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

\[ \hat{H} = \sum_{\alpha \beta m n} \left( h_{\alpha m, \beta n} + \Delta V_{\alpha m, \beta n}^{\text{ion}} \right) \hat{d}_{\alpha m \sigma} \hat{d}_{\beta n \sigma} \]

\[ + \frac{1}{2} \sum_{\alpha \beta \gamma \delta m n o p} \sum_{\sigma \sigma'} V_{\alpha \beta \gamma \delta m n o p}^{mnop} \hat{d}_{\alpha m \sigma} \hat{d}_{\alpha \beta n \sigma'} \hat{d}_{\gamma \delta m \sigma'} \hat{d}_{\beta n \sigma}, \]

(1)

where \( \hat{d}^{\dagger}_{\alpha m \sigma} \) creates an electron in the atomic orbital \( |\alpha m \sigma\rangle \) with orbital quantum number \( m \) and spin \( \sigma \) centered at atom \( \alpha \). Further we have defined

\[ h_{\alpha m, \beta n} := \epsilon_{\alpha m} \delta_{\alpha \beta} \delta_{m n} + b_{\alpha m, \beta n}, \]

(2)

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

\[ \Delta V_{\alpha m, \beta n}^{\text{ion}} := \sum_{\gamma \neq \alpha, \beta} \langle \alpha m \sigma | \hat{V}_{\gamma} | \beta n \sigma \rangle, \]

(3)

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

The \( h_{\alpha m, \beta n} \) are elements of a matrix \( h \) 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 \( h \) 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:

\[ \hat{H} = \sum_{i j \sigma} \left( \epsilon_{i j} \delta_{i j} + \Delta V_{ij}^{\text{ion}} \right) \hat{d}_{i \sigma}^{\dagger} \hat{d}_{j \sigma} \]

\[ + \frac{1}{2} \sum_{i j k l \sigma \sigma'} V_{i j k l \sigma \sigma'} \hat{d}_{i \sigma}^{\dagger} \hat{d}_{k \sigma'}^{\dagger} \hat{d}_{l \sigma'} \hat{d}_{j \sigma}, \]

(4)

where \( \Delta V_{ij}^{\text{ion}} \) now is

\[ \Delta V_{ij}^{\text{ion}} = \sum_{\alpha \beta m n} c_{i \alpha m}^{*} c_{j \beta n} \Delta V_{\alpha m, \beta n}^{\text{ion}}. \]

(5)