Supporting Information

for

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

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Transformation from the atomic to the molecular orbital basis

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The Hamiltonian of a molecule in Born-Oppenheimer approximation, after dismissing terms which only depend on the positions of the nuclei and are therefore constant, can be written as

$$\begin{aligned}\hat{\mathrm{H}} =& \sum_{\substack{\alpha\beta\sigma\\ mn}} \left(h_{\alpha m,\beta n} + \Delta V^{\mathrm{ion}}_{\alpha m,\beta n} \right) \hat{\mathrm{d}}^\dagger_{\alpha m\sigma} \hat{\mathrm{d}}_{\beta n\sigma} \\ &+ \frac{1}{2} \sum_{\substack{\alpha\beta\gamma\delta\\ mnop}} \sum_{\sigma\sigma'} V^{mnop}_{\alpha\beta\gamma\delta}\, \hat{\mathrm{d}}^\dagger_{\alpha m\sigma} \hat{\mathrm{d}}^\dagger_{\gamma p\sigma'} \hat{\mathrm{d}}_{\delta q\sigma'} \hat{\mathrm{d}}_{\beta n\sigma}, \end{aligned} \tag{1}$$

where $\hat{\mathrm{d}}^\dagger_{\alpha m\sigma}$ creates an electron in the atomic orbital $|\alpha m\sigma\rangle$ with orbital quantum number m and spin σ centered at atom α. Further we have defined

$$h_{\alpha m,\beta n} := \epsilon_{\alpha m}\delta_{\alpha\beta}\delta_{mn} + b_{\alpha m,\beta n}, \tag{2}$$

where $\epsilon_{\alpha m}$ is the energy of orbital m on atom α and $b_{\alpha m,\beta n}$ is the hopping integral between orbital m on atom α and orbital n on atom β. All non-hopping terms can be condensed in the crystal field correction

$$\Delta V^{\mathrm{ion}}_{\alpha m,\beta n} := \sum_{\gamma}^{\gamma\neq\alpha,\beta} \langle \alpha m\sigma | \hat{\mathrm{V}}_\gamma | \beta n\sigma \rangle \,, \tag{3}$$

where $\hat{V}_\gamma$ is the atomic core potential at $\mathbf{r}_\gamma$. Equation (3) defines the crystal field correction to the single particle Hamiltonian. Finally, we have the ordinary matrix elements $V^{mnop}_{\alpha\beta\gamma\delta}$ of the Coulomb interaction.

The $h_{\alpha m,\beta n}$ are elements of a matrix $\mathbf{h}$ which corresponds to the single particle Hamiltonian of the molecule with only onsite energies and hopping terms. After performing a transformation to the molecular orbital basis, in which $\mathbf{h}$ is diagonal, $|i\sigma\rangle = \sum_{\alpha m} c_{i\alpha m}\, |\alpha m\sigma\rangle$, and using the approximation that the basis $|\alpha m\sigma\rangle$ is orthogonal, the Hamiltonian reads:

$$\begin{aligned}\hat{\mathrm{H}} =& \sum_{ij\sigma} \left(\epsilon_i \delta_{ij} + \Delta V^{\mathrm{ion}}_{ij} \right) \hat{\mathrm{d}}^\dagger_{i\sigma} \hat{\mathrm{d}}_{j\sigma} \\ &+ \frac{1}{2} \sum_{ijkl} \sum_{\sigma\sigma'} V_{ijkl}\, \hat{\mathrm{d}}^\dagger_{i\sigma} \hat{\mathrm{d}}^\dagger_{k\sigma'} \hat{\mathrm{d}}_{l\sigma'} \hat{\mathrm{d}}_{j\sigma}, \end{aligned} \tag{4}$$

where $\Delta V^{\mathrm{ion}}_{ij}$ now is

$$\Delta V^{\mathrm{ion}}_{ij} = \sum_{\substack{\alpha\beta\\ mn}} c^*_{i\alpha m} c_{j\beta n}\, \Delta V^{\mathrm{ion}}_{\alpha m,\beta n}. \tag{5}$$