

# **Supporting Information**

for

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

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**Symmetries in the frontier orbitals basis**

## Symmetries in the frontier orbitals basis

One huge simplification which is possible in the molecular orbital basis is the reduction of the size of our Hilbert space  $\mathcal{H}$ , which occurs by retaining few relevant molecular orbitals only. To this end we split the full molecular basis into frozen and dynamic orbitals, where  $N_f$  of the frozen orbitals are assumed to be always fully occupied and the remaining  $N_e$  set to be always empty. We do not make any assumption about the occupation of the  $N_d$  dynamic states. Whether these  $N_d$  frontier orbitals are full or empty depends on the electrochemical potential of the molecule, and on whether an exchange of electrons with the environment is possible.

In the occupation number representation a general state of the Fock space then looks like

$$|\Psi\rangle \approx \underbrace{|11 \dots 11\rangle}_{2N_f} \otimes \underbrace{|n_{k\uparrow}n_{k\downarrow} \dots n_{l\uparrow}n_{l\downarrow}\rangle}_{2N_d} \otimes \underbrace{|00 \dots 00\rangle}_{2N_e}. \quad (1)$$

In this work we assume the molecule to be neutral under equilibrium conditions, with 195 valence electrons. Thus, the orbitals we choose to build up the subspace of dynamic orbitals are orbitals Nrs. 97-100, see Fig. 1 (b) in the main text. This choice results in the lowest 96 molecular orbitals being doubly filled. Note that the choice of the LUMO states  $L\pm$  rather than  $L_{zx/yz}$  is convenient due to the fact that these orbitals acquire a definite phase upon rotations of 90 degrees around the main symmetry axis of the molecule. Specifically, for the four frontier orbitals  $S$ ,  $H$  and  $L\pm$ , the acquired phases are  $\phi_S = \pi$ ,  $\phi_H = 0$  and  $\phi_{L\pm} = \pm \frac{\pi}{2}$ , respectively. This in turn imposes symmetry constraints on the Hamiltonian. Consider e.g. the Coulomb interaction

$$V_{ijkl} = \frac{1}{4\pi\epsilon_0} \iint d^3r_1 d^3r_2 \psi_i^*(\mathbf{r}_1) \psi_j(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_k^*(\mathbf{r}_2) \psi_l(\mathbf{r}_2). \quad (2)$$

Then, in the frontier orbital basis it holds that:

$$V_{ijkl} = e^{-i(\phi_i - \phi_j + \phi_k - \phi_l)} V_{ijkl}. \quad (3)$$

Therefore a given matrix element of the Coulomb interaction  $V_{ijkl}$  is different from zero only if the sum of the corresponding phases adds up to multiples of  $2\pi$ :  $\phi_i - \phi_j + \phi_k - \phi_l = 2\pi \cdot n$ ,  $n \in \mathbb{Z}$ . In Tab. 1 we list all nonvanishing matrix elements of the Coulomb interaction which are used in this work. For the crystal field correction  $\Delta V_{ij}^{\text{ion}}$  it can be shown that:

$$\Delta V_{ij}^{\text{ion}} = e^{-i(\phi_i - \phi_j)} \Delta V_{ij}^{\text{ion}} \quad (4)$$

$$\Rightarrow \Delta V_{ij}^{\text{ion}} = \Delta V_{ii}^{\text{ion}} \delta_{ij}, \quad (5)$$

since all phases  $\phi_i$  are different;  $\phi_i \neq \phi_j$  for  $i \neq j$ . Hence  $\Delta V_{ij}^{\text{ion}}$  is diagonal in the  $\{S, H, L\pm\}$  basis. In the following we treat the  $\Delta V_{ii}^{\text{ion}}$  as free parameters and include them in the parameter  $\delta_i$  entering Eq. 3 in the main text.

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

Table 1: Major nonvanishing Coulomb integrals between the SOMO( $S$ ), the HOMO( $H$ ), the LUMO+ and the LUMO-. When the LUMOs need to be distinguished, they are denoted as  $L+$  or  $L-$ , otherwise just by  $L$ . All values are calculated numerically using Monte Carlo integration [1] of the real space orbitals and renormalized by a constant  $\epsilon_r = 2.2$ .

## References

- [1] M. Galassi et al., *GNU Scientific Library Reference Manual*, 3rd ed., <https://www.gnu.org/software/gsl/manual/>