The role of the tip symmetry on the STM topography of $\pi$-conjugated molecules

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We present an STM theory based on the reduced density matrix (RDM) formalism which is able to describe transport properties of an STM junction for $\pi$-conjugated molecules on thin insulating films. It combines a very popular derivation of STM tunneling matrix elements [1], based on Bardeen’s tunneling formalism [2], with a generalized master equation approach for interacting molecular systems. We show that this method allows the efficient implementation of different tip symmetries in STM simulations. With the example of hydrogen phthalocyanine ($H_2Pc$), we study the influence of s- and p-wave tip symmetries on the constant-height current maps of $\pi$-conjugated molecules.

1 Introduction Since its invention in 1982 by Binning and Rohrer [3], scanning tunneling microscopy has been gathering enormous attention in- and outside the physics community. There already exist many theories describing STM junctions [4–11], and a comprehensive review can be found in Ref. [12]. One of the most famous theories of STM was initially proposed by Tersoff and Hamann [13–15] based on the theory of tunneling of Bardeen [2]: They modeled the tip as a spherical potential well and showed that the tunneling current is proportional to the local density of states of the sample. Although not capable of explaining atomic resolution in STM experiments, this theory laid the foundations for the understanding of STM images. A more sophisticated description of the tip-sample tunneling was proposed by Chen [1] which took into account higher angular momentum states and therefore different tip symmetries. A major benefit of his proposal is of rather technical nature; he concluded in his “derivative rule” that tunneling matrix elements involving a given tip symmetry are proportional to corresponding spatial derivatives of the sample wavefunction evaluated at the apex of the tip. He further stated that higher corrugation amplitudes and thus atomic resolution can be ascribed to $d_z^2$-tip symmetries [16]. In recent years, STM experiments with molecules on thin insulating films [17–19] are enjoying increasing interest. The insulating layers, only few ångström thin and grown on the conductive substrate, are effectively decoupling the molecular electrons from the electrons in the substrate. Thus, there is essentially no hybridization of substrate and sample wavefunction, which allows to study the electronic properties of the pristine molecule at low temperatures.

In this work we combine the reduced density matrix (RDM) formalism [20] with the STM tunneling theory of Chen [1]. The RDM formalism is a powerful tool to investigate the transport properties of interacting nanosystems weakly coupled to leads. It is applicable also to molecular quantum dots [21–23] where it can be used to study many-body quantum interference in three-terminal [24] and STM setups [25, 26]. Its combination with Chen’s theory allows

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and can be described by the Hamiltonian

\[ H = H_{\text{mol}} + H_S + H_T + H_{\text{tun}}. \]  

The presence of the insulating layer allows to neglect hybridization of the molecular wavefunction with the wavefunction of the substrate and thus to work in the weak coupling sequential tunneling regime. The Hamiltonian of the molecule \( H_{\text{mol}} = H_0 + V_{ee} \) is given by

\[ H_{\text{mol}} = \sum_{\nu} \epsilon_\nu d^\dagger_\nu d_\nu + \sum_{\langle \nu, \nu' \rangle} b_{\nu,\nu'} d^\dagger_\nu d_{\nu'} + V_{ee}, \]  

where the multi-indices \( \nu, \nu' \) include the atomic site \( r_\nu = (x_\nu, y_\nu, z_\nu) \), the orbital index \( l_\nu \in \{ 1s, 2s, 2p_x, 2p_y, 2p_z \} \) of a hydrogen-like atomic orbital and the spin index. We set the \( z \)-coordinate of the molecule to \( d \), where \( z = 0 \) defines the metal–insulator interface (see Fig. 1).

The operator \( d^\dagger_\nu \) creates an electron in the molecule with the set of quantum numbers \( \nu \) with the onsite energy \( \epsilon_\nu \). The values for the different onsite energies were taken from Ref. [27]. We consider the set of all 2s (1s for hydrogen), 2p_x and 2p_y orbitals as the \( \sigma \)-system, and consequently the set of 2p_z orbitals as the \( \pi \)-system. The hopping parameters \( b_{\nu,\nu'} \) are calculated using the Slater–Koster LCAO method [28] with the overlap parameters taken from Refs. [27, 29] and the geometrical parameters taken from Refs. [30–32]. For the electron–electron interaction \( V_{ee} \) we are using a constant-interaction term [33]:

\[ V_{ee} = \frac{U}{2} (N - N_0)^2, \]  

where \( U \) quantifies the strength of the Coulomb interaction. \( N = \sum_\nu d^\dagger_\nu d_\nu \) and \( N_0 \) is the number of electrons occupying the neutral molecule. Under consideration that the grandcanonical energy of the molecule,

\[ E_0 = \langle H_0 \rangle = \langle H - \mu_0 N \rangle, \]  

with \( \mu_0 \) being the chemical potential of the leads in equilibrium, has to be minimal in its neutral state, we adjusted the parameter \( U \) and renormalized the single-particle eigenenergies by a constant value. This criterion only fixes a range of possible \( U \) and single particle shifts. The final values have been obtained by fitting our transport calculations to experimental results [34, 35]. Image charge effects are known to produce such renormalizations of onsite energies and Coulomb interactions [36]. A microscopic evaluation of this effect lies outside the scope of this paper and will be considered for later work.

The substrate and the tip are assumed to act as reservoirs of noninteracting electrons, \( H_S = \sum_{\kappa_\nu} \epsilon_\kappa^S c^\dagger_\kappa c_\kappa \), where \( \eta = S, T \) denotes substrate or tip. The tunneling Hamiltonian \( H_{\text{tun}} \) describes tunneling between the molecule and substrate and between the tip and the molecule:

\[ H_{\text{tun}} = \sum_{\eta \kappa j \sigma} \tilde{t}_{\eta j}^\dagger c^\dagger_{\eta \kappa} d_{j \sigma} + \text{h.c.}, \]  

where \( \eta \) again denotes substrate or tip, \( \kappa = (k_x, k_y, k_z) \) is the wavevector of an electron in lead \( \eta \), \( \sigma \) is the spin of the electron and the index \( j \) denotes a molecular orbital (MO) of the \( \pi \)-system. The tunneling amplitudes \( \tilde{t}_{\eta j} \) depend on the wavevector \( \kappa \) and the MO index \( j \).

The single-particle MOs of the system are obtained by numerical diagonalization of \( H_0 \). Due to the planar geometry of \( \text{H}_2\text{Pc} \) [30, 37, 38] the \( \pi \)-system is decoupled from the \( \sigma \)-system and thus not influenced by the presence of the central hydrogen atoms. The reduced symmetry can be recovered also in the \( \pi \)-system if we introduce a spatial modulation of the on-site energies \( \epsilon_\kappa^\pi \) associated to the electron density of the filled \( \sigma \)-orbitals. For this purpose, we introduce the Mulliken charge [39] relative to all occupied \( \sigma \)-orbitals at

Figure 1. (Left) Artistic view of the STM setup. (Right) Sketch of the potential profile of the STM setup along the direction perpendicular to the molecular plane.
where $\epsilon$ is the absolute value of the electron charge and $c_{i(a,l_o)}$ is the LCAO coefficient of the orbital $l_o$ at the atomic site $a$ in the MO $j$. The Mulliken charge reflects the non-uniform delocalization of the MOs over all atomic valence orbitals in the $\sigma$-system. If we exclude the electron occupying the $p_z$ orbital, an isolated carbon (nitrogen) atom has $3(4)$ $\sigma$-like valence electrons. We denote the associated charge $Q_a^0$ the expected Mulliken charge. From the difference between the expected and the actual Mulliken charge one can deduce a local variation of the onsite energy for the valence electron in the $p_z$ orbital at site $a$:

$$\Delta a^e = \frac{2Q_a^M - Q_a^0}{Q_a^0 \epsilon}_a,$$

(7)

where $\epsilon_a$ is the dielectric constant of the underlying insulator. This variation is derived as follows: We assume $\epsilon_a^n$ to be the energy of a second shell orbital of a hydrogen-like atom with charge $Q_a^e$,

$$\epsilon_a^e = \left(\frac{Q_a^e}{\epsilon}\right)^2 = E^0_1(\epsilon),$$

(8)

where $E^0_1(\epsilon) = -13.6$ eV. The non-uniform delocalization of the $\sigma$-orbitals introduces a variation of the expected Mulliken charge $\delta_a = (Q_a^M - Q_a^0)$ and thus a screening of $Q_a^e$:

$$E^0_2 \left(Q_a^e + \delta_a\right)_{a} - E^0_2(Q_a^e) \approx 2E^0_1(\epsilon) \frac{Q_a^e}{2\epsilon^2\epsilon_a} \delta_a$$

$$= 2 \frac{Q_a^M - Q_a^0}{Q_a^e} \epsilon_a^e.$$

(9)

Note that the variation of the charge has been screened by the underlying insulator. Using these energy corrections, we can establish an effective Hamiltonian for the $\pi$-system:

$$H^e_{\pi} = \sum_a \left(\epsilon^e_a + \Delta a^e\right) d^e_a d^e_a.$$

(11)

Diagonalizing this effective Hamiltonian yields the MOs of the $\pi$-system:

$$\langle r | J \sigma \rangle = \sum_a c_{aJ} \langle r | \sigma \rangle = \sum_a c_{aJ} p_a(r - r_a) u_a,$$

(12)

where $\epsilon_j$ is the energy of the MO $j$ and $\langle r | \sigma \rangle$ denotes a $p_z$-orbital with spinor component $u_a$ centered at the atomic site $r_a$,

$$p_a(r - r_a) = N_a(z - z_a) e^{-\frac{Q_a^M + \delta_a}{2\epsilon_a^e}(r - r_a)},$$

(13)

with normalization $N_a$ and $\alpha_0$ being Bohr’s radius. The tunneling region between the substrate and the molecule is modelled as a one-dimensional potential barrier. Due to the $z$-localization of the molecular orbitals one can prove that for the substrate tunneling amplitudes it holds [25]:

$$t^S_{kJ} = \epsilon_j \langle \mathbf{S} k | \sigma \rangle = \epsilon_j \sum_a c_{aJ} \langle \mathbf{S} k | \sigma \rangle,$$

(14)

where $\langle \mathbf{S} k | \sigma \rangle$ is an eigenstate of the substrate Hamiltonian. The latter is modelled as a quantum well, only confined in $z$-direction, see Fig. 1. A product ansatz for the substrate wavefunction yields plane waves in the $xy$-plane and the solution of a one-dimensional finite potential well in $z$-direction:

$$\langle r | \mathbf{S} k | \sigma \rangle = \frac{1}{\sqrt{S}} e^{ik_x x + ik_y y} \psi_{k}(z) u_a,$$

(15)

with $u_a$ being its spinor part and $S$ the surface area of the substrate. The wavefunction in $z$-direction reads

$$\psi_{k}(z) = \Omega \left\{ \begin{array}{ll} -\sin(k_z z_0) & z < z_0, \\
\cos(k_z z) - \frac{k_z}{k} \sin(k_z z), & z_0 \leq z \leq 0, \\
e^{-|k_z|z} & z > 0. \end{array} \right.$$}

(16)

For the wavevectors, we have $k^2_{\perp \perp} = \frac{2m}{\hbar^2} e_{i y z}$ and $k^2 = \frac{2m}{\hbar^2} (\epsilon^b_i + \phi^b_i - \epsilon_i)$ for the decay constant of the evanescent parts of the piecewise-defined wavefunction.

Consequently, the matrix element between substrate wavefunction and a $p_z$ orbital in Eq. (14),

$$\langle \mathbf{S} k | \sigma \rangle = \int d^3r e^{-ik_x x -ik_y y} \psi_{k}(z) p_z(r - r_a),$$

(17)

can be calculated as

$$\langle \mathbf{S} k | \sigma \rangle = V_a(k_z, k_1, \kappa) e^{-ik_z r_a},$$

(18)

where the scalar product $k_\| \cdot r_a = k_x x_a + k_y y_a$ results from the shifting of the integrand in Eq. (17) by $+r_a$ and the function $V_a(k_z, k_1, \kappa)$, equivalent to $O_\perp(k)$ in Ref. [25], condenses the results of the integration. Ultimately, the tunneling amplitudes for the substrate read:

$$t^S_{kJ} = \epsilon_j \sum a c_{aJ} V_a(k_z, k_1, \kappa) e^{-ik_z r_a}.$$

(19)

For an even more detailed description of the derivation of the eigenstates of the substrate Hamiltonian and the calculation of the tunneling amplitudes for the substrate, we refer to Refs. [25, 26], respectively.

For the derivation of the tip tunneling amplitudes, we follow in this paper the derivation proposed in Ref. [1] rather
than the one in Ref. [26]. The advantage of this approach is that it is independent of the explicit form of the wavefunction inside the tip; it rather models the exponentially decaying part of the tip wavefunction and allows to consider different symmetries of tip wavefunctions, which are reflected in the form of their vacuum tails. It is based on Bardeen’s tunneling theory [2], which states that a tunneling matrix element between two wavefunctions \( \chi \) and \( \psi \) living in two different spatial regions can be represented by the integral

\[
M(\chi, \psi) = -\frac{\hbar^2}{2m} \int_{\Sigma} dS (\chi^{*} \nabla \psi - \psi^{*} \nabla \chi),
\]

(20)

where \( \Sigma \) is the separation surface of the two regions. Following Ref. [1], we write the wavefunction of the tip \( \chi_{l}(r) \) in a separation ansatz as a linear combination of real-valued spherical harmonics (cubic harmonics) \( Y_{l}(\theta, \phi) \) and spherical modified Bessel functions of the third kind \( k_{l}(\kappa r) \) [40]:

\[
\begin{align*}
\chi_{l}(r) &= \sum_{\kappa} C_{l\kappa} \chi_{l\kappa}(r), \\
\chi_{l\kappa}(r) &= N_{l\kappa} k_{l}(\kappa r) Y_{l}(\theta, \phi),
\end{align*}
\]

(21)

(22)

where \( \kappa = \sqrt{\frac{2m}{\hbar^2} (\epsilon_{l}^{2} + \phi_{l}^{2} - \epsilon_{k})} \), \( \rho = |r - r_{tip}| \). The \( C_{l\kappa} \) are dimensionless mixing coefficients and the \( N_{l\kappa} \) are ensuring that the resulting tunneling matrix element has the right dimension of energy. They are calculated using a cutoff of \( \kappa^{-1} \) for the lower integration limit, since the \( k_{l}(x) \) are not regular at \( x = 0 \) for \( l > 1 \). In the present work we are considering an idealized choice of the coefficients \( C_{l\kappa} \), restricting to pure s, pure p, or equally mixed s and p states. In order to better describe realistic tips the \( C_{l\kappa} \) can be determined from first principle calculations, following, e.g., the lines of Ref. [41].

By using the recurrence relations of the spherical modified Bessel functions and relating \( k_{l}(\kappa r) \) to the Green’s function of the spherical Helmholtz equation, Ref. [1] arrives at his “derivative rule,” stating that a tunneling amplitude involving tip states with symmetries different from s-wave symmetries can be related to the respective spatial derivatives of the sample wavefunction, evaluated at the position of the tip. Finally, by inserting Eq. (22) into Eq. (20) and following the procedure in Ref. [1], the tunneling amplitudes for the tip are obtained as:

\[
\begin{align*}
\tau_{l\kappa} &\equiv \sum_{\ell} C_{l\ell} M_{\ell\kappa}^{\ell} \equiv \sum_{\ell} C_{l\ell} M(\chi_{\ell\kappa}^{*}, \psi_{\ell}),
\end{align*}
\]

(23)

Tunneling amplitudes \( M_{\ell\kappa}^{\ell} \) for s states (\( l = 0 \)), p states (\( l = 1 \)), and d states (\( l = 2 \)) are listed in Table 1.

The dynamics of our system is calculated using the reduced density matrix approach [20]. We give in this work only a short overview over the derivation of the equation of motion for the reduced density matrix (RDM). A more detailed discussion can be found for example in Refs. [23–25]. The starting point is the density matrix of the complete system in the interaction picture. Its time evolution is described by the Liouville–von Neumann equation,

\[
\frac{i\hbar}{\frac{d}{dt}} = [H_{\text{run}}^{\ell}(t), \rho^{\ell}(t)]
\]

(24)

with the tunneling Hamiltonian acting as a perturbation. Eq. (24) has the formal solution

\[
\rho^{\ell}(t) = \rho^{\ell}(t_{0}) - \frac{i}{\hbar} \int_{t_{0}}^{t} dt_{1} [H_{\text{run}}^{\ell}(t_{1}), \rho^{\ell}(t_{1})].
\]

(25)

By reinserting Eq. (25) into Eq. (24) and tracing out the degrees of freedom of the substrate and the tip, we obtain the generalized master equation:

\[
\dot{\rho}_{\text{loc}}^{\ell}(t) = -\frac{i}{\hbar} \text{tr}_{S,T} \left\{ [H_{\text{run}}^{\ell}(t), \rho^{\ell}(t_{0})] \right\} + \left( \frac{i}{\hbar} \right)^{2} \int_{t_{0}}^{t} dt_{1} \text{tr}_{S,T} \left\{ [H_{\text{run}}^{\ell}(t_{1}), [H_{\text{run}}^{\ell}(t_{1}), \rho^{\ell}(t_{1})]] \right\},
\]

(26)

Table 1: Tunneling matrix elements for the tip for \( l = 0 \) (s state), \( l = 1 \) (p states), and \( l = 2 \) (d states).

<table>
<thead>
<tr>
<th>Tip state (l( \ell ))</th>
<th>Tunneling amplitude ( M_{\ell\kappa}^{\ell} )</th>
<th>Tip state (l( \ell ))</th>
<th>Tunneling amplitude ( M_{\ell\kappa}^{\ell} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>( \frac{2\pi \hbar^{2} C_{s}}{m_{s}} ) ( \psi(r_{\text{tip}}) )</td>
<td>d( \ell )</td>
<td>( \frac{2\pi \hbar^{2} C_{d\ell}}{m_{d\ell}} ) ( \frac{\Theta_{d\ell}}{2} \frac{\delta^{2}}{\delta r_{\text{tip}}^{2}} \psi(r_{\text{tip}}) )</td>
</tr>
<tr>
<td>( p_{\ell} )</td>
<td>( \frac{2\pi \hbar^{2} C_{p\ell}}{m_{p\ell}} ) ( \frac{\partial}{\partial r_{\text{tip}}} \psi(r_{\text{tip}}) )</td>
<td>d( \ell )</td>
<td>( \frac{2\pi \hbar^{2} C_{d\ell}}{m_{d\ell}} ) ( \frac{\Theta_{d\ell}}{2} \frac{\delta^{2}}{\delta r_{\text{tip}}^{2}} \psi(r_{\text{tip}}) )</td>
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<td>( \frac{2\pi \hbar^{2} C_{d\ell}}{m_{d\ell}} ) ( \frac{\Theta_{d\ell}}{2} \frac{\delta^{2}}{\delta r_{\text{tip}}^{2}} \psi(r_{\text{tip}}) )</td>
</tr>
</tbody>
</table>
which describes the time evolution of the RDM up to second order in the tunneling Hamiltonian. In the secular approximation, after retransforming the reduced density matrix to the Schrödinger picture we project it onto subblocks of particle number \( N \) and energy \( E \) as

\[
\rho^{\text{NE}} = \mathcal{P}_{\text{NE}} \rho_{\text{red}}^\text{S} \mathcal{P}_{\text{NE}},
\]

(27)

where we used the projection operator

\[
\mathcal{P}_{\text{NE}} = \sum_j |NE_j\rangle \langle NE_j|.
\]

(28)

Equation (26) finally becomes:

\[
\dot{\rho}^{\text{NE}} = -\sum_{\eta} \sum_{i,j} \sum_{E'} \left\{ \Gamma_{ij}^{+} (E - E') \mathcal{P}_{\text{NE}} d_{i}^{\dagger} \mathcal{P}_{N+1E} d_{j}^{\dagger} \rho^{\text{NE}} + \Gamma_{ij}^{-} (E - E') \mathcal{P}_{\text{NE}} d_{i}^{\dagger} \mathcal{P}_{N-1E} d_{j} \rho^{\text{NE}} - \Gamma_{ij}^{-} (E - E') \mathcal{P}_{\text{NE}} d_{i} \mathcal{P}_{N+1E} d_{j}^{\dagger} \rho^{\text{NE}} - \Gamma_{ij}^{+} (E - E') \mathcal{P}_{\text{NE}} d_{i} \mathcal{P}_{N-1E} d_{j}^{\dagger} \rho^{\text{NE}} \right\}. \]

(29)

Furthermore, we restrict our transport calculations to the many-body ground states of the molecule. The rate \( \Gamma_{ij}^{\pm} (\Delta E) \) in Eq. (29) is given by

\[
\Gamma_{ij}^{\pm} (\Delta E) = \frac{2\pi}{h} \sum_{k} \left( f_{i}^{\pm}(\epsilon_{k}) \right)^{\dagger} f_{j}^{\pm}(\epsilon_{k}) \delta(\epsilon_{k} - \Delta E),
\]

(30)

where \( f_{i}^{\pm}(\epsilon_{k}) \) is the Fermi distribution of an electron in lead \( \eta = (S, T) \) with chemical potentials \( \mu_{\eta} = -\phi_{0}^{\eta} + ceV_{h} \), \( \mu_{S} = -\phi_{0}^{S} - (1-c)eV_{h} \) and \( f_{i}^{\pm}(\epsilon_{k}) = 1 - f_{i}^{\pm}(\epsilon_{k}) \). Note that in STM setups there is an asymmetric bias drop \( c \) across the junction.

Its value can be estimated as follows: Let us consider an empty capacitor (substrate–tip) with capacitance \( C_{0} \). After replacing half of the vacuum inside the capacitor by a dielectric with relative permittivity \( \epsilon_{i} \) (substrate + insulating layer – tip), the effective capacitance of this system then reads \( C_{\text{eff}} = \frac{C_{0} \epsilon_{i}}{1 + \epsilon_{i}} \), yielding the parameter for the bias drop as \( c = \frac{C_{\text{eff}}}{C_{0}} = \frac{\epsilon_{i}}{1 + \epsilon_{i}} \). This estimation relies on the assumption of equal tip–molecule and molecule–substrate distances. They are comparable in typical STM setups with insulating films. Taking the relative permittivity of NaCl \( \epsilon_{i}^{\text{NaCl}} = 5.92 \) [42] yields \( c = 0.86 \). At present we neglect a possible dependence of the bias drop on the tip and substrate workfunction. We believe that this effect would be captured by a self-consistent solution of the Poisson equations for the junction that goes beyond the scope of this publication.

Equation (29) can be put in a shorter form,

\[
\dot{\rho}_{\text{red}} = \mathcal{L} \rho_{\text{red}}.
\]

(31)

The operator \( \mathcal{L} \) is called the Liouvillian of the system. We calculate the stationary solution \( \rho_{\text{stat}}^{\text{red}} \) which is given by the nullspace of \( \mathcal{L} \). Ultimately, the stationary current through contact \( \eta \) is calculated as

\[
\langle I_{\eta} \rangle = \text{tr}_{\text{sys}} \left\{ \mathcal{L} \rho_{\text{stat}}^{\text{red}} \right\},
\]

(32)

where the current operator \( I_{\eta} \) can be obtained from the time-derivative of the average charge on the system and is defined as [25, 26]:

\[
I_{\eta} = e \sum_{i,j} \sum_{N,E,E'} \mathcal{P}_{\text{NE}} \left\{ d_{i}^{\dagger} \mathcal{P}_{N+1E} d_{j}^{\dagger} \Gamma_{ij}^{\eta+} (E' - E) - d_{i}^{\dagger} \mathcal{P}_{N-1E} d_{j} \Gamma_{ij}^{\eta-} (E' - E') \right\} \mathcal{P}_{\text{NE}}.
\]

(33)

### 3 Results

In all calculations we used a substrate–molecule distance of \( d = 7 \, \text{Å} \) and the workfunctions of the substrate and the tip were chosen to be equal: \( \phi_{0}^{S} = \phi_{0}^{T} = -\mu_{G} \), see also Fig. 1. In Fig. 2, we show the \( I-V \) characteristics and a stability diagram of H₂Pc. From Fig. 2a, we are able to inhere the state of the system according to the values of the workfunction and the bias voltages. In analogy with stability diagrams associated to single electron transistors, what we see in the central part of this figure is a Coulomb diamond. Varying the workfunction acts as ramping an effective gate voltage. Transitions occur if the chemical potential of the substrate \( \mu_{S} = \mu_{G} - (1-c)eV_{h} \) or the chemical potential of the tip \( \mu_{T} = \mu_{G} + ceV_{h} \) matches the chemical potential of the molecule \( \mu_{N} = E_{N} - E_{N-1}. \) At zero bias, going left through the diamonds increases the particle number in the system, while going right decreases it. Due to the asymmetric bias drop \( c \), the Coulomb diamond is tilted. Its steeper borders mark transitions where the chemical potential of the substrate aligns with the chemical potential of the system, while its flatter borders indicate a resonance with the chemical potential of the tip.

The bias trace in Fig. 2b, taken at \( \mu_{G} = -2.9 \, \text{eV} \), shows two resonances at \( V_{h} = 0.13 \, \text{V} \) and \( V_{h} = -0.8 \, \text{V} \). The corresponding constant-height STM images in both cases resemble the LUMO orbital of H₂Pc. The reason for this is the transition from an \( N \) to an \( N+1 \)-particle state (see Fig. 2a), which is mediated by the LUMO single particle MO. The \( I-V \) characteristic in Fig. 2c corresponds instead to \( \mu_{G} = -4 \, \text{eV} \). The constant-height STM images corresponding to the two resonances now resemble different orbitals. The current map at positive bias still reflects the LUMO orbital of H₂Pc, which is consistent with the corresponding \( N-1 \) to \( N \) transition. This regime, where there is an anionic resonance at positive bias and a cationic resonance at negative bias is usually the most common in STM experiments with molecules on thin insulating films [17, 18]. In the following we will discuss the influence of different tip symmetries on the STM topography of H₂Pc.
Figure 2 Stability diagram (a) and $I$–$V$ characteristics (b, c) for H$_2$Pc on a thin insulating film of thickness $d = 7 \text{ Å}$ and a tip height of $4.3 \text{ Å}$. In the central region in panel a transport is blocked due to Coulomb blockade and the molecule is neutral, with $N = 42$ electrons populating the $\pi$-system. The current traces shown in panels b and c correspond to the two dashed lines in panel a. The small insets show constant-height STM images computed at the bias voltage of the respective resonance, indicated by the arrows.

with the workfunctions of the tip and the substrate chosen to be $\phi_T^0 = \phi_S^0 = -\mu_G = 4 \text{ eV}$.

For the s-wave tip symmetry the recorded constant-height STM images, Fig. 3a and d, are showing the characteristic patterns of nodal planes and orbital lobes of the corresponding MOs.

A striking difference to the STM images with the s-wave tip can be seen in Fig. 3b and e, where constant-height STM

Figure 3 Constant-height STM images of H$_2$Pc for different tip configurations at a tip-sample distance of $5 \text{ Å}$ and a thickness of the insulating layer $d = 7 \text{ Å}$. Panels a–c show current maps recorded at the cationic resonance at $V_b = -1.1 \text{ V}$, while panels d–f show current maps recorded at the anionic resonance at $V_b = 1.4 \text{ V}$. The white bar indicates a length of $5 \text{ Å}$.
images are shown for a tip with $p_z$ and $p_y$ symmetry. The nodal plane patterns of the MOs disappeared; instead the current now has maxima and minima at the positions of the nodal planes and of the orbital lobes, respectively. By considering the tunneling matrix elements as the derivatives of the molecular wavefunction in the $x$- and $y$-directions, this result is not surprising. However, as put forward in Ref. [19], there exists a nice empirical explanation of these findings, namely that if the tip is directly placed above a nodal plane, the contributions of the $p_z$-orbital of the molecule, the contributions of the $p_y$-orbital in the tip are cancelling each other due to their phases, differing in their signs. By placing the tip above a nodal plane, that is between two $p_z$ orbitals which differ in their signs, there is no such cancellation of the contributions of the $p_y$-orbital in the tip and tunneling is occurring.

Finally, in Fig. 3c and f we show the results of a simulated mixed $s$–$p$ wave tip, which we modeled as an equally weighted linear combination of $s$, $p_z$, and $p_y$ orbitals. They show the non-uniform competition of the contributions of the $s$ and the $p$ orbitals in the tip. In the inner parts of the molecule there are still maxima in the current occurring at the positions of the nodal planes. In the outer parts, however, the contribution of the $s$-wave tip state outweighs the $p$-wave contribution, and there are maxima at orbital lobes. Additionally, in contrast to Fig. 3b and e, the overall image appears more smeared out, what also can be attributed to the $s$-wave part of the tip state.

4 Conclusions In this work we have presented a semi-quantitative transport theory for STM-setups involving π-conjugated molecules on thin insulating films. To this end we derived tunneling matrix elements that account for the conditions under which tunneling between the molecule and the contacts takes place. For the substrate we started from a microscopic point of view [26], using the solutions of a Schrödinger equation for a potential well in the $z$-direction. For the tunneling matrix elements of the tip we used the approach in Ref. [1], which only considers the shape of the tip wave function in the vacuum between tip and sample, but allows for the inclusion of spatially different tip states.

Finally, we derived the generalized master equation for the reduced density matrix in secular approximation with the tunneling Hamiltonian treated in second order. The current through the system was calculated using the stationary solution for the reduced density matrix.

In order to model the investigated molecule we used the Slater–Koster LCAO approach [28] to get its single-particle eigenstates and a constant-interaction model to calculate the energies of the many-particle ground states of the molecule.

We presented our numerical calculations for the case of hydrogen phthalocyanine. As in a recent experimental work [19], which addressed the same question, we confirm that different tip symmetries have strong influence on the topography of STM images.

All in all we showed that our formalism is able to mirror experimental findings quite well, despite the limitations induced by our applied approximations. A natural improvement of our model is a better treatment of screening and image charge effects induced by the contacts, as they could be responsible for negative differential conductance and the breaking of molecular symmetries [36]. Also the role of vibronic excitations would be an interesting topic to address. For example, it has been experimentally shown in Ref. [18] for the case of a naphthalocyanine that vibrations can be crucial in the current-induced switching of the positions of the central hydrogen atoms of the molecule.

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References