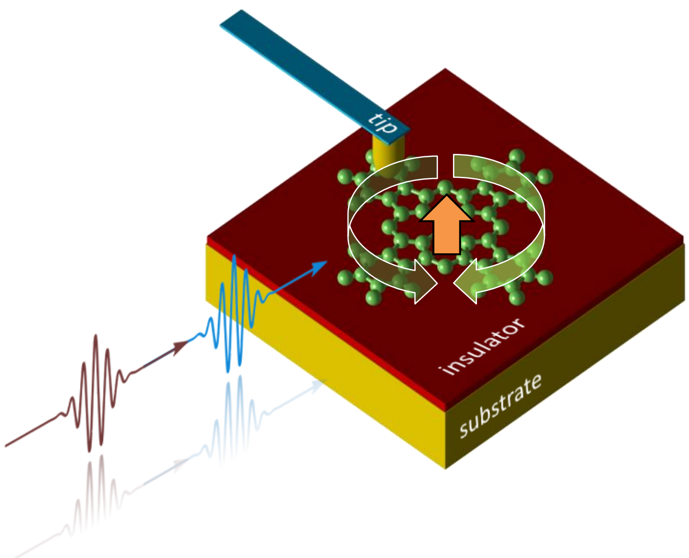
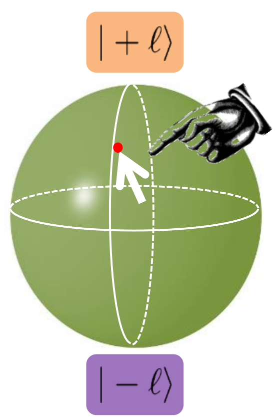
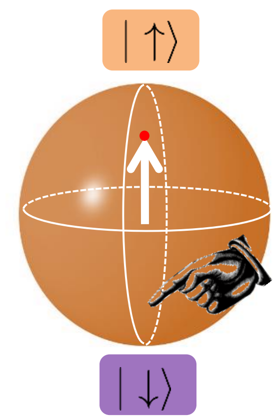
Pulse driven interacting single molecule junctions

Andrea Donarini







Schneefernerhaus, 29.05.2019

Time dependent driving

External driving introduces explicit time dependence in the Hamiltonian

$$\hat{H}(t) = \hat{H}_{\rm mol}(t) + \hat{H}_{\rm leads}(t) + \hat{H}_{\rm tun}(t)$$

The Liouville von Neumann (LvN) equation in interaction picture remains

$$\dot{\hat{\rho}}_{{\rm tot},I}(t) = -\frac{i}{\hbar}[\hat{H}_{{\rm tun},I}(t), \hat{\rho}_{{\rm tot},I}(t)]$$

where the operators in interaction picture read

$$\hat{O}_I(t) = \hat{U}_0^\dagger(t,t_0)\hat{O}_S(t)\hat{U}_0(t,t_0)$$

$$\hat{U}_0(t,t_0) = T_{\rightarrow}\exp\left\{-\frac{i}{\hbar}\int_{t_0}^{t}\left[\hat{H}_{\rm mol}(t') + \hat{H}_{\rm leads}(t')\right]\,{\rm d}t'\right\}$$

Weak coupling limit

The LvN equation can be recast into the integro-differential form

$$\dot{\hat{\rho}}_I(t) = -\frac{i}{\hbar}\left[\hat{H}_{\mathrm{tun},I}(t), \hat{\rho}_(t_0)\right] + \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} \left[\hat{H}_{\mathrm{tun},I}(t), \left[\hat{H}_{\mathrm{tun},I}(t'), \hat{\rho}_I(t')\right]\right] \mathrm{d}t'$$

We further assume initial time factorization for the density operator

$$\hat{\rho}(t_0) = \hat{\rho}_{\mathrm{mol}}(t_0) \otimes \hat{\rho}_{\mathrm{leads}}(t_0)$$

Thus, it holds true:

$$\hat{\rho}_I(t) = \hat{\rho}_{\mathrm{red},I}(t) \otimes \hat{\rho}_{\mathrm{leads}}(t_0) + O\left(\hat{H}_{\mathrm{tun}}\right)$$

Where the reduced density operator reads:

$$\hat{\rho}_{\mathrm{red},I}(t) = \mathrm{Tr}_{\mathrm{leads}}\left\{\hat{\rho}_I(t)\right\}$$

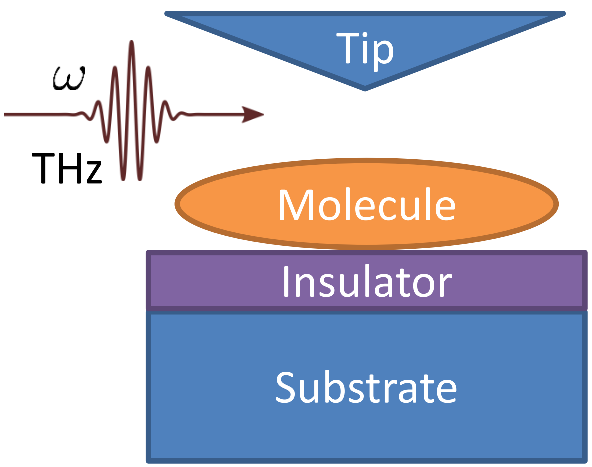
Weak coupling limit

The reduced density operator obeys the integro-differential equation

$$\dot{\hat{\rho}}_{\mathrm{red},I}(t) = \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} \mathrm{Tr}_{\mathrm{leads}} \left\{ \left[\hat{H}_{\mathrm{tun},I}(t), \left[\hat{H}_{\mathrm{tun},I}(t'), \hat{\rho}_{\mathrm{red},I}(t') \otimes \hat{\rho}_{\mathrm{leads}}(t_0) \right] \right] \right\} \mathrm{d}t'$$

$$= \int_{t_0}^{t} \mathcal{K}_I(t,t') \hat{\rho}_{\mathrm{red},I}(t') \, \mathrm{d}t'$$

The properties of the propagation kernel depend on the specific model at hand



$$\mathrm{Re}[\epsilon_r(\omega)] = 1 - \frac{\omega_p^2}{\omega^2} \qquad \omega = cq \gg qv_F \qquad \omega_p/\omega \approx 10^3$$

$$\hat{H}_{\mathrm{leads}} = \sum_{\eta \mathbf{k} \sigma} [\epsilon_{\eta \mathbf{k}} + \alpha_\eta e V_{\mathrm{bias}}(t)] \hat{c}^\dagger_{\eta \mathbf{k} \sigma} \hat{c}_{\eta \mathbf{k} \sigma}$$ Fermi seas

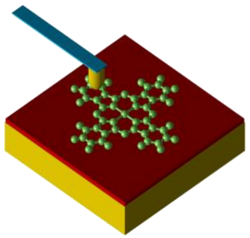
$$\mu_\eta(t) = \mu_0 + \alpha_\eta e V_{\mathrm{bias}}(t)$$ No charge accumulation in the leads

$$\alpha_{\mathrm{sub}} - \alpha_{\mathrm{tip}} = 1$$
$$\hat{H}_{\mathrm{mol}}(t) = \hat{H}_{\mathrm{mol}}(t_0)$$ No potential drop on the molecule

Adiabatic limit

The **tunnelling** Hamiltonian is bilinear in the leads and molecule operators:

$$\hat{H}_{\text{tun}} = \sum_{\ell \mathbf{k} \sigma} t^{\text{tip}}_{\ell \mathbf{k} \sigma}(\mathbf{r}_{\text{tip}})\, \hat{c}^{\dagger}_{\text{tip},\mathbf{k}\sigma} \hat{d}_{\ell\sigma} + t^{\text{sub}}_{\ell \mathbf{k} \sigma}\, \hat{c}^{\dagger}_{\text{sub},\mathbf{k}\sigma} \hat{d}_{\ell\sigma} + h.c.$$



The asymptotic behaviour of the propagation kernel can be analysed

$$\mathcal{K}_I(t,t') \propto \sum_{\eta \mathbf{k} \sigma} \mathrm{Tr}_{\text{leads}} \left\{ \hat{c}^{\dagger}_{\eta\mathbf{k}\sigma,I}(t) \hat{c}_{\eta\mathbf{k}\sigma,I}(t') \hat{\rho}_{\text{leads}}(t_0) \right\}$$
$$\to \exp\left(-\pi \frac{t-t'}{\hbar\beta}\right) \sum_{\eta} \exp\left(-\frac{i}{\hbar}\mu_0(t'-t) - \frac{i}{\hbar}\int_t^{t'} \alpha_\eta e V_{\text{bias}}(t'')\mathrm{d}t''\right)$$

The adiabatic limit is given by $\beta\hbar\omega \ll 1$

$$\mathcal{K}_I(t,t') \propto \exp\left(-\pi \frac{t-t'}{\hbar\beta}\right) \sum_{\eta} \exp\left(-\frac{i}{\hbar}[\mu_0 + \alpha_\eta e V_{\text{bias}}(t)](t'-t)\right)$$

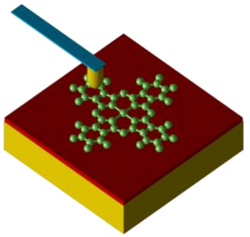
The theory is the same as in stationary non-equilibrium, with the replacement:

$$V_{\text{bias}} \to V_{\text{bias}}(t)$$

Markovian limit

The reduced density operator in the interaction picture evolves on time scales

$$\Gamma = \max(\Gamma_{\rm tip}, \Gamma_{\rm sub})$$



where

$$\Gamma_\eta = \frac{2\pi}{\hbar}|t^\eta|^2 D_\eta$$

In the limit $\beta\hbar\Gamma \ll 1$ we obtain the Generalized Master Equation:

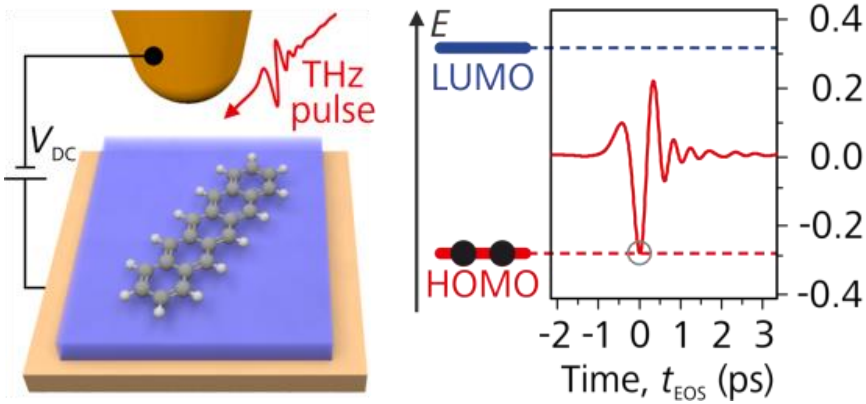
$$\dot{\hat\rho}_{{\rm red},I}(t) = \int_{t_0}^{t} \mathcal{K}_I(t,t')[\hat\rho_{{\rm red},I}(t')]\,{\rm d}t' \approx \int_0^\infty \mathcal{K}_I(t,t-t'){\rm d}t'\,[\hat\rho_{{\rm red},I}(t)]$$

More explicitly, in the Schrödinger picture

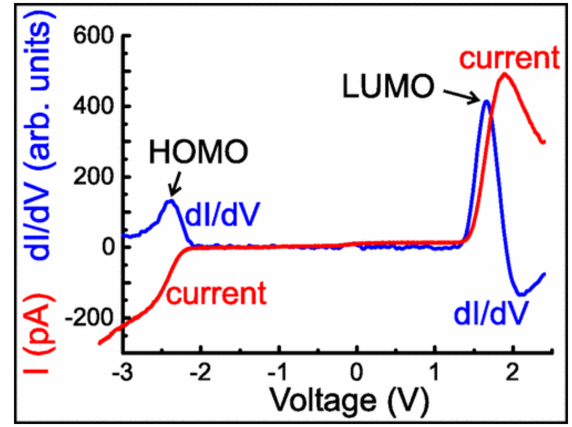
$$\dot{\hat\rho}_{\rm red}(t) = -\frac{i}{\hbar}[\hat H_{\rm mol}, \hat\rho_{\rm red}(t)] - \frac{i}{\hbar}[\hat H_{\rm LS}(t), \hat\rho_{\rm red}(t)] + \mathcal{L}_{\rm tun}(t)[\hat\rho_{\rm red}(t)]$$

Coherent dynamics relevant for quasi degenerate states: $\Delta\epsilon < \Gamma$

Time scales



T. Cocker et al. Nature (2016)



J. Repp et al. Phys. Rev. Lett. (2005)

The experiments are performed at $T = 10\,\mathrm{K}$ $\quad \hbar\beta \approx 4\,\mathrm{ps}$ **Non adiabatic ?**

The spectral resolution in the dc case is $\Delta E = 100\,\mathrm{meV}$ ➡ $\tau_{\mathrm{rel}} \approx 40\,\mathrm{fs}$

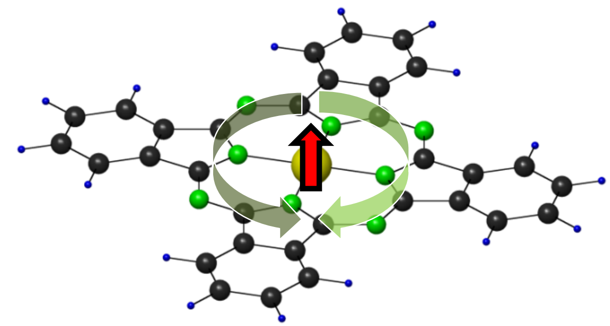
Decaying time of the correlator dominated by electron phonon coupling in the substrate.

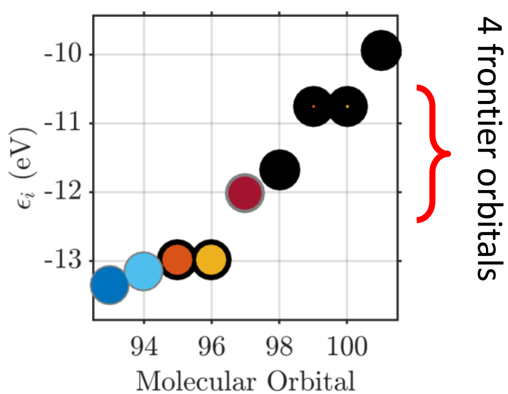
Tunnelling rates at the substrate $\hbar\Gamma_{\mathrm{sub}} \approx 1\,\mathrm{meV}$ $\quad 1/\Gamma_{\mathrm{sub}} \approx 1\,\mathrm{ps}$

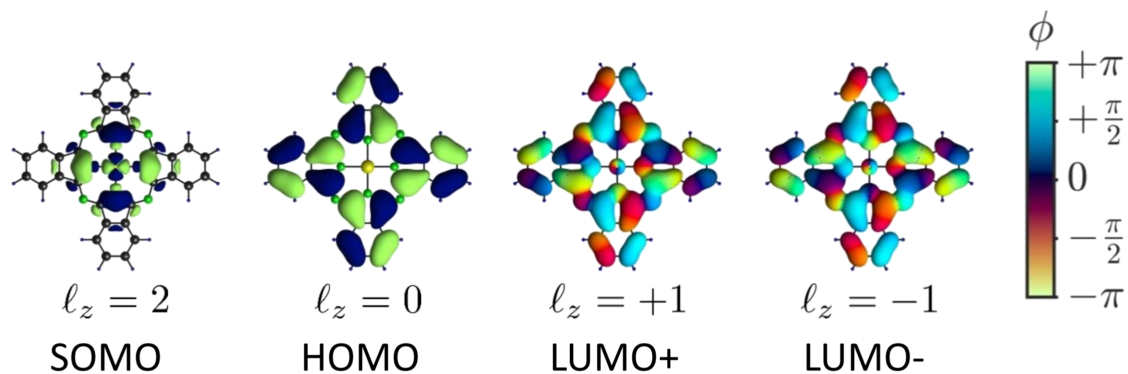
$(1/\Gamma_{\mathrm{tip}} \approx 1\,\mathrm{ns})$

Frontier orbitals in CuPc

The single particle Hamiltonian is constructed following LCAO schemes of Harrison and Slater-Koster.





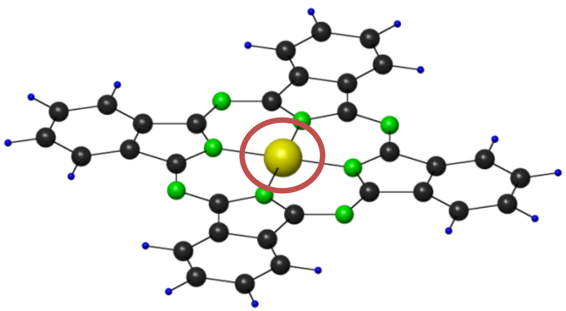


S. Froyen and W.A. Harrison, *PRB* **20,** 2420 (1979)

J. C. Slater and G. F. Koster, *Phys. Rev.* **94**, 1498 (1954)

SOI in the frontier orbital basis

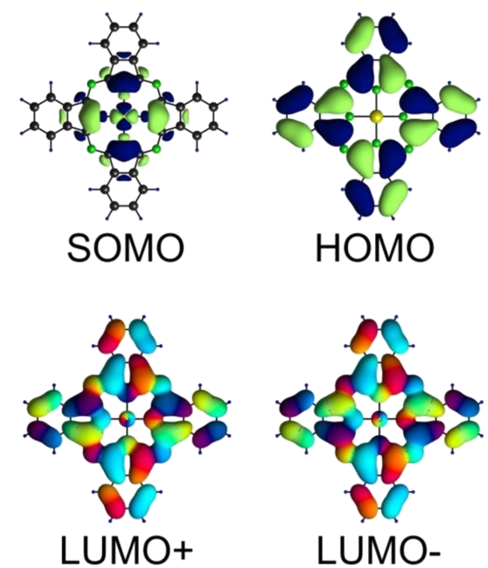
$$\hat{H}_{mol} = \hat{H}_0 + \hat{V}_{ee} + \boxed{\hat{V}_{SO}} + \hat{V}_Z$$



$$\hat{V}_{\mathrm{SO}} = \sum_{\alpha,\ell_\alpha} \xi_{\ell_\alpha}\, \boldsymbol{\ell}_\alpha \cdot \mathbf{s}_\alpha$$

Projection onto the frontier orbital basis yields

$$\begin{aligned}\hat{V}_{\mathrm{SO}} =& \lambda_1 \sum_{\tau=\pm} \tau \left(d^\dagger_{L\tau\uparrow} d_{L\tau\uparrow} - d^\dagger_{L\tau\downarrow} d_{L\tau\downarrow} \right) \\ &+ \lambda_2 \left(d^\dagger_{S\uparrow} d_{L-\downarrow} + d^\dagger_{L+\uparrow} d_{S\downarrow} + \mathrm{h.c.} \right)\end{aligned}$$

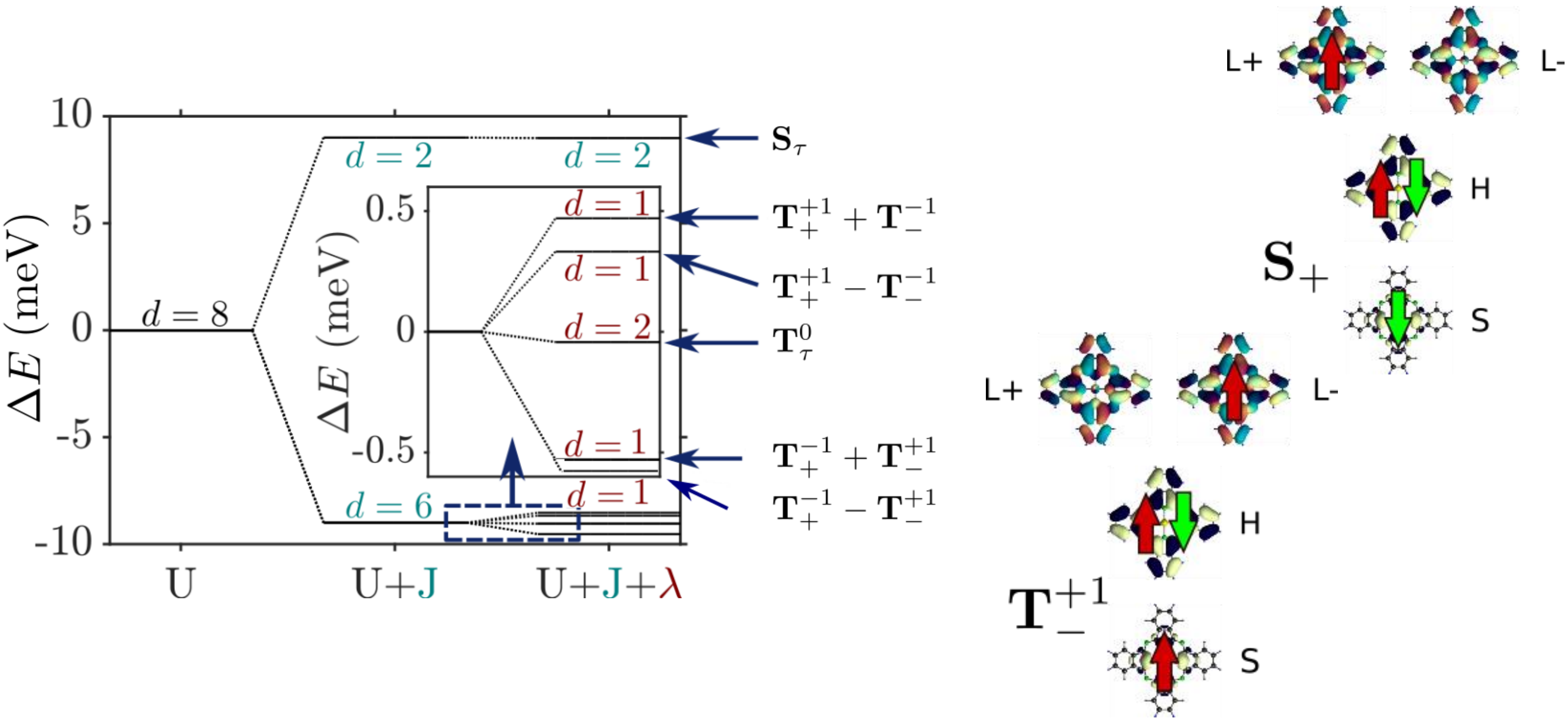


where $\lambda_1 = \frac{1}{2}\xi_{\mathrm{Cu}}\,|c_L|^2 = 0.47\ \mathrm{meV}$, $\lambda_2 = \xi_{\mathrm{Cu}}\,\frac{c_S c_L}{\sqrt{2}} = 6.16\ \mathrm{meV}$

and $\xi_{Cu} = 100\ \mathrm{meV}$

Anionic low energy spectrum

H_{mol} contains three different energy scales $U > J > \lambda$



B. Siegert, A. Donarini and M. Grifoni, *Beilstein J. of Nanotech.* **6**, 2452 (2015)

Spin-orbit hamiltonian

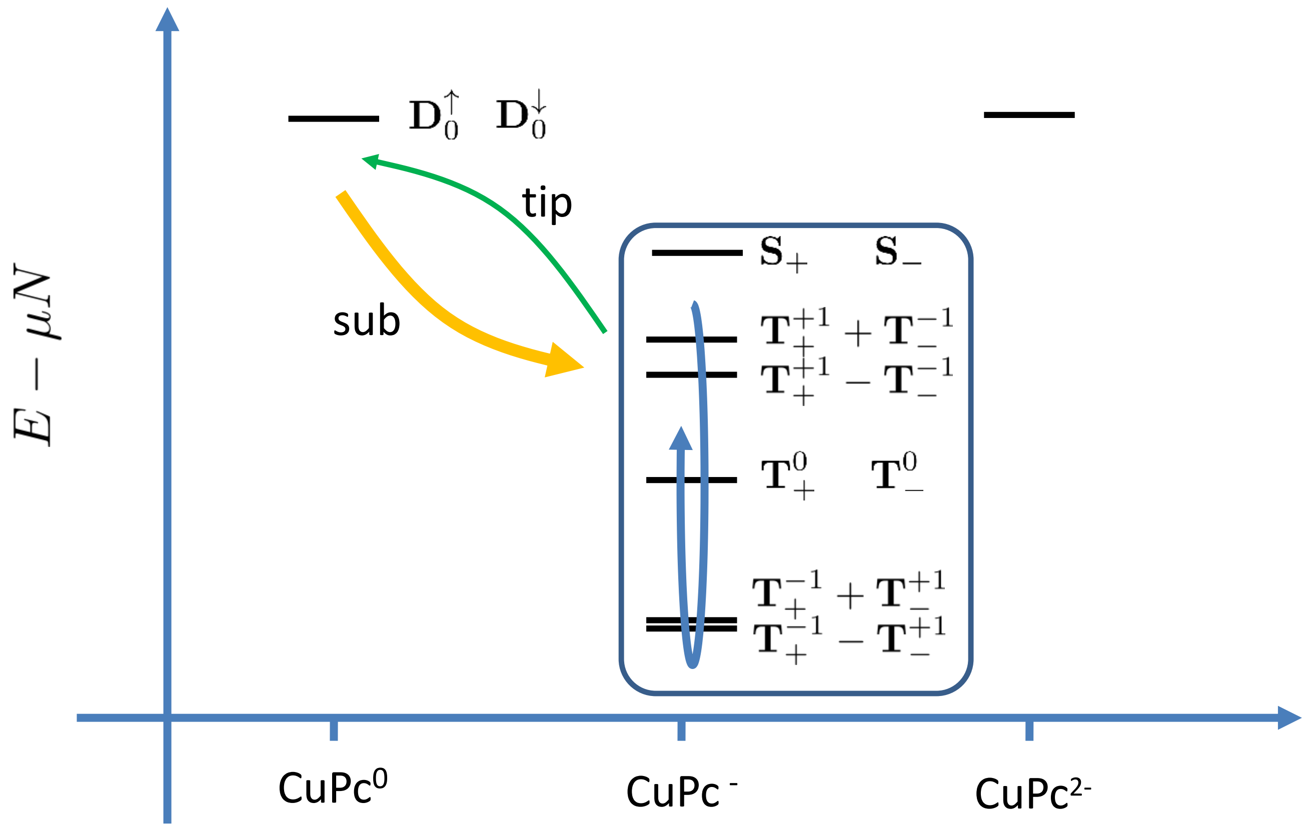
The spin orbit Hamiltonian in the triplet subspace is parametrized by 4 constants:

$$\hat{H}_{\mathrm{SOI}}^{\mathrm{eff}} = \begin{array}{c} \begin{matrix} T_+^{+1} & T_+^{0} & T_+^{-1} & T_+^{+1} & T_+^{0} & T_+^{-1} \end{matrix} \\ \begin{pmatrix} \alpha_1/2 & 0 & 0 & 0 & 0 & \alpha_2 \\ 0 & \alpha_4 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\alpha_1/2 & \alpha_3 & 0 & 0 \\ 0 & 0 & \alpha_3 & -\alpha_1/2 & 0 & 0 \\ 0 & 0 & 0 & 0 & \alpha_4 & 0 \\ \alpha_2 & 0 & 0 & 0 & 0 & \alpha_1/2 \end{pmatrix} \end{array}$$

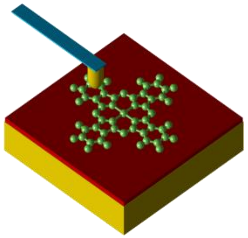
$\alpha_1 = 0.86\,\mathrm{meV}$ $\quad \alpha_2 = 0.02\,\mathrm{meV}$ $\quad \alpha_3 = 0.01\,\mathrm{meV}$ $\quad \alpha_4 = -0.01\,\mathrm{meV}$

Tunnelling and precession

$$\Delta E < \hbar\Gamma,\ k_\mathrm{B}T \ll U$$



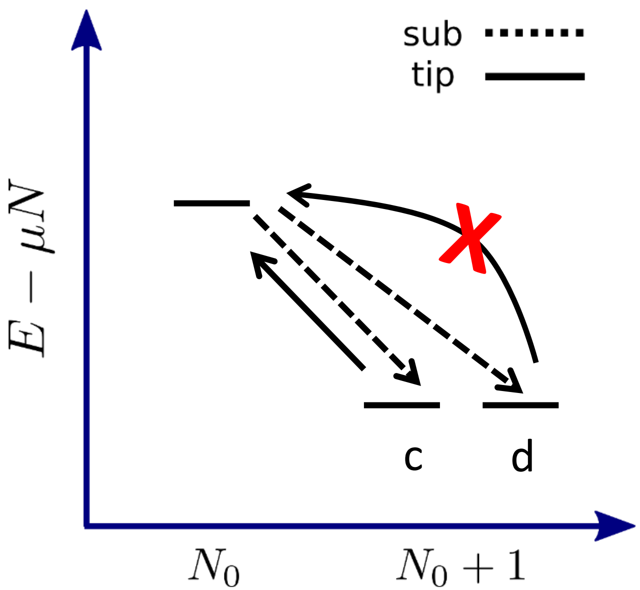
Tunnelling rate matrices



The single particle rate matrices consist of an angular momentum and a spin part. The coupling is asymmetric.

$$\Gamma^{\rm tip}_{\ell_z\sigma\ell'_z\sigma'} = \tilde{\Gamma}^{\rm tip}_0 \psi^*_{\ell_z}(\mathbf{r}_{\rm tip})\psi_{\ell'_z}(\mathbf{r}_{\rm tip}) \otimes \left(\frac{\mathbb{1}}{2} + \mathbf{P}_{\rm tip}\right)_{\sigma\sigma'}$$

$$\Gamma^{\rm sub}_{\ell_z\sigma\ell'_z\sigma'} = \tilde{\Gamma}^{\rm sub}_0 \delta_{\ell_z\ell'_z} \otimes \left(\frac{\mathbb{1}}{2} + \mathbf{P}_{\rm sub}\right)_{\sigma\sigma'}$$

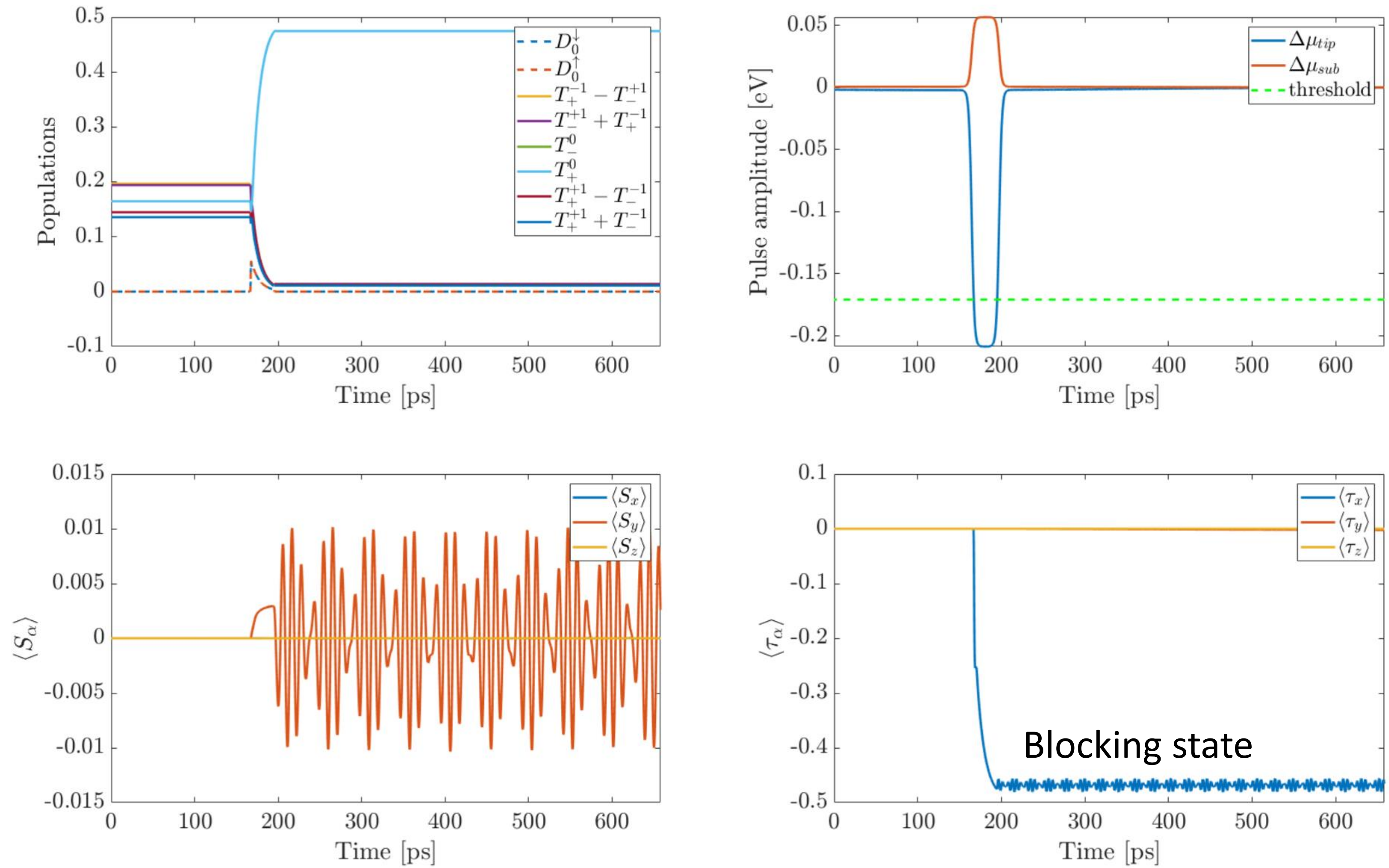


There are states **coupled** to the substrate but **decoupled** from the tip

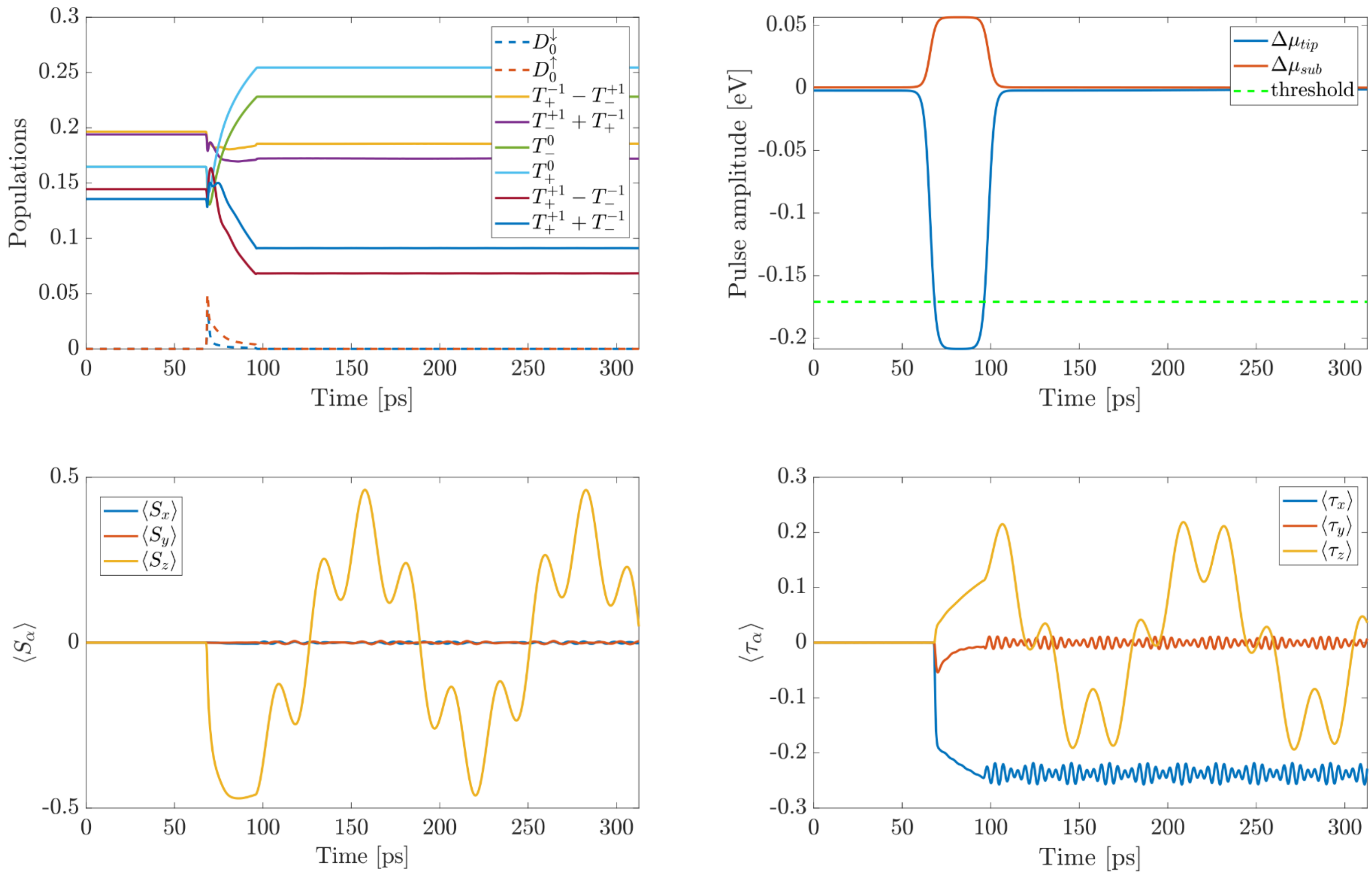
Blocking states

S. Sobczyk, A. Donarini, and M. Grifoni *Phys. Rev. B* **85**, 205408 (2012)

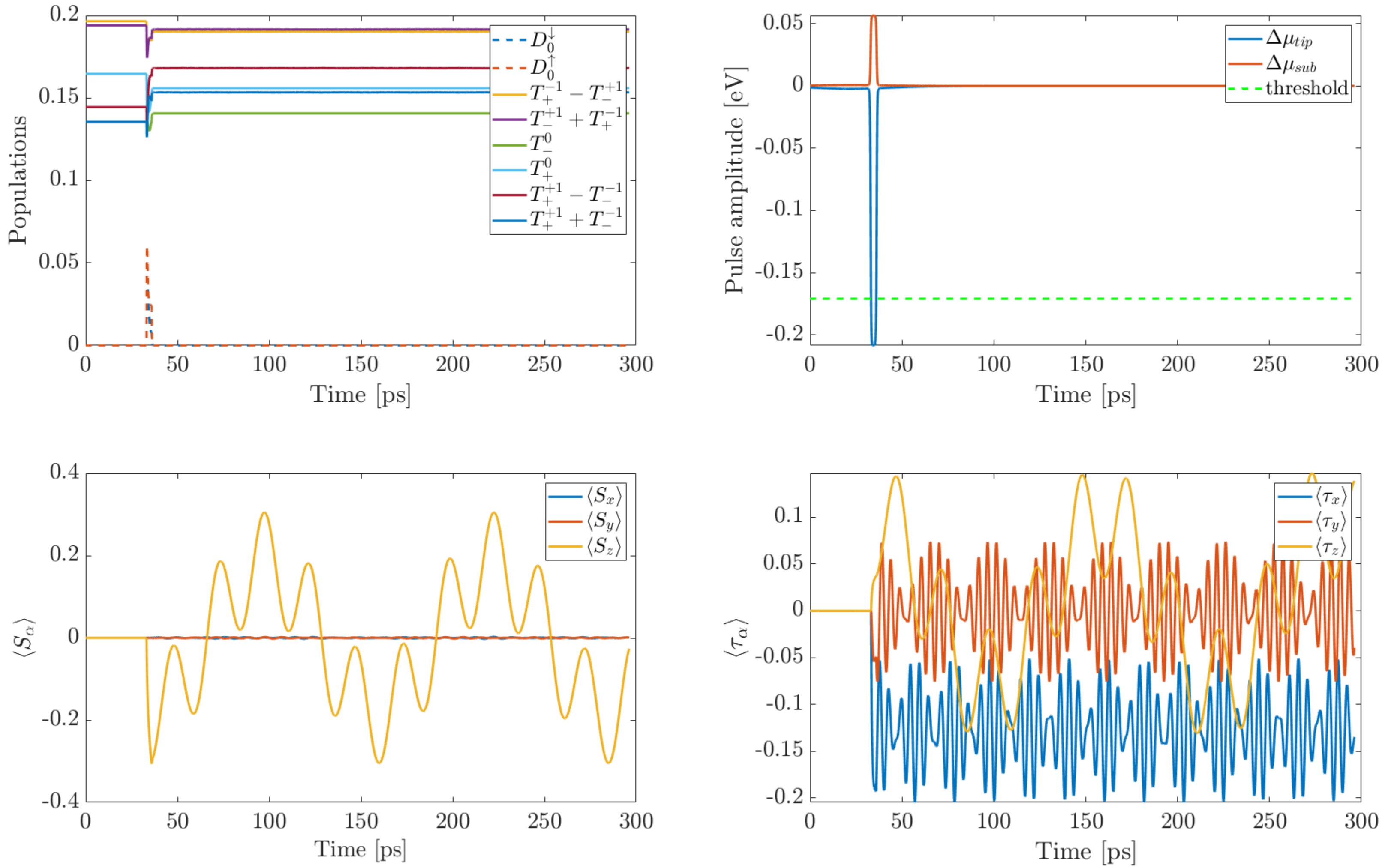
Pseudospin valve



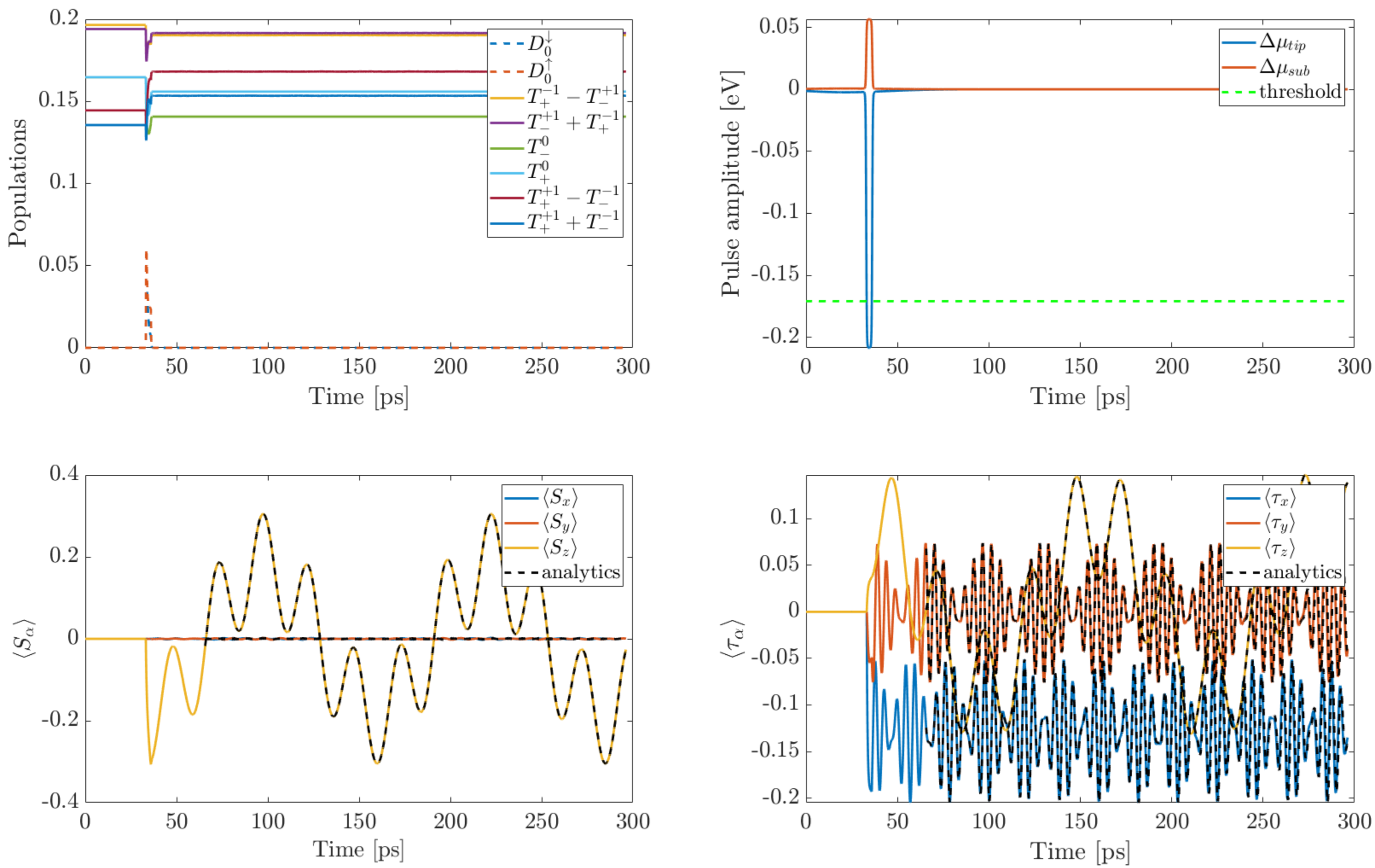
Spin polarized tip



Short pulse to drive the system



Analytic evaluation of the dynamics



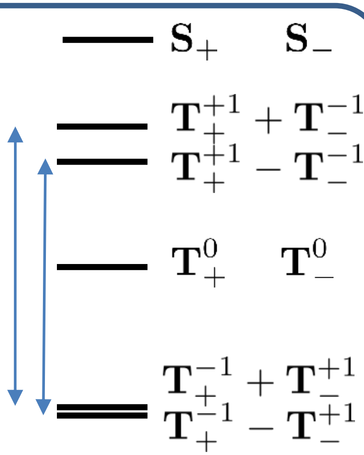
Mixed correlators

$$
\begin{aligned}
\langle \tau_x(t) \rangle = & \tfrac{1}{3}(\langle \tau_x \rangle - \langle \tau_x S_{z^2} \rangle) + \\
& \left(\tfrac{1}{3}\langle \tau_x \rangle + \tfrac{1}{4}\langle S_{x^2y^2} \rangle + \tfrac{1}{6}\langle \tau_x S_{z^2} \rangle\right) \cos[(\alpha_1 + \alpha_2 - \alpha_3)t] \\
& \left(\tfrac{1}{3}\langle \tau_x \rangle - \tfrac{1}{4}\langle S_{x^2y^2} \rangle + \tfrac{1}{6}\langle \tau_x S_{z^2} \rangle\right) \cos[(\alpha_1 - \alpha_2 + \alpha_3)t] \\
& \tfrac{1}{2}(\langle \tau_y S_z \rangle + \langle \tau_z S_{xy} \rangle) \sin[(\alpha_1 + \alpha_2 - \alpha_3)t] \\
& \tfrac{1}{2}(\langle \tau_y S_z \rangle - \langle \tau_z S_{xy} \rangle) \sin[(\alpha_1 - \alpha_2 + \alpha_3)t]
\end{aligned}
$$

Two close frequencies

⇓

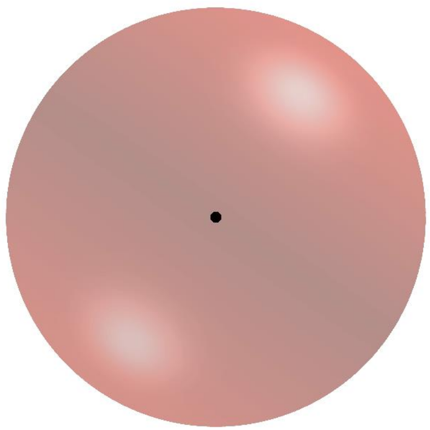
Beating oscillations

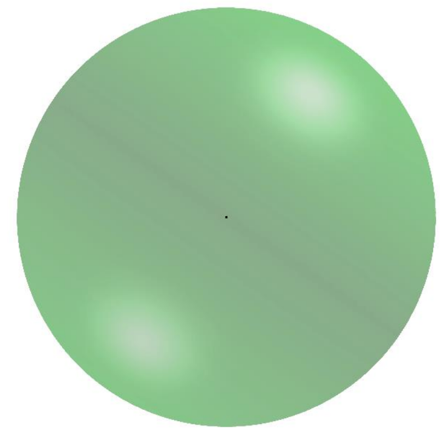


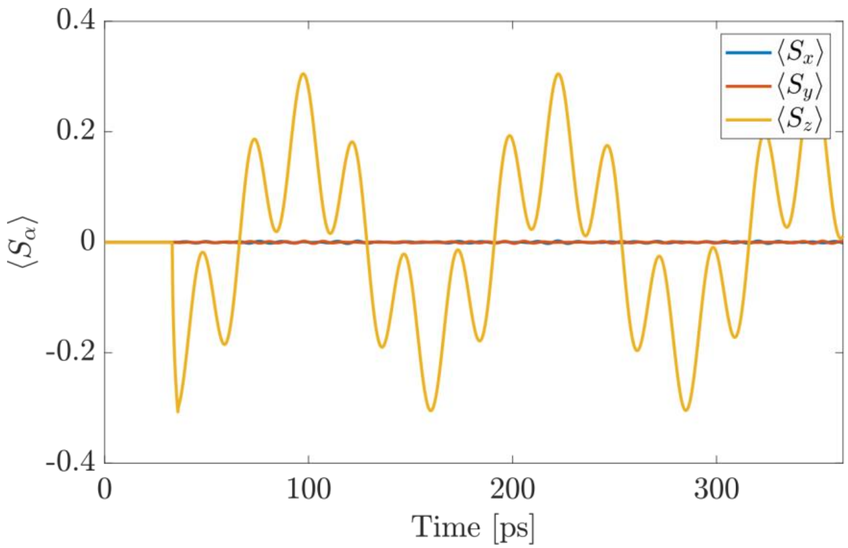
Triplet states: complete description requires information on the spin quadrupoles

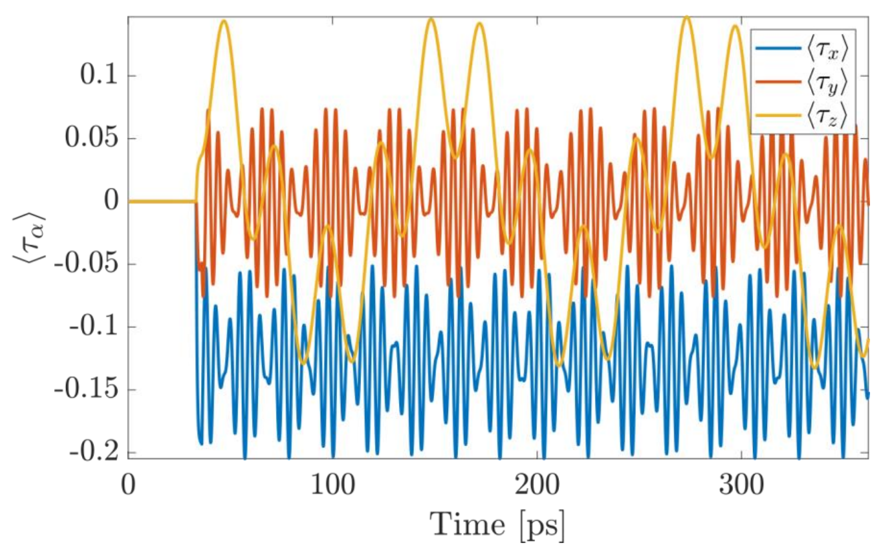
Spin orbit coupling: generates entangled spin and pseudo spin dynamics

More than spin precession

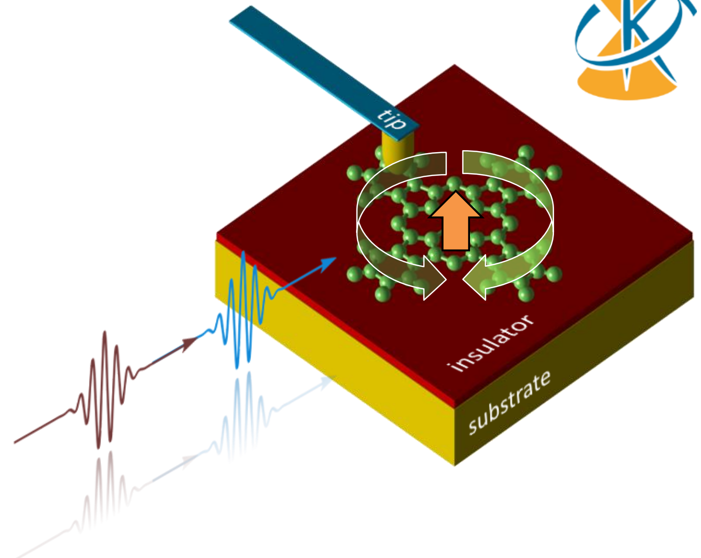




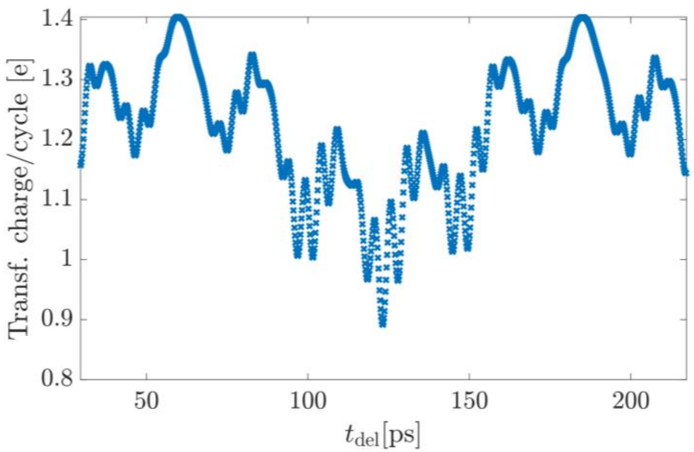




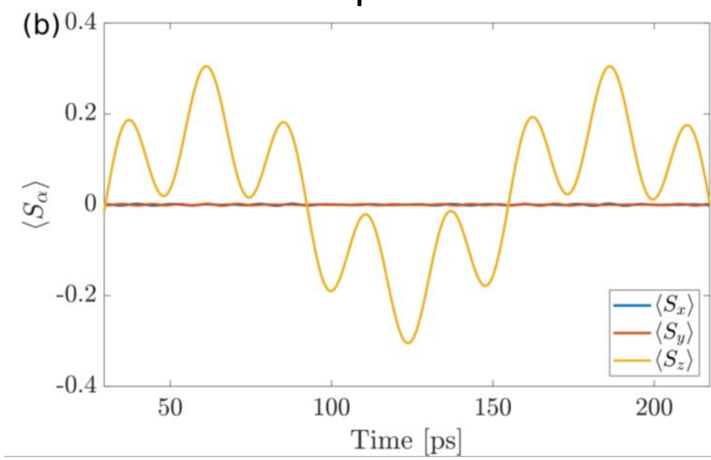
Read out



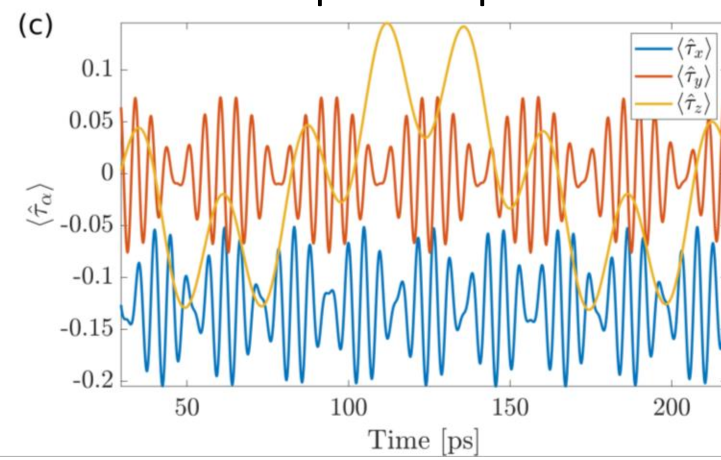
Transf. charge/cycle



spin



pseudospin



Conclusions

- **Pulsed driven dynamics** of an open interacting system in terms of **generalized master equation** for the **reduced density matrix**
- Time scale separation allows for an **adiabatic** and **Markovian** dynamics
- Pumping with a THz laser pulse generates spin-orbit induced dynamics
- Analytic description of the free system dynamics reveals spin orbit induced correlation between spin and pseudospin
- Fingerprints of spin and pseudospin valve effects are detected in the transferred charge per pump probe cycle

Thank you for your attention

Many body Hamiltonian

The minimal many body Hamiltonian, in the frontier orbital basis, of CuPc is given by:

$$\hat{H}_{mol} = \hat{H}_0 + \hat{V}_{ee} + \hat{V}_{SO} + \hat{V}_Z$$

Single particle Hamiltonian: $$\hat{H}_0 = \sum_{i\sigma} (\epsilon_i + \delta)\, \hat{n}_{i\sigma}$$

$\delta = 1.83\ eV$: renormalization for ionic background and crystal field

Electronic interactions: $$\hat{V}_{ee} = \sum_{ijkl} \sum_{\sigma\sigma'} V_{ijkl} \hat{d}^{\dagger}_{i\sigma} \hat{d}^{\dagger}_{k\sigma'} \hat{d}_{l\sigma'} \hat{d}_{j\sigma}$$

V_{ijkl} : Coulomb integrals between all dynamical orbitals

U_S	11.352 eV	$J^{\mathrm{ex}}_{HL} = -\tilde{J}^{\mathrm{p}}_{H+-}$	548 meV
U_H	1.752 eV	J^{ex}_{+-}	258 meV
$U_L = U_{+-}$	1.808 eV	J^{p}_{+-}	168 meV
U_{SH}	1.777 eV	$J^{\mathrm{ex}}_{SL} = -\tilde{J}^{\mathrm{p}}_{S+-}$	9 meV
U_{SL}	1.993 eV	$J^{\mathrm{ex}}_{SH} = J^{\mathrm{p}}_{SH}$	2 meV
U_{HL}	1.758 eV		