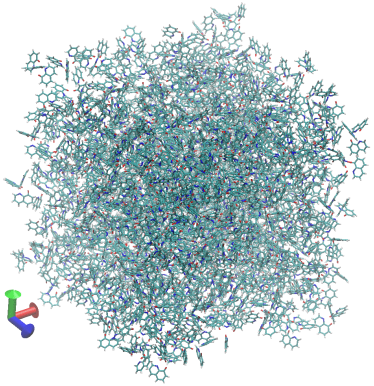

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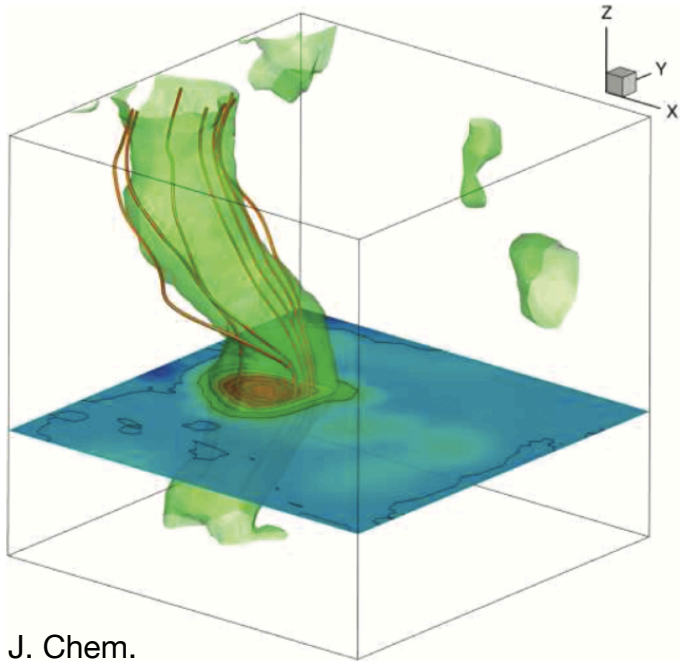
- Single molecular dynamics snapshot from glassy phase of bulk Alq3

- Large internal variations in molecular …
  - internal geometry
  - density
  - relative orientation

- … lead to large variations in
  - single molecule SOC
  - local hyperfine fields
  - current density

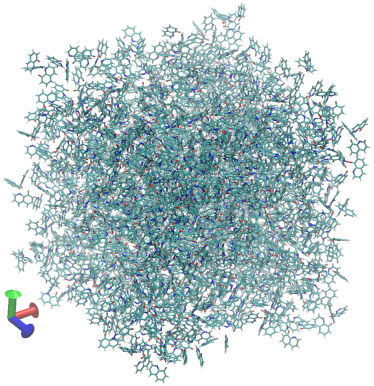


current density isocontour[1]

1. V. Rühle, A. Lukyanov, F. May et al, J. Chem. Theory Comput. 7, 3335 (2011)

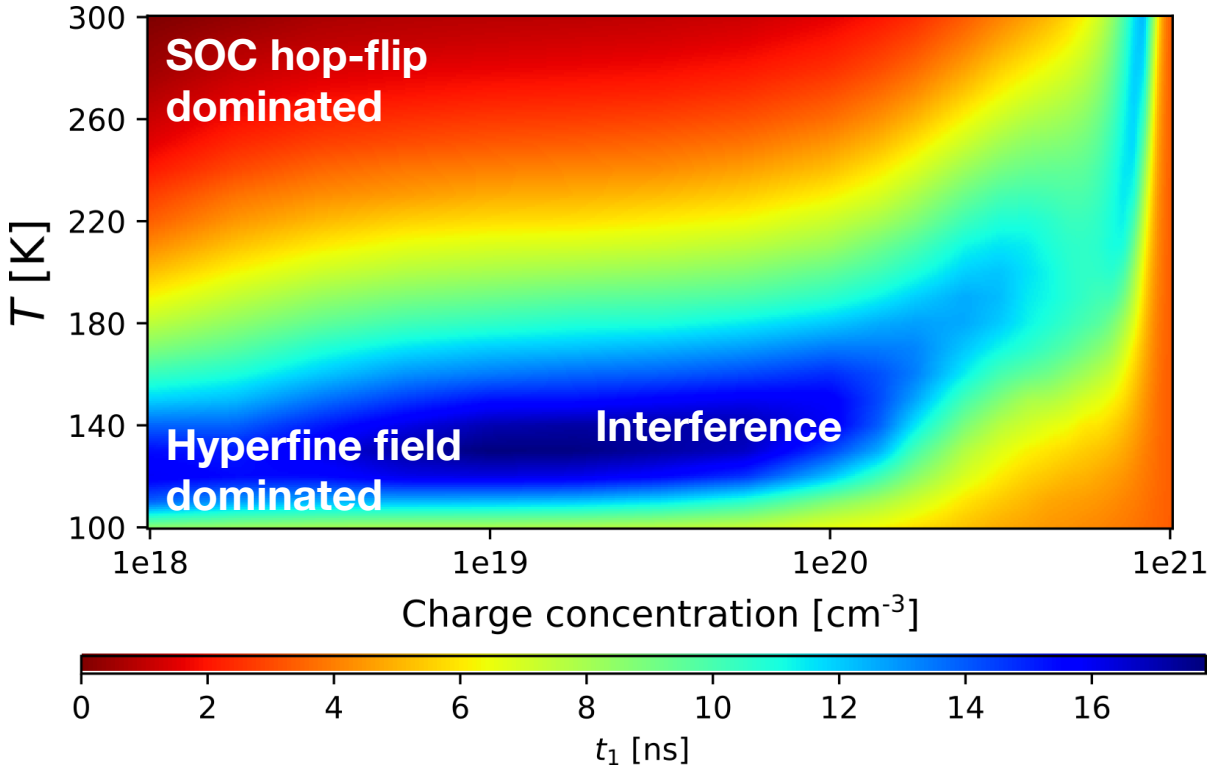
T_1 Spin Relaxation Time in Bulk Alq_3

- Proof of concept: bulk Alq_3 longitudinal spin relaxation time
- Amorphous bulk model: 4096 molecule cell, periodic boundary conditions, monopolaronic transport approximation



- thermal relaxation **negligible**
- With **no exchange**, 'hockey-stick' T_1 shape:

- HFI and hop-flipping interfere, slowing T_1
- Charge hopping blocked as concentration increases, slower HFI relaxation dominates



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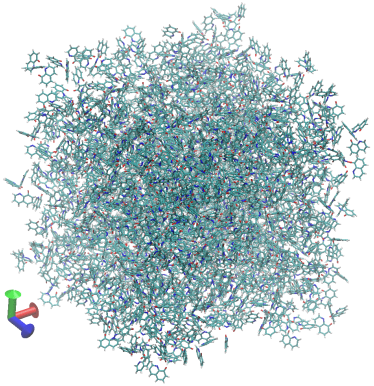
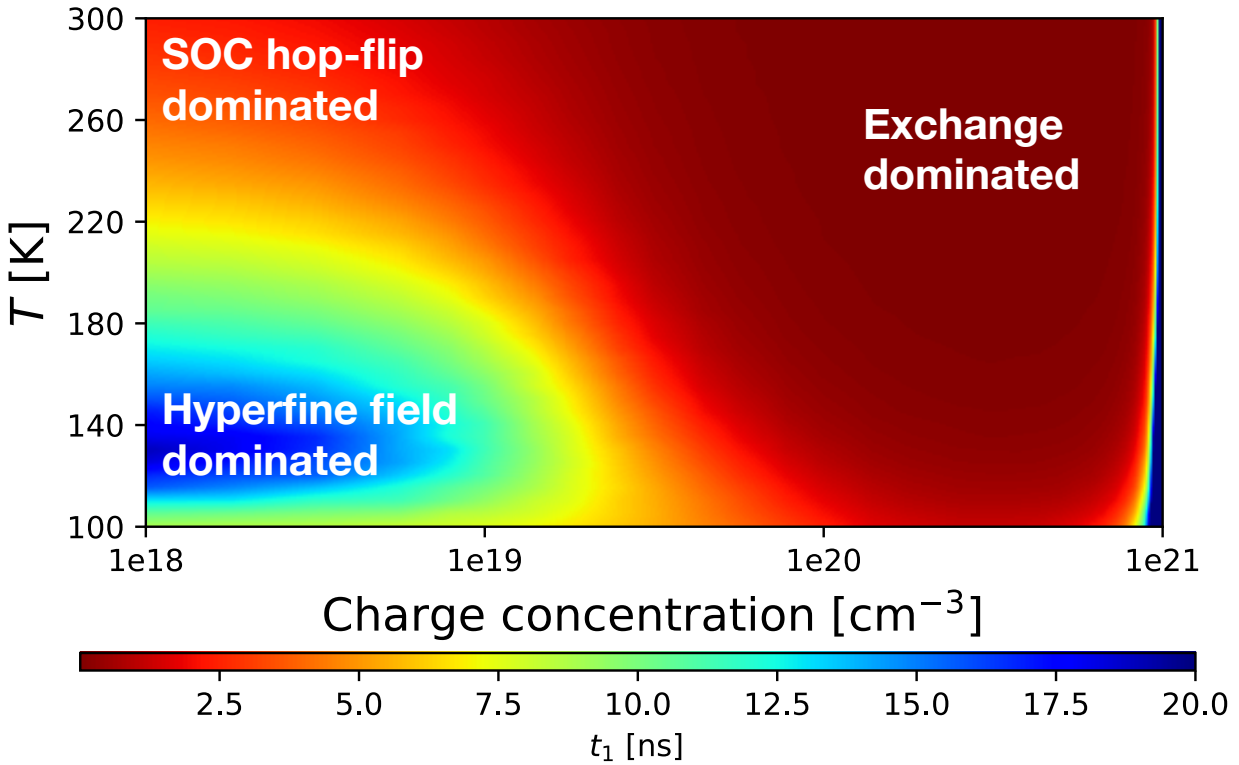


- With **exchange included,** large speedup in high concentration regime
- Due to relaxation **traps**:
- Exchange-mediated spin diffusion enhances access to fast relaxation sites
- Complex balance of effects



Summary

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- Theoretical modeling offers **otherwise unattainable** insights through
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  - **complementarity** to experiment
- Models highlight **complexity** of molecular spin dynamics - exciting!
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Thank You!