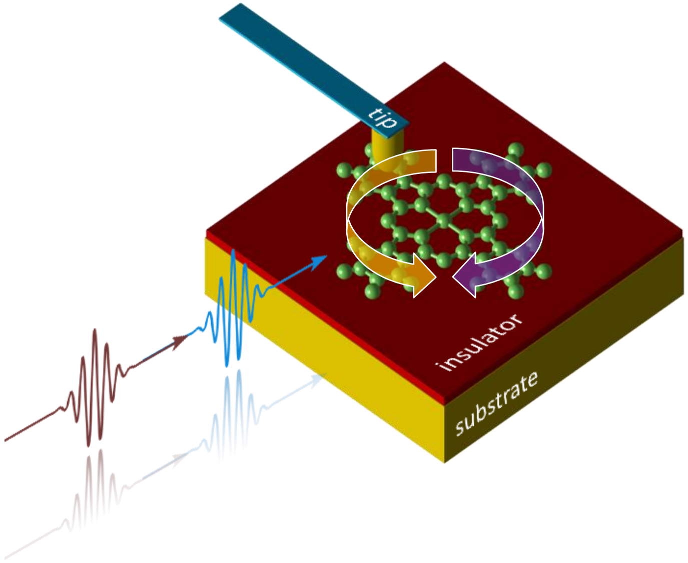
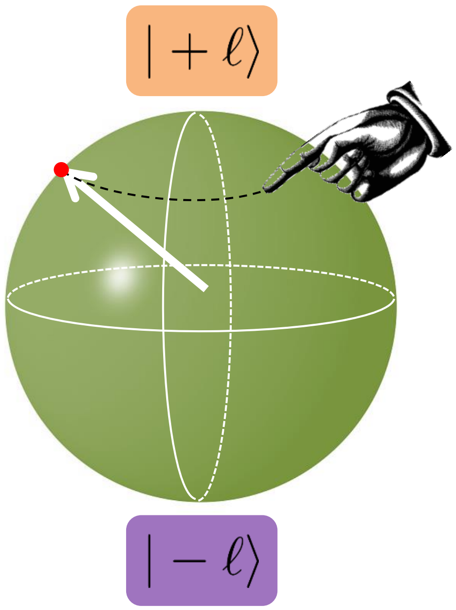
# Time-dependent dynamics in molecular junctions

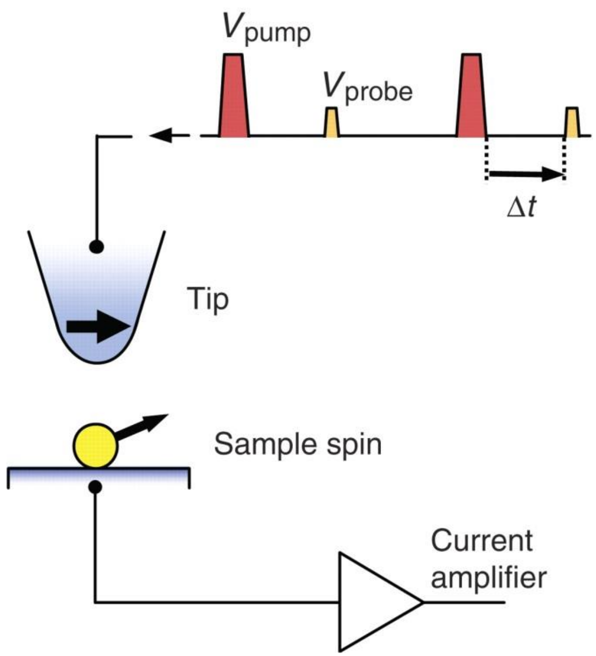
Moritz Frankerl, Andrea Donarini and Milena Grifoni

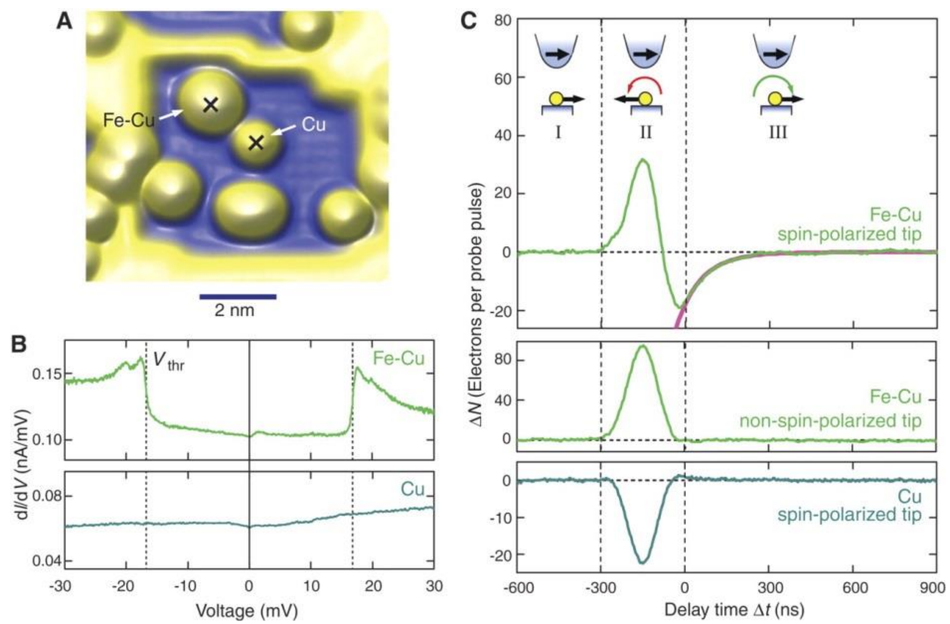



Frauenchiemsee 4.10.2017

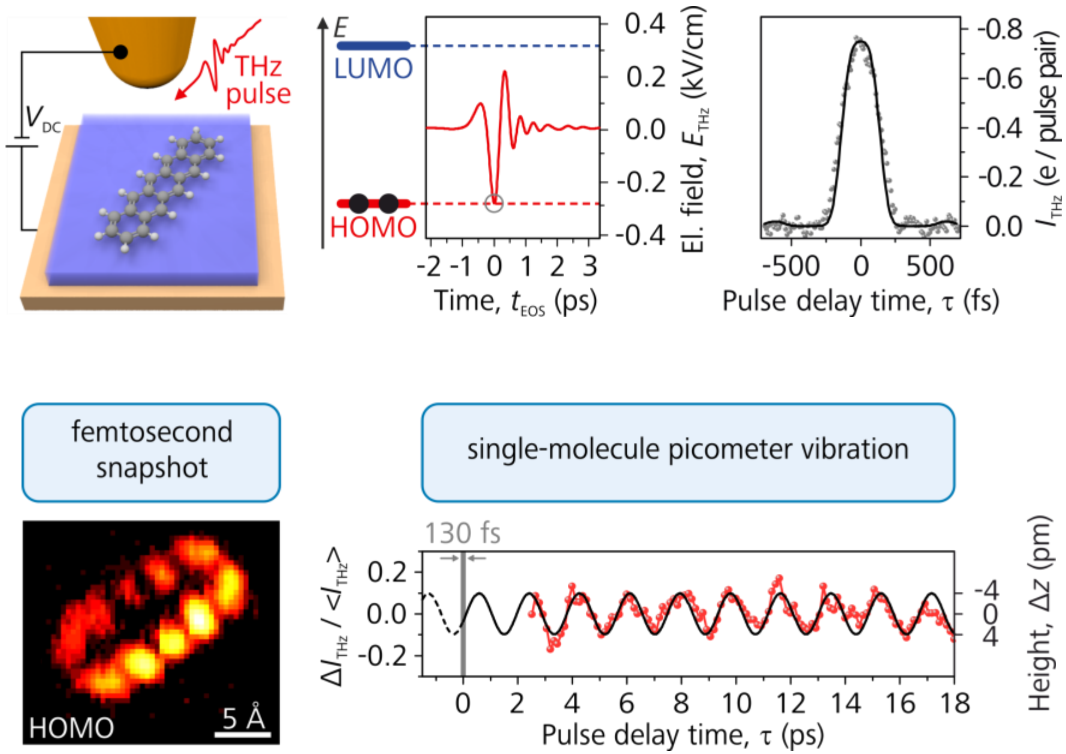
# Spin-relaxation with atomic resolution



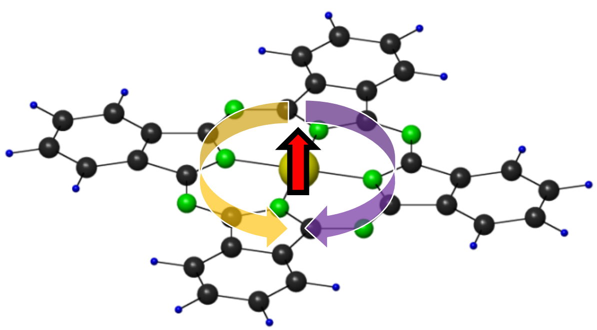

S. Loth, M. Etzkorn, C. P. Lutz, D. M. Eigler and A. J. Heinrich, *Science* **329,** 1628 (2010)

# Femtosecond orbital imaging



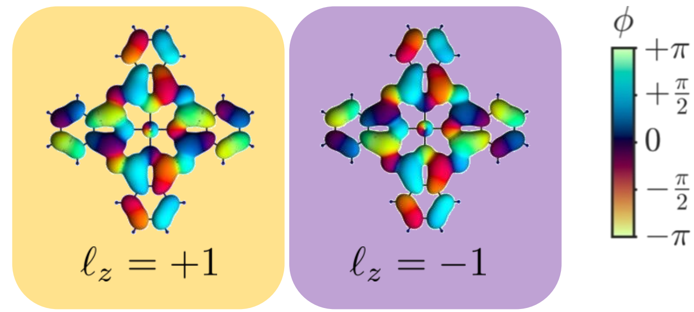

T. L. Cocker, D. Peller, P. Yu, J. Repp and R. Huber, *Nature* **539,** 263 (2016)

# Spin-orbit in Cu-Phthalocynine



The neutral molecule has an unpaired spin on the metallic center

The lowest unoccupied molecular orbitals (LUMOs) are orbitally degenerate

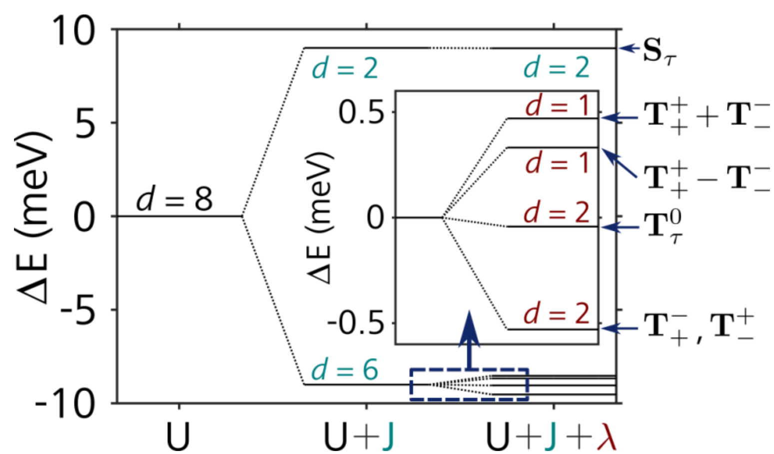



The spectrum of the **anion** is determined by the three energy scales

Charging energy $U \approx 1 \text{ eV}$

Exchange coupling $J \approx 10^{-2} \text{ eV}$

Spin-orbit coupling $\lambda \approx 10^{-3} \text{ eV}$



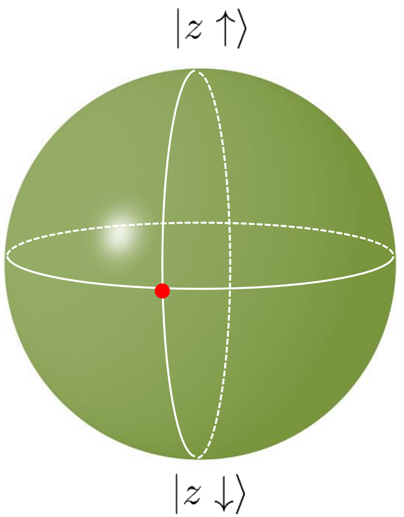

B. Siegert, A. Donarini and M. Grifoni, *Beilstein J. of Nanotech.* **6**, 2452 (2015)

# Qubit coherent oscillations

$$\hat{H} = \hbar\omega\, \hat{S}_z$$

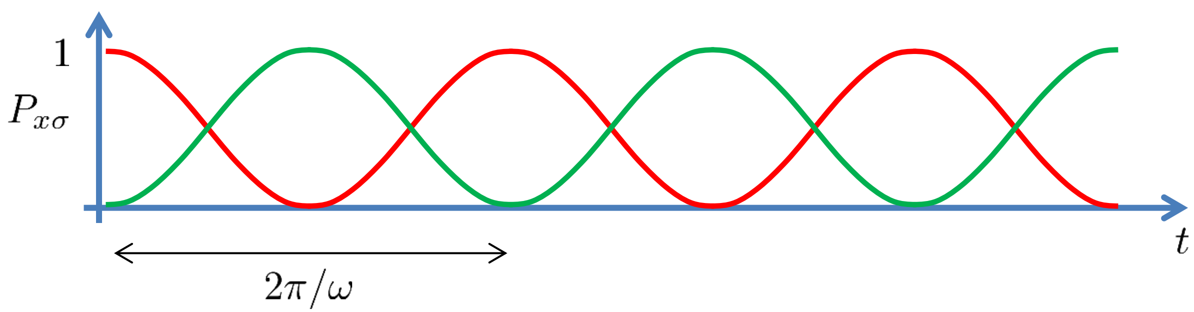
$$|\psi\rangle(0) = \frac{1}{\sqrt{2}}\left(|z\uparrow\rangle + |z\downarrow\rangle\right) = |x\uparrow\rangle$$

$$|\psi\rangle(t) = \frac{1}{\sqrt{2}}\left(e^{+i\frac{\omega}{2}t}|z\uparrow\rangle + e^{-i\frac{\omega}{2}t}|z\downarrow\rangle\right)$$



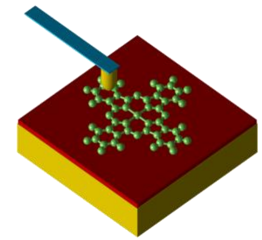


$$P_{z\sigma} = \frac{1}{2}$$



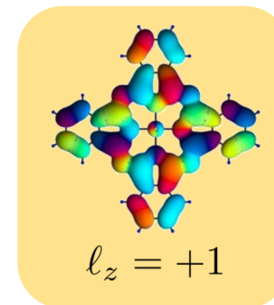

$$P_{x\sigma} = \tfrac{1}{2}[1 + \sigma\cos(\omega t)]$$

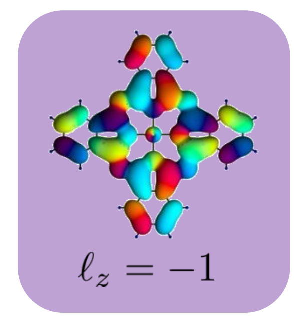
# The two orbitals model



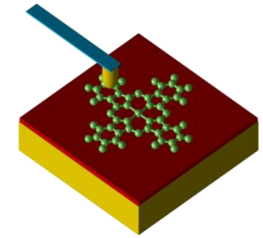
We consider for simplicity a **spinless** model for the CuPc LUMOs:

$$\hat{H}_{\mathrm{mol}} = \sum_{\ell_z=\pm 1} \left( \epsilon + \ell_z \frac{\hbar\omega}{2} \right) \hat{d}^{\dagger}_{\ell_z} \hat{d}_{\ell_z} + U \hat{N}(\hat{N} - 1).$$



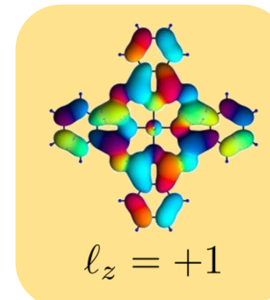
# The two orbitals model



We consider for simplicity a **spinless** model for the CuPc LUMOs:

$$\hat{H}_{\text{mol}} = \sum_{\ell_z=\pm 1} \epsilon \hat{N} + \hbar\omega \hat{T}_z + U\hat{N}(\hat{N}-1).$$

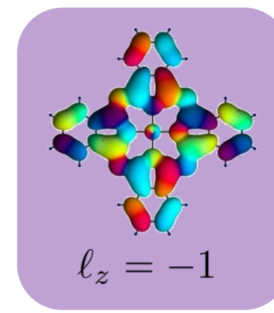
Pseudo-spin




The **tip** and **substrate** are non-interacting Fermi seas with adiabatically modulated energies

Laser pulse

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

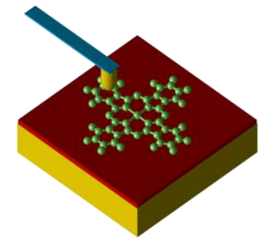



kept at the quasi-equilibrium chemical potentials $\mu_\eta(t) = \mu_0 + \alpha_\eta e V_{\text{bias}}(t).$

The **tunnelling** Hamiltonian reads:

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

# Tunnelling rate matrices



The single particle rate matrices $$\Gamma^{\eta}_{\ell_z \ell'_z}(E) = \frac{2\pi}{\hbar} \sum_{\mathbf{k}} t^{\eta}_{\ell_z \mathbf{k}}{}^{*} t^{\eta}_{\ell'_z \mathbf{k}} \delta(E - \epsilon_{\eta \mathbf{k}})$$

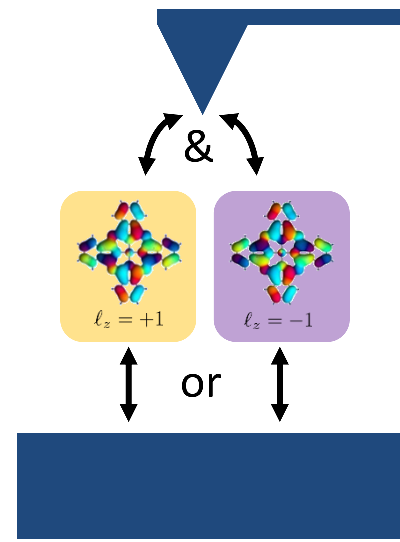
contain the geometrical information concerning the tunnelling process:

$$\Gamma^{\mathrm{tip}}_{\ell_z \ell'_z} = \tilde{\Gamma}^{\mathrm{tip}}_{0} \psi^{*}_{\ell_z}(\mathbf{r}_{\mathrm{tip}}) \psi_{\ell'_\mathbf{z}}(\mathbf{r}_{\mathrm{tip}})$$

Local tunnelling:
angular momentum mixing

$$\Gamma^{\mathrm{sub}}_{\ell_z \ell'_z} = \Gamma^{\mathrm{sub}}_{0} \delta_{\ell_z \ell'_z}$$

Extendend tunnelling:
angular momentum conservation




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

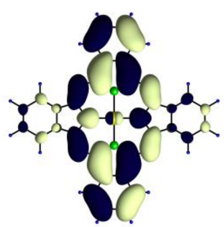
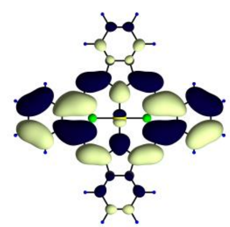
# Tunnelling rate matrices

We express the tunnelling matrix in terms of Pauli matrices and pseudo-spin polarization

$$\Gamma^{\mathrm{tip}} = \Gamma_0^{\mathrm{tip}}(\mathbf{1} + \mathbf{P}_{\mathrm{tip}} \cdot \boldsymbol{\sigma})$$

$$\mathbf{P}_{\mathrm{tip}} = \begin{pmatrix} \cos\phi_{\mathrm{tip}} \\ \sin\phi_{\mathrm{tip}} \\ 0 \end{pmatrix} \qquad \phi_{\mathrm{tip}} = \arctan\left(\frac{2\psi_x\psi_y}{\psi_y^2 - \psi_x^2}\right) + \frac{\pi}{2}[\mathrm{sgn}(\psi_y^2 - \psi_x^2) - 1]$$

where we introduced the real orbitals

$\psi_x =$  $\psi_y =$  $\psi_{\ell_z} = \frac{1}{\sqrt{2}}(\psi_x - i\ell_z\psi_y)$

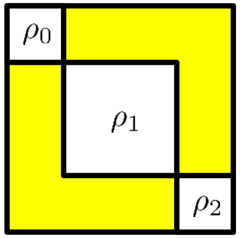
$|\mathbf{P}_{\mathrm{tip}}|$ is a measure of the tip **sharpness** and $\phi_{\mathrm{tip}}$ is the direction of the tip **polarization**

# Open system dynamics

We describe the dynamics of this **driven open system** with a generalized master equation for the **reduced density operator** $\hat{\rho} = \mathrm{Tr}_{\mathrm{leads}}\{\hat{\rho}_{\mathrm{tot}}\}$

$$\dot{\hat{\rho}} = \underbrace{-\frac{i}{\hbar}[\hat{H}_{\mathrm{mol}}, \hat{\rho}]}_{\text{internal dynamics}} \underbrace{- \frac{i}{\hbar}[\hat{H}_{\mathrm{LS}}(t), \hat{\rho}] + \mathcal{L}_{\mathrm{tun}}(t)[\hat{\rho}]}_{\text{time dependent coupling to the leads}}$$

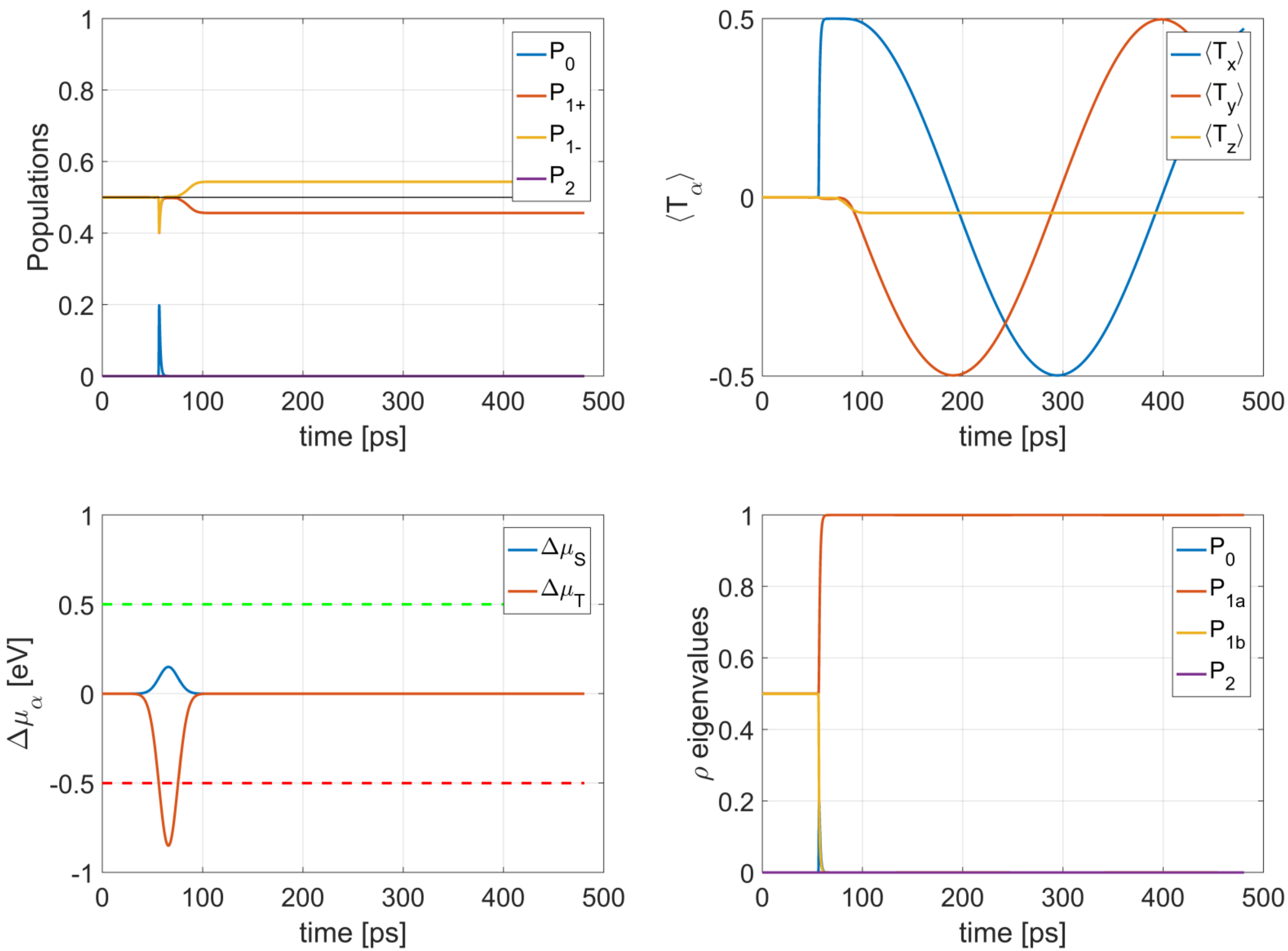
The density operator assumes a block-diagonal form in the basis of the molecular eigenstates




We represent the dynamics in terms of **occupation probabilities** and **pseudo-spin**

$$\rho_0 = P_0 \qquad \rho_1 = \frac{P_1}{2}\mathbf{1} + \mathbf{T}\cdot\boldsymbol{\sigma} \qquad \rho_2 = P_2$$

# Pseudo-spin dynamics



# Pseudo-spin dynamics

At the charge neutrality point $\mu_0 = \epsilon + \frac{U}{2}$ , and deep in the Couolomb blockade regime $k_B T \ll U$

we distinguish **three** dynamical regimes:

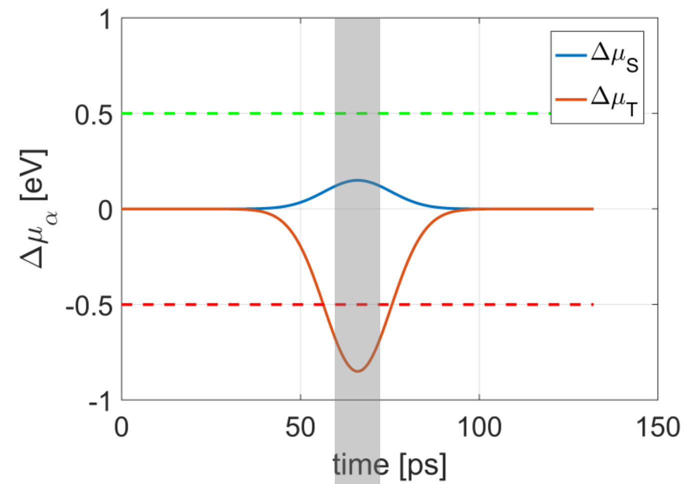
**Above threshold**

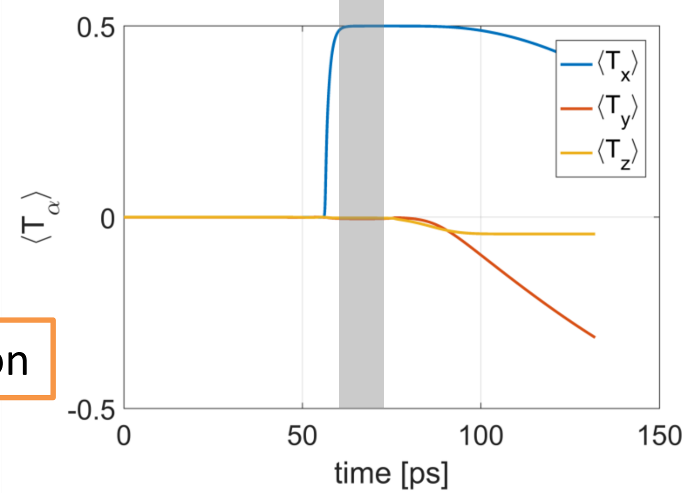
$$\dot{P}_0 = -2\Gamma_0^{\text{sub}} P_0 + 2\Gamma_0^{\text{tip}}(\tfrac{P_1}{2} + \mathbf{P}_{\text{tip}} \cdot \mathbf{T})$$

$$\dot{P}_1 = -2\Gamma_0^{\text{tip}}(\tfrac{P_1}{2} + \mathbf{P}_{\text{tip}} \cdot \mathbf{T}) + 2\Gamma_0^{\text{sub}} P_0 + 2\sum_\eta \Gamma_0^\eta P_2$$

$$\dot{P}_2 = -2\sum_\eta \Gamma_0^\eta P_2$$

$$\dot{\mathbf{T}} = [\omega \mathbf{e}_z - \Gamma_0^{\text{tip}} \frac{1}{\pi}(\bar{p}_{01,\text{tip}} - \bar{p}_{12,\text{tip}})\mathbf{P}_{\text{tip}}] \times \mathbf{T} - \Gamma_0^{\text{tip}}[\mathbf{T} + (\tfrac{P1}{2} + P_2)\mathbf{P}_{\text{tip}}]$$




After a short excursion into the 0-particle state, the system is **trapped** in the 1-particle pure state:

$P_1 = 1$ $\quad \mathbf{T} = -\frac{1}{2}\mathbf{P}_{\text{tip}}$

Qubit preparation

# Pseudo-spin dynamics

At the charge neutrality point $\mu_0 = \epsilon + \frac{U}{2}$ , and deep in the Couolomb blockade regime $k_B T \ll U$

we distinguish **three** dynamical regimes:

**Under threshold**

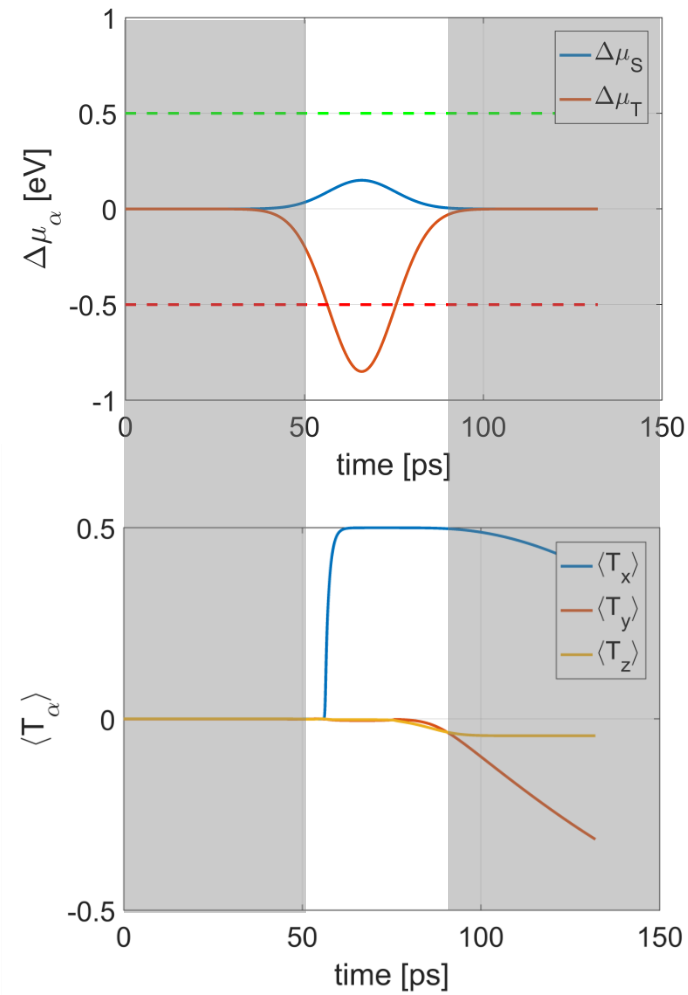
$$\left.\begin{aligned} \dot{P}_0 &= -2\sum_\eta \Gamma_0^\eta P_0 \\ \dot{P}_1 &= 2\sum_\eta \Gamma_0^\eta (P_0 + P_2) \\ \dot{P}_2 &= -2\sum_\eta \Gamma_0^\eta P_2 \end{aligned}\right\}$$

To be complemented with

$$P_0 + P_1 + P_2 = 1$$

$$\dot{\mathbf{T}} = \omega(\mathbf{e}_z \times \mathbf{T}) + \Gamma_0^{\text{tip}}(P_0 - P_2)\mathbf{P}_{\text{tip}}$$

The system remains in the 1-particle subspace with the pseudo-spin  precessing around the z axis.




Free evolution

# Pseudo-spin dynamics

At the charge neutrality point $\mu_0 = \epsilon + \frac{U}{2}$ , and deep in the Couolomb blockade regime $k_B T \ll U$

we distinguish **three** dynamical regimes:

**Close to resonance**

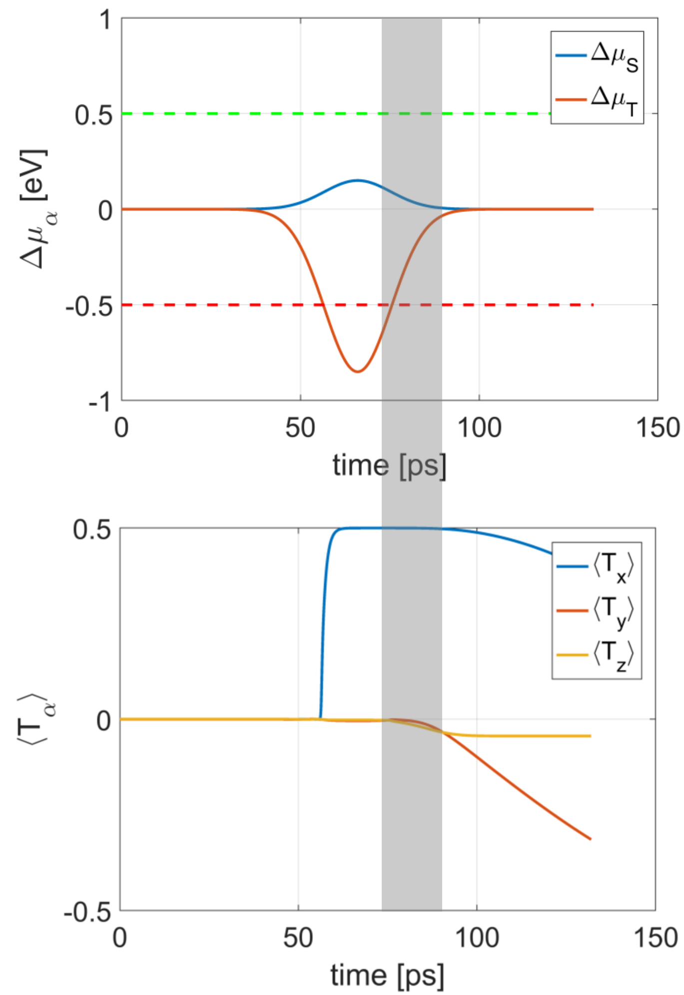
$$\left.\begin{aligned}\dot{P}_0 &= -2\sum_\eta \Gamma_0^\eta P_0 \\ \dot{P}_1 &= 2\sum_\eta \Gamma_0^\eta (P_0 + P_2) \\ \dot{P}_2 &= -2\sum_\eta \Gamma_0^\eta P_2\end{aligned}\right\}$$

To be complemented with

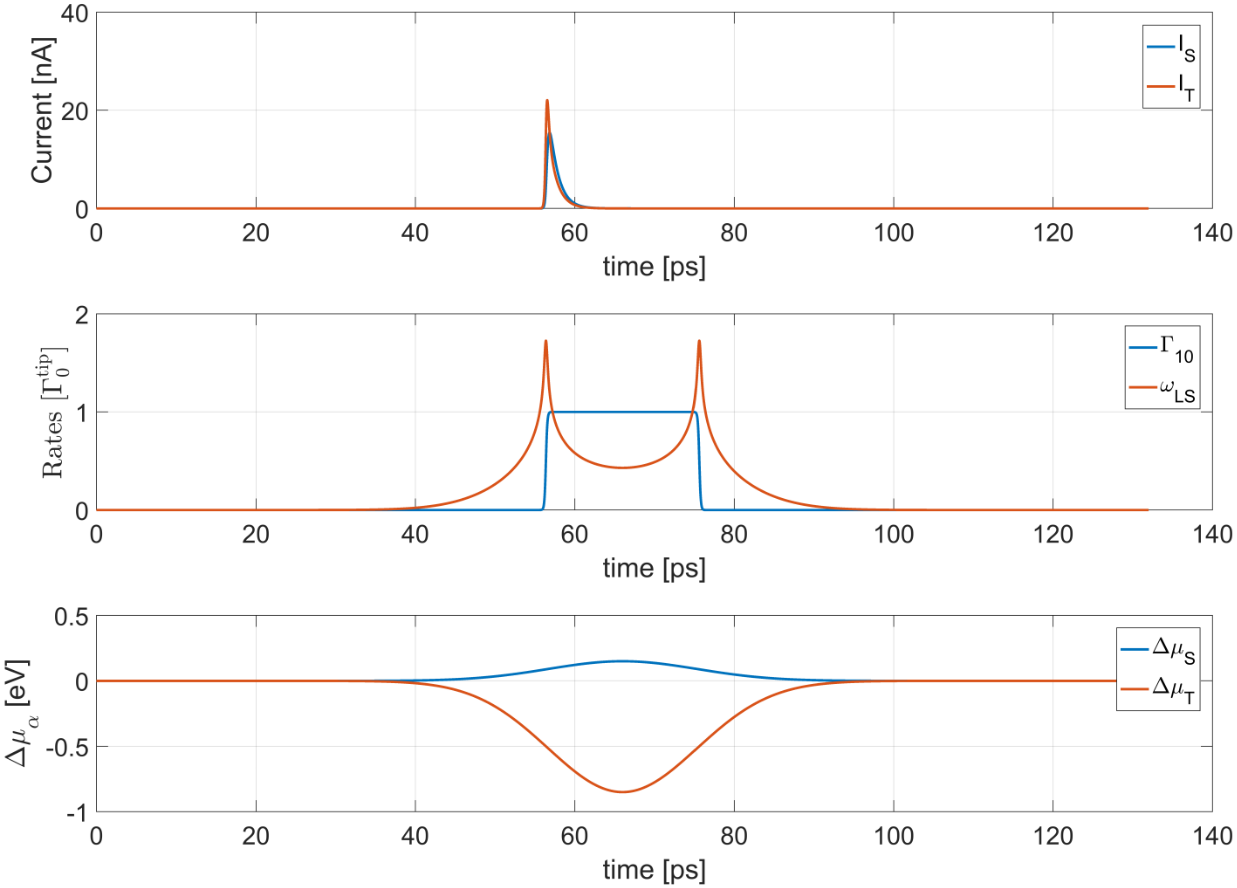
$$P_0 + P_1 + P_2 = 1$$

$$\dot{\mathbf{T}} = [\underbrace{\omega \mathbf{e}_z - \Gamma_0^{\text{tip}} \frac{1}{\pi} (\bar{p}_{01,\text{tip}} - \bar{p}_{12,\text{tip}}) \mathbf{P}_\text{tip}}_{\omega_{LS}}] \times \mathbf{T}$$

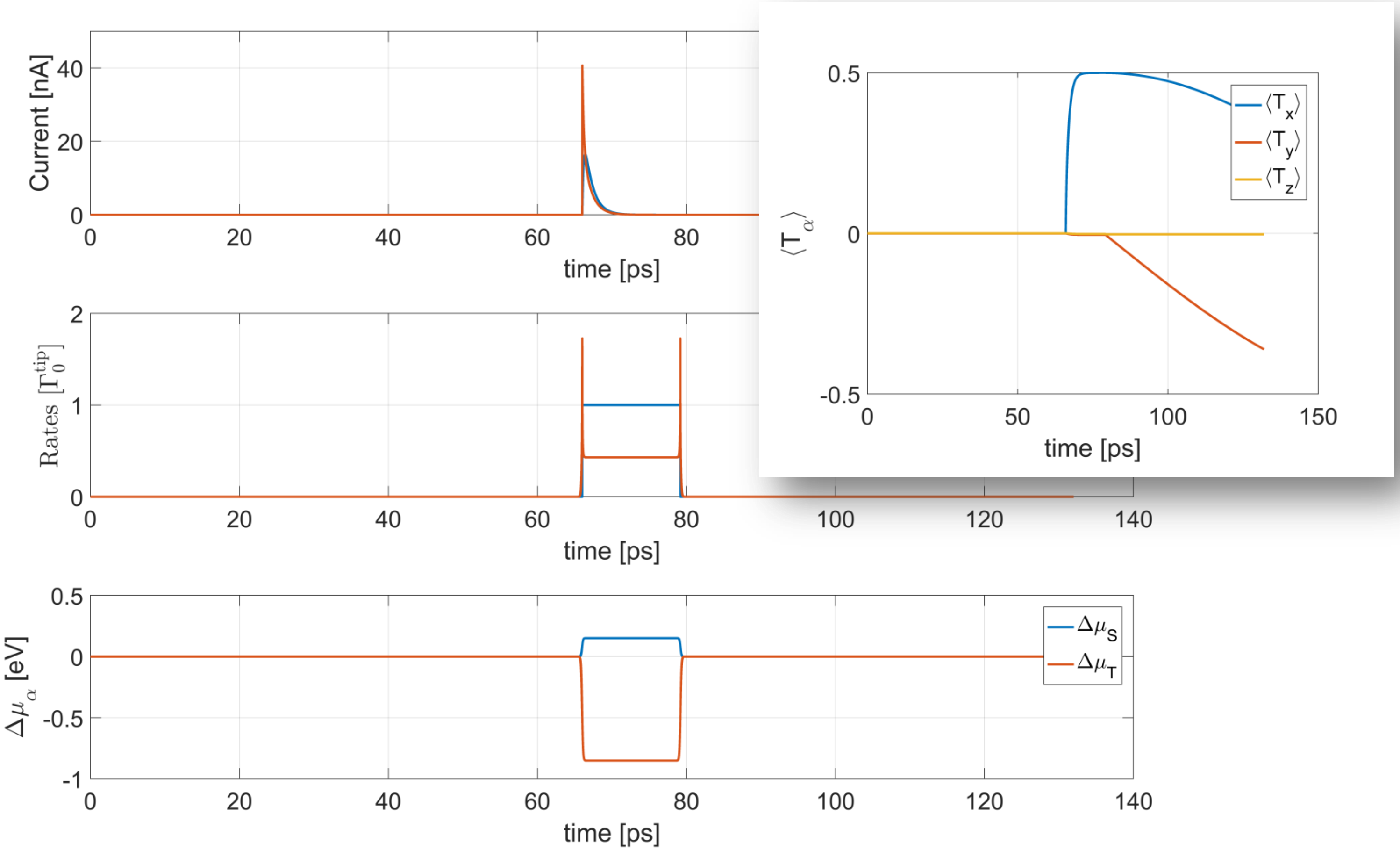
The Lamb shift correction is most effective in this regime.



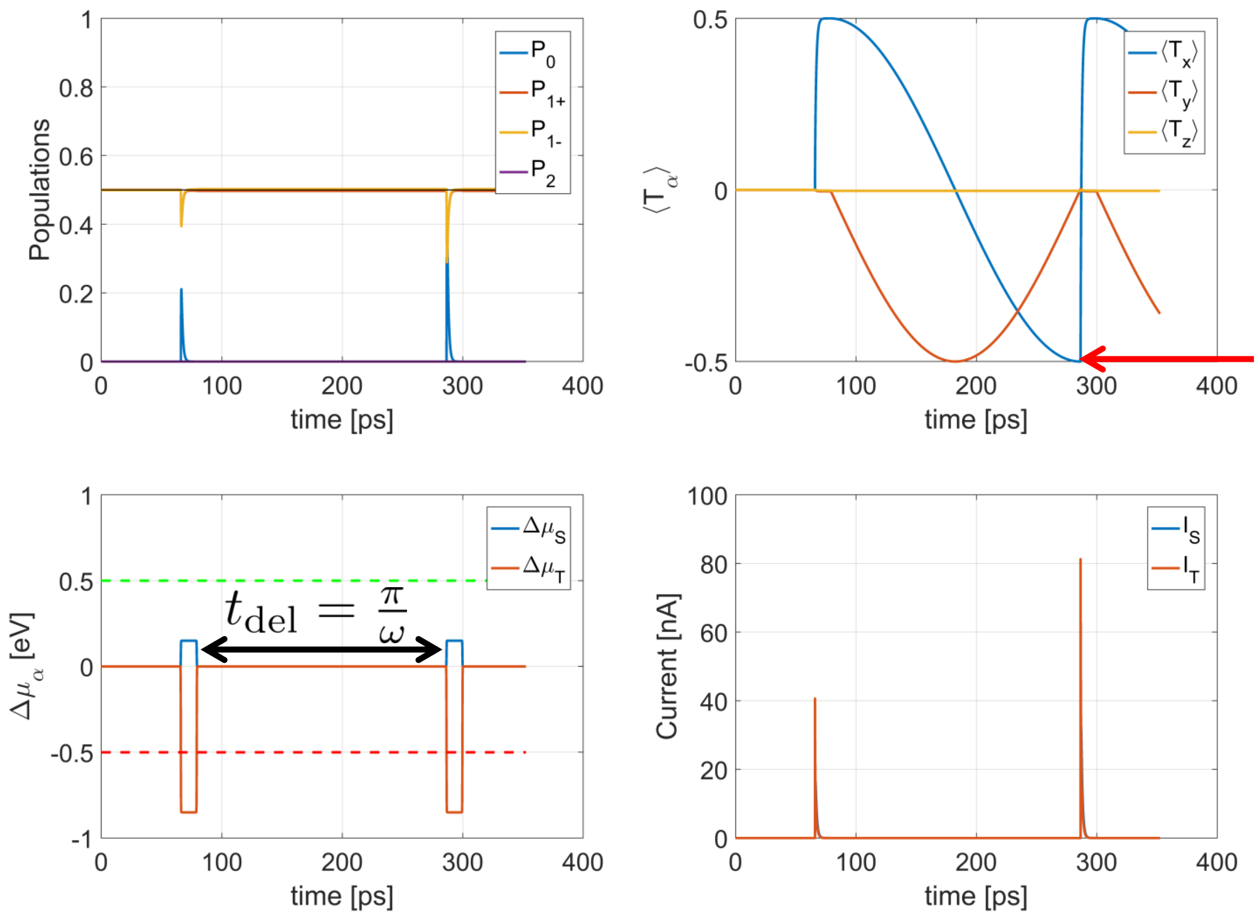
# Pump pulse optimization



# Pump pulse optimization



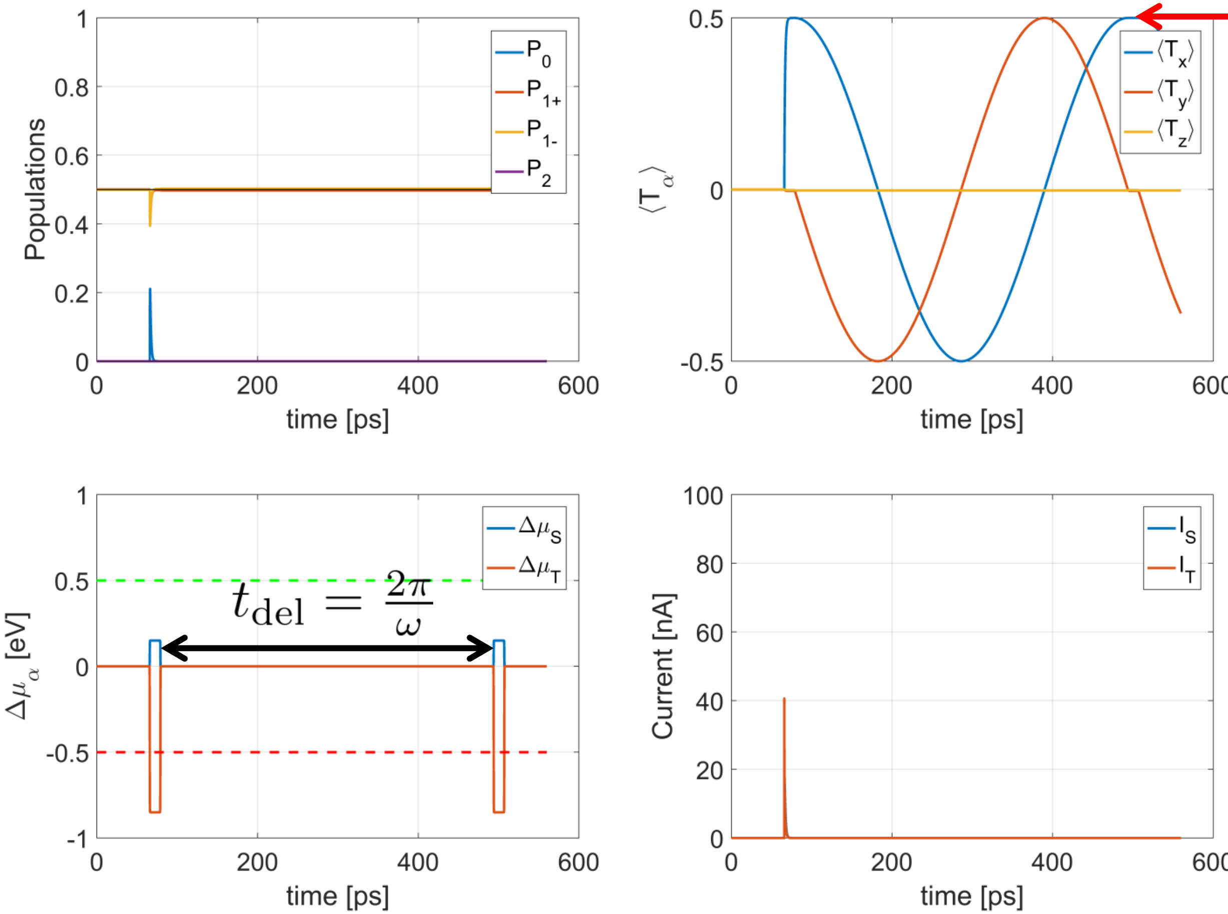
# Read-out mechanism




$$\mathbf{T} = \frac{1}{2}\mathbf{P}_{\rm tip}$$

Strong read-out pulse

# Read-out mechanism

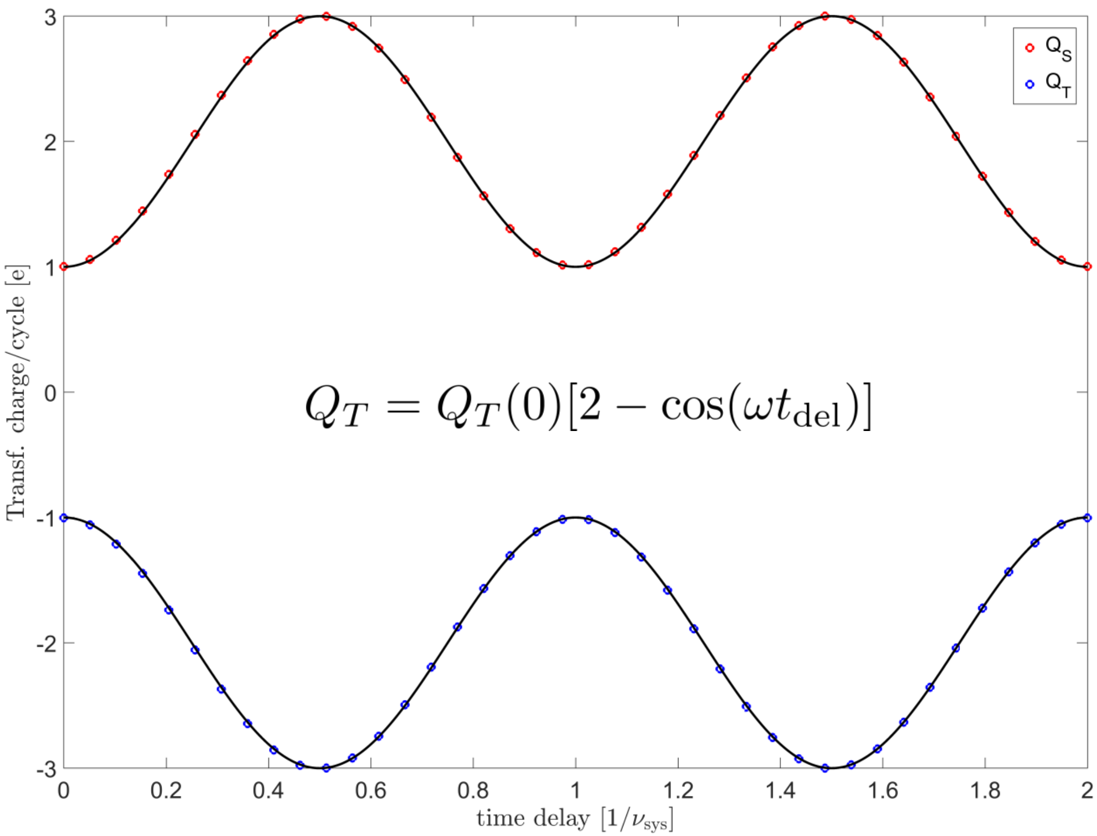



$$\mathbf{T} = -\frac{1}{2}\mathbf{P}_{\rm tip}$$

No read-out pulse

# Transmitted charge

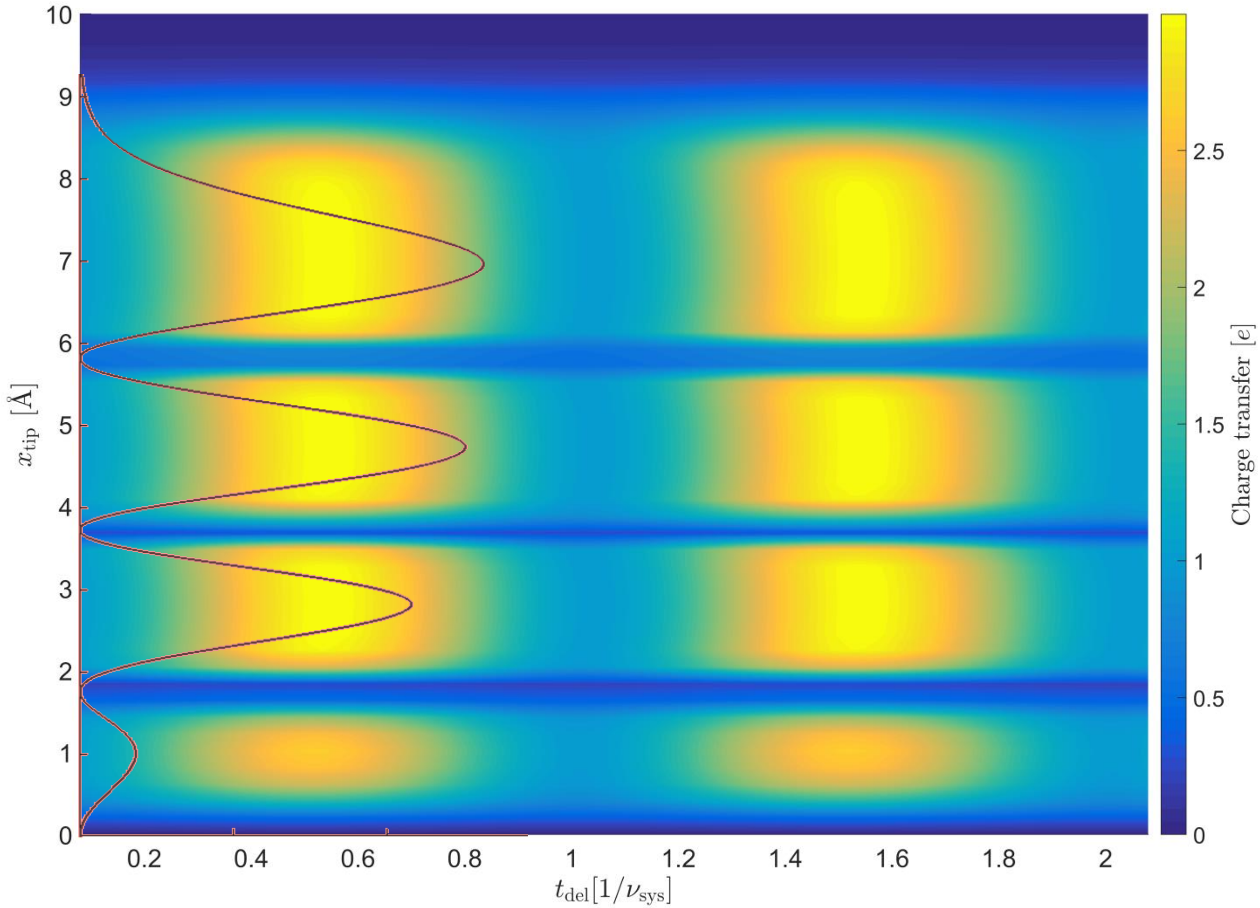
Square pulse $\mathbf{r}_{\text{tip}} = (5 \quad 0 \quad 3)$ Å




$$\hbar\omega = 10^{-5}\ \text{eV},\ k_B T = 5 \times 10^{-3}\ \text{eV},\ \Gamma_0 = 10^{-3}\ \text{eV},\ U = 1\ \text{eV}$$

# Transmitted charge

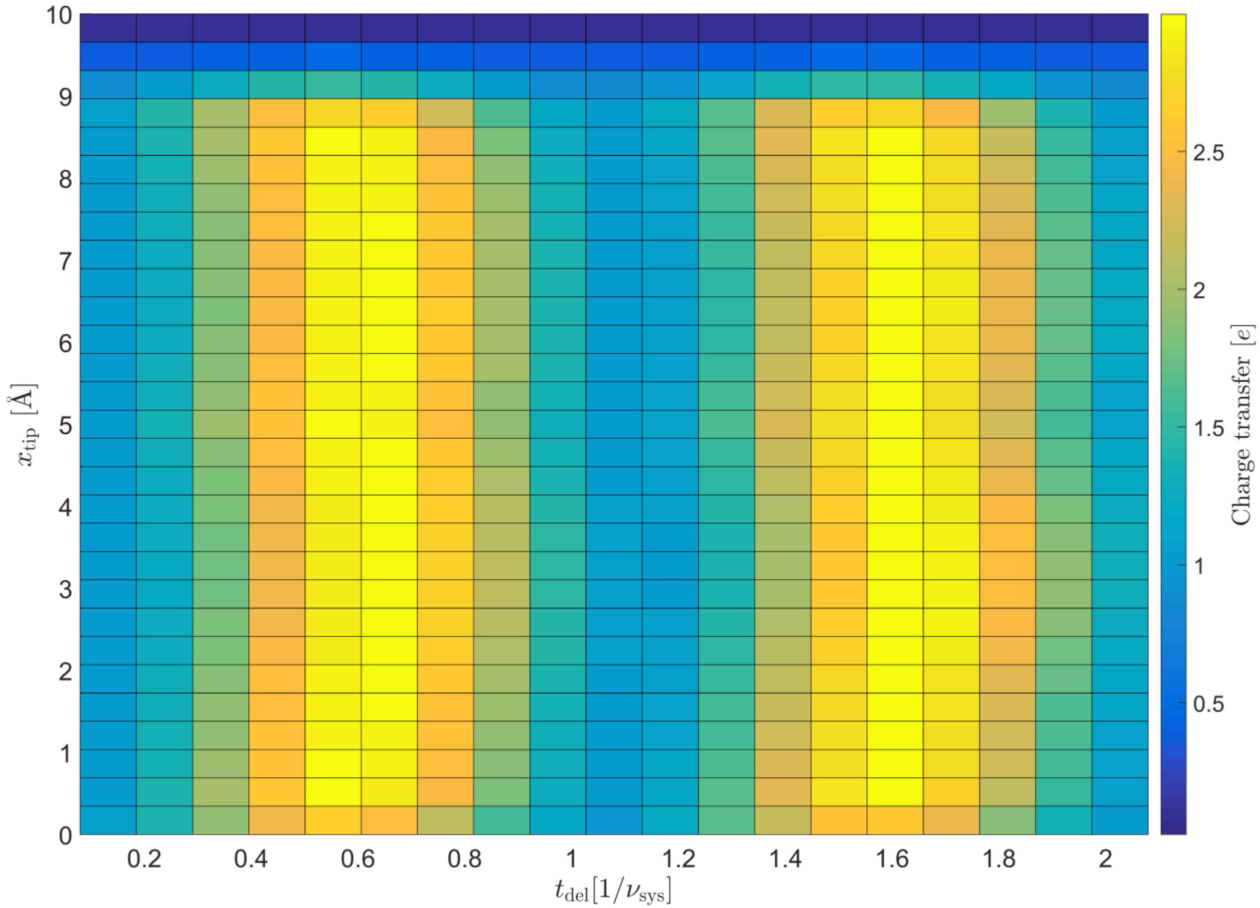
Gaussian pulse $y_{\text{tip}} = 0\text{Å},\ z_{\text{tip}} = 3\text{Å}$




$$\hbar\omega = 10^{-5}\ \text{eV},\ k_B T = 5 \times 10^{-3}\ \text{eV},\ \Gamma_0 = 10^{-3}\ \text{eV},\ U = 1\ \text{eV},\ D = \frac{10}{\Gamma_0}$$

# Transmitted charge

Gaussian pulse $y_{\text{tip}} = 1\text{Å},\ z_{\text{tip}} = 3\text{Å}$




$$\hbar\omega = 10^{-5}\ \text{eV},\ k_B T = 5\times 10^{-3}\ \text{eV},\ \Gamma_0 = 10^{-3}\ \text{eV},\ U = 1\ \text{eV},\ D = \frac{10}{\Gamma_0}$$

# Conclusions and outlook

- The two orbitals model for Cu-Pc shows **pseudo-spin dynamics** with tip depenent driving

- With a bias pulse we prepare the molecular qubit in an tip dependent anionic **pure state**.

- The **charge transfer** per pump-probe cycle allows for the **electrical read-out** of the coherent pseudo-spin precession.

- Spin and pseudo –spin dynamics will be combined for a more realistic model of Cu-Pc single molecule junction

- Impact of dephasing and relaxation processes which go beyond charge tunnelling shall be considered (e.g. Jahn-Teller effect)

**Thank you for your attention !**