Supporting Information

for

Effects of spin–orbit coupling and many-body correlations in STM-transport through copper phthalocyanine

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Details on the perturbative treatment of the SOI

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In addition to the states introduced in Eq. 14 in the main text, the following states must be also taken into account when performing second order perturbation theory:

$$
\begin{aligned}
|L\tau\uparrow, L\tau\downarrow\rangle &= \hat{\mathrm{d}}^{\dagger}_{L\tau\uparrow}\hat{\mathrm{d}}^{\dagger}_{L\tau\downarrow}|\Omega\rangle\,, \\
|L\tau\sigma, L\bar{\tau}\sigma'\rangle &= \hat{\mathrm{d}}^{\dagger}_{L\tau\sigma}\hat{\mathrm{d}}^{\dagger}_{L\tau\sigma'}|\Omega\rangle\,, \\
|S\uparrow, S\downarrow\rangle &= \hat{\mathrm{d}}^{\dagger}_{S\uparrow}\hat{\mathrm{d}}^{\dagger}_{S\downarrow}|\Omega\rangle\,,
\end{aligned}
\tag{1}
$$

with $E_{L\tau\uparrow,L\tau\downarrow} = E_{L\tau\sigma,L\bar{\tau}\sigma'} = \Delta_1$ and $E_{S\uparrow,S\downarrow} = \Delta_2$. In the basis introduced in Eqs. 14 in the main text and Eq. (1), $\hat{\mathrm{V}}_{\mathrm{SO}}$ is blockdiagonal and decomposes into six subblocks: two three-dimensional, two two-dimensional, one four-dimensional and one one-dimensional subblocks.

The four dimensional subblock describes the effects of SOI on the $\mathbf{T}^{+}_{+}$ and $\mathbf{T}^{-}_{-}$ states. Written in the basis $\{|\mathbf{T}^{+}_{+}\rangle, |\mathbf{T}^{-}_{-}\rangle, |L^{+}\uparrow, L^{-}\downarrow\rangle, |S\uparrow, S\downarrow\rangle\}$, the Hamiltonian reads

$$
\begin{aligned}
H = &\begin{pmatrix} -J^{\mathrm{ex}}_{SL} & 0 & 0 & 0 \\ 0 & -J^{\mathrm{ex}}_{SL} & 0 & 0 \\ 0 & 0 & \Delta_1 & 0 \\ 0 & 0 & 0 & \Delta_2 \end{pmatrix} \\
&+ \begin{pmatrix} \lambda_1 & 0 & -\sqrt{2}\lambda_2 & \sqrt{2}\lambda_2 \\ 0 & \lambda_1 & \sqrt{2}\lambda_2 & -\sqrt{2}\lambda_2 \\ -\sqrt{2}\lambda_2 & \sqrt{2}\lambda_2 & \lambda_1 & 0 \\ \sqrt{2}\lambda_2 & -\sqrt{2}\lambda_2 & 0 & 0 \end{pmatrix}.
\end{aligned}
\tag{2}
$$

The degeneracy of the unperturbed states $\mathbf{T}^{+}_{+}$ and $\mathbf{T}^{-}_{-}$ and the fact that there are no matrix-elements which couple these states require the use of second order degenerate perturbation theory. Applying it yields the following matrix M:

$$
M = A \cdot \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}, \tag{3}
$$

where the prefactor A is given by

$$
A = -2\lambda_2^2 \left(\frac{1}{\Delta_1 + J^{\mathrm{ex}}_{SL}} + \frac{1}{\Delta_2 + J^{\mathrm{ex}}_{SL}} \right). \tag{4}
$$

Diagonalization of M gives the second-order energy corrections

$$
\Delta E(\alpha) = \lambda_1, \tag{5}
$$

$$
\Delta E(\beta) = \lambda_1 - 4\lambda_2^2 \left(\frac{1}{\Delta_1 + J^{\mathrm{ex}}_{SL}} + \frac{1}{\Delta_2 + J^{\mathrm{ex}}_{SL}} \right), \tag{6}
$$

and the correct linear combinations of the states $\mathbf{T}_+^+$ and $\mathbf{T}_-^-$:

$$|\alpha\rangle = \frac{1}{\sqrt{2}}\Big(|\mathbf{T}_+^+\rangle + |\mathbf{T}_-^-\rangle \Big) \tag{7}$$

$$|\beta\rangle = \frac{1}{\sqrt{2}}\Big(|\mathbf{T}_+^+\rangle - |\mathbf{T}_-^-\rangle \Big). \tag{8}$$

Writing H in the basis $\{|\alpha\rangle, |\beta\rangle, |L^+\uparrow, L^-\downarrow\rangle, |S\uparrow, S\downarrow\rangle\}$ yields:

$$\begin{aligned}\tilde{H} = &\begin{pmatrix} -J_{SL}^{\mathrm{ex}} & 0 & 0 & 0 \\ 0 & -J_{SL}^{\mathrm{ex}} & 0 & 0 \\ 0 & 0 & \Delta_1 & 0 \\ 0 & 0 & 0 & \Delta_2 \end{pmatrix} \\ &+ \begin{pmatrix} \lambda_1 & 0 & 0 & 0 \\ 0 & \lambda_1 & -2\lambda_2 & 2\lambda_2 \\ 0 & -2\lambda_2 & \lambda_1 & 0 \\ 0 & 2\lambda_2 & 0 & 0 \end{pmatrix}. \end{aligned} \tag{9}$$

We see that $|\alpha\rangle$ stays unaffected by the perturbation, whereas $|\beta\rangle$ will change:

$$\begin{aligned}|\beta\rangle \rightarrow |\beta\rangle &+ 2\,\frac{\lambda_2}{\Delta_1 + J_{SL}^{\mathrm{ex}}}\,|L^+\uparrow, L^-\downarrow\rangle \\ &- 2\,\frac{\lambda_2}{\Delta_2 + J_{SL}^{\mathrm{ex}}}\,|S\uparrow, S\downarrow\rangle\,. \end{aligned} \tag{10}$$

The mixing of $\mathbf{T}_+^-$ and $\mathbf{T}_-^+$ is caused by a pair-hopping term in the Hamiltonian, more precisely by

$$\frac{1}{2} J_{L+L-}^{\mathrm{p}} \sum_\sigma \Big(\hat{\mathrm{d}}_{L+\sigma}^\dagger \hat{\mathrm{d}}_{L+\bar{\sigma}}^\dagger \hat{\mathrm{d}}_{L-\bar{\sigma}} \hat{\mathrm{d}}_{L-\sigma} + \mathrm{h.c.} \Big)\,, \tag{11}$$

which couples $\mathbf{T}_+^-$ and $\mathbf{T}_-^+$ to the following states:

$$\begin{aligned} |a\rangle &= \frac{1}{\sqrt{2}} \hat{\mathrm{d}}_{H\uparrow}^\dagger \hat{\mathrm{d}}_{H\downarrow}^\dagger \Big(\hat{\mathrm{d}}_{L+\uparrow}^\dagger \hat{\mathrm{d}}_{L+\downarrow}^\dagger - \hat{\mathrm{d}}_{L-\uparrow}^\dagger \hat{\mathrm{d}}_{L-\downarrow}^\dagger \Big) |0\rangle\,, \\ |b\rangle &= \frac{1}{\sqrt{2}} \hat{\mathrm{d}}_{H\uparrow}^\dagger \hat{\mathrm{d}}_{H\downarrow}^\dagger \Big(\hat{\mathrm{d}}_{L+\uparrow}^\dagger \hat{\mathrm{d}}_{L+\downarrow}^\dagger + \hat{\mathrm{d}}_{L-\uparrow}^\dagger \hat{\mathrm{d}}_{L-\downarrow}^\dagger \Big) |0\rangle\,, \end{aligned} \tag{12}$$

with corresponding energies E_a and $E_b = E_a + 2J_{L+L-}^{\mathrm{p}}$. Then, after introducing

$$\begin{aligned} |\mathbf{T}_1\rangle &= \frac{1}{\sqrt{2}} \left(|\mathbf{T}_+^-\rangle + |\mathbf{T}_-^+\rangle \right), \\ |\mathbf{T}_2\rangle &= \frac{1}{\sqrt{2}} \left(|\mathbf{T}_+^-\rangle - |\mathbf{T}_-^+\rangle \right), \end{aligned} \tag{13}$$

the Hamiltonian in the basis of these four states can be written as

$$H = \begin{pmatrix} H_{1b} & 0 \\ 0 & H_{2a} \end{pmatrix}, \tag{14}$$

with

$$H_{1b} = \begin{pmatrix} -J_{SL}^{\mathrm{ex}} - \lambda_1 & \lambda_2 \\ \lambda_2 & E_b \end{pmatrix} \tag{15}$$

and

$$H_{2a} = \begin{pmatrix} -J_{SL}^{\mathrm{ex}} - \lambda_1 & \lambda_2 \\ \lambda_2 & E_a \end{pmatrix}. \tag{16}$$

Diagonalization finally yields the four states

$$\begin{aligned}
|1\rangle &= \frac{1}{\sqrt{1-\gamma_b^2}} \left(|\mathbf{T}_1\rangle + \gamma_b \, |b\rangle \right), \\
|2\rangle &= \frac{1}{\sqrt{1-\gamma_a^2}} \left(|\mathbf{T}_2\rangle + \gamma_a \, |a\rangle \right), \\
|\tilde{1}\rangle &= \frac{1}{\sqrt{1-\gamma_b^2}} \left(|b\rangle - \gamma_b \, |\mathbf{T}_1\rangle \right), \\
|\tilde{2}\rangle &= \frac{1}{\sqrt{1-\gamma_a^2}} \left(|a\rangle - \gamma_a \, |\mathbf{T}_2\rangle \right),
\end{aligned} \tag{17}$$

with the admixture $\gamma_{a/b} \approx \frac{-\lambda_2}{E_{a/b} + J_{SL}^{\mathrm{ex}}}$. Their energies are approximately

$$\begin{aligned}
E_1 &\approx -\lambda_1 - \frac{\lambda_2^2}{E_b + J_{SL}^{\mathrm{ex}} + \lambda_1}, \\
E_2 &\approx -\lambda_1 - \frac{\lambda_2^2}{E_a + J_{SL}^{\mathrm{ex}} + \lambda_1}, \\
E_{\tilde{1}} &\approx E_b + \frac{\lambda_2^2}{E_b + J_{SL}^{\mathrm{ex}} + \lambda_1}, \\
E_{\tilde{2}} &\approx E_a + \frac{\lambda_2^2}{E_a + J_{SL}^{\mathrm{ex}} + \lambda_1}.
\end{aligned} \tag{18}$$

This analysis reproduces mixing and energy splittings consistent with our numerical calculations.