

Theoretical framework for the interpretation of STM images of adsorbates

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A theoretical formalism for the interpretation of STM images of adsorbates is developed by approaching the calculation of the observed current as a transport problem in quantum statistical mechanics. The STM configuration is treated as a system of three groups of states – the substrate, the adsorbate and the tip – in contact with a thermal reservoir, with which it exchanges energy. A new definition of current is introduced, and shown to be related to that given in the traditional transfer Hamiltonian approach. The transport instrument used for the description is the stochastic Liouville equation, known to have the advantage of allowing the incorporation of thermal effects as well as arbitrary degree of coherence in the quantum transport. Some preliminary calculations of STM images of simple adsorbate models are presented.

1. Introduction

Since the invention of the scanning tunneling microscopy (STM) [1] a large number of high-resolution images of atoms [2,3] and molecules [4–8] adsorbed on conductive substrates have been obtained. Despite the abundance of data, the mechanism of tunneling through an adsorbate placed in the gap remains unclear, although the relevant questions have been approached by several groups in the past few years [9–16]. The commonly accepted formalism for the interpretation of STM images is the Tersoff–Hamann theory [17], which relates the tunneling current to the substrate local density of states, evaluated at the tip position, and is based on first-order time-dependent perturbation theory [18]. STM images of adatoms have been simulated [9–13] within the transfer Hamiltonian framework [18], but several authors [14,19–23] have pointed out the inadequacy of this perturbative approach to the STM current, proposing current definitions which go beyond

the perturbative regime. Traditional approaches appear to invoke several conditions, among them interaction weak enough to be treated as a perturbation, temperature which is not high enough to complicate simple quantum mechanical transfer considerations among sharp levels, and incoherence in the transfer which allows use of the Fermi golden rule. We have felt that it might be useful to have a theoretical expression for the STM current valid beyond the above restrictions. Such an expression could lead to an understanding of how the unperturbed levels and eigenstates of the eigenstates of the adsorbate, often out of resonance with respect to the Fermi level of the electrodes, participate in the image. The understanding could, in its turn, help realize the potential of STM as a probe to measure the local properties of the adsorbates from their images. The construction of a formalism capable of treating strong transfer interactions would be invaluable in the analysis of chemisorption or strong physical adsorption. Obviously, it would also be

of considerable practical interest to incorporate into the formalism the ability to deal with arbitrary degree of coherence in electron transport, and to account explicitly for the interactions of the system with a thermal bath at arbitrary temperatures.

With these ideas in mind, we have begun the construction of a formalism for the interpretation of STM images of adsorbates. This paper is a brief report of our preliminary results. Our formalism contains an alternate definition of the STM current, which can be shown to reduce, in appropriate limits, to the usual definition involving transition rates between tip and substrate levels. The formulation is designed to be used along with transport equations of arbitrary degree of sophistication (e.g. master equations, density matrix equations) but, for the presentation in the present paper, utilizes the stochastic Liouville equation (SLE) [24–31] to describe the electron transfer in the STM experiment. It is thereby able to treat both the complexity of large adsorbate molecules and interacting reservoirs; and the quantum nature of the electron motion. As inputs, it takes the Hamiltonian of the tip, the substrate and the adsorbate molecule, and, in its simplest form, analyzes the interaction of the reservoir via the introduction of a coherence damping rate, which can be treated as an adjustable parameter, and eventually eliminated by a set of independent measurements.

A central entity in our formalism is the propagator for electron motion within the tip–substrate–adsorbate system. The formalism is divided naturally into two parts: (i) the calculation of the propagators from the system Hamiltonian and the basic transport instrument, the SLE, and (ii) the acquisition of the current from the propagators. We comment on (i) in section 2 below, treat (ii) in section 3, and obtain and discuss STM images for simple systems in section 4.

2. Stochastic Liouville equation applied to STM

The natural starting point of most electron transfer calculations is the Schrödinger equation,

which may be written alternatively as the Von Neumann equation,

$$i\hbar \frac{\partial \rho}{\partial t} = [H, \rho], \quad (1)$$

for the density matrix ρ , the system Hamiltonian being H . The stochastic Liouville equation (SLE) is a generalization of eq. (1) to incorporate thermal balance effects and reservoir interactions, and, in its *simplest* form, is given by

$$i\hbar \frac{\partial \rho_{mn}}{\partial t} = [H, \rho - \rho^{\text{thermal}}]_{mn} - \alpha(1 - \delta_{mn})(\rho_{mn} - \rho_{mn}^{\text{thermal}}). \quad (2)$$

In (2), α is the coherence damping or dephasing rate (taken here to have a single value for simplicity) which, as a result of reservoir interactions, destroys off-diagonal elements of the density matrix in the relevant representation of states m, n , etc, and ρ^{thermal} is the thermal value of the density matrix. The most suitable choice for the m, n representation is that of localized (Wannier) states. As is well known [26,27], the simple form eq. (2) is an approximation whose range of validity is essentially the same as that of the Boltzmann equation under the relaxation time approximation. More elaborate forms of the SLE would represent α as an operator rather than a single c -number.

In the absence of dephasing, i.e. for $\alpha = 0$, the SLE describes purely coherent motion. It is then possible [28] to show that the SLE is equivalent to the generalized master equation (GME)

$$\frac{dP_m(t)}{dt} = \int_0^t ds \sum_n [W_{mn}^c(t-s)P_n(s) - W_{mn}^c(t-s)P_m(s)]. \quad (3)$$

The GME is characterized by its time non-local nature and governs, through the memory functions W_{mn}^c , the evolution of the probabilities P_m of the electron being in states m . In W_{mn}^c , the superscript c denotes that the motion is purely coherent. These coherent memory functions can be calculated from the Hamiltonian and system details. The procedure and the technical informa-

tion may be found in several reviews by Kenkre [28,29] in the context of the transport of excitons in molecular crystals.

What makes the present calculational procedure possible is a simple prescription [28–30] which allows one to obtain W_{mn} , the memory functions in the presence of reservoir interactions, from W_{mn}^c , which are their counterpart in the absence of those interactions. For instance, at large temperatures, the SLE (2) is equivalent to the GME (3) with the replacement of W_{mn}^c by

$$W_{mn}(t) = W_{mn}^c(t) \exp(-\alpha t). \quad (4)$$

Space limitation prevents us from presenting the full details here. Suffice it to say that the procedure for calculating the propagators from the SLE is to convert the SLE to the GME, to obtain the memory functions, and to follow straightforward techniques detailed in refs. [28,29]. The propagators so obtained are denoted by $\Pi_{mn}(t)$, represent the probability that the electron is in state m at time t , given that it was in state n at time 0, and contain information of the Hamiltonian H of the tip–substrate–adsorbate system as well as of the reservoir interactions and temperature.

3. Calculation of the current from the propagators

To illustrate the method, let us consider each of the three parts of the STM system, viz. the tip, substrate and adsorbate molecule, to consist of a single state, which we denote by T, S, M, respectively. The states T and S exchange electrons with their respective reservoirs (the tip far from the apex and the substrate far from the STM junction). When the two reservoirs are held at a constant difference of potential, a driving agency is created, which forces the current through the system in the STM configuration. Let us denote by R_S and R_T the rates at which the electrons are depleted from the substrate and tip states, respectively, as a result of the driving agency.

The propagators $\Pi_{mn}(t)$, with m and n taking on the values T, S, M, describe the evolution of

the tip–substrate–adsorbate system if they constituted a closed system. It is then straightforward to write down a master equation for the probability evolution in the open system and to solve it in terms of the rates R and the probability propagators $\Pi_{mn}(t)$:

$$\tilde{P}_m(\epsilon) = \tilde{\eta}_m(\epsilon) + [\tilde{\Gamma}_{mT}(\epsilon) - \tilde{\Gamma}_{mS}(\epsilon)] R_S \tilde{P}_S(\epsilon). \quad (5)$$

Here and henceforth tildes denote Laplace transforms, ϵ is the Laplace variable, η is the homogeneous solution, i.e. the solution in the absence of the current-driving agency, and is given by

$$\eta_m(t) = \sum_n \Pi_{mn}(t) P_n(0). \quad (6)$$

Eq. (5) has been obtained under the assumption that the rate R_T for the electrons to leave the tip–substrate–adsorbate system into the circuit in a direction opposite to that imposed by the direction of the current is negligible in comparison to the rate R_S . The latter corresponds to the direction imposed by the current. At the end of this section, we shall relax this assumption and exhibit the full expressions involving R_T as well.

The current j is proportional to the product of the probability of the substrate state and the rate to leave the STM system from the substrate state. Eqs. (5) and (6) lead, therefore, to the following expression in the Laplace domain

$$\tilde{j}(\epsilon) = \frac{\tilde{\eta}_S(\epsilon)}{(1/R_S) + [\tilde{\Gamma}_{SS}(\epsilon) - \tilde{\Gamma}_{ST}(\epsilon)]}. \quad (7)$$

Here and henceforth we suppress all proportionality constants in the expressions for the current. By taking the limit $\epsilon \rightarrow 0$, and using an Abelian theorem, viz.

$$\lim_{\epsilon \rightarrow 0} \epsilon \tilde{f}(\epsilon) = \lim_{t \rightarrow \infty} f(t), \quad (8)$$

one can finally obtain our primary result for j , the steady-state current, in terms of the *thermal* pop-

ulation of the substrate state and the time integrals of the difference of the propagators:

$$j = \frac{P_S^{\text{thermal}}}{\int_0^\infty dt [\Pi_{SS}(t) - \Pi_{ST}(t)]}. \quad (9)$$

Here, P_S^{thermal} is the thermal population of the substrate in the closed tip–molecule–substrate system. In order to obtain the simple expression (9), we have made the further simplifying assumption that R_S is so large that its reciprocal may be neglected in the denominator of (9).

Under this simplifying assumption, the steady-state tunneling current depends only on the variables of the STM system. The time integral of the propagator contains all the information about the interactions between the sites, the nature of the system and the degree of coherence in the transport. Temperature effects enter through this term as well as through P_S^{thermal} .

It can be shown quite easily that, if the system considered is a two-state system consisting of only the tip and the substrate, and a simple master equation is assumed to govern the evolution, one gets

$$\Pi_{SS}(t) - \Pi_{ST}(t) = \exp[-t(F_{ST} + F_{TS})], \quad (10)$$

$$P_S^{\text{thermal}} = F_{ST}/(F_{ST} + F_{TS}), \quad (11)$$

where the F 's are transition rates between the tip and the substrate. The substitution of (10) and (11) in (9) yields

$$j = F_{ST}, \quad (12)$$

which is the standard result that the current is given by the golden rule transition rate from the tip to the substrate.

Eq. (9) is our principal result. It goes beyond weak-coupling approximations and incorporates thermal effects and reservoir interactions. We have displayed its simplest form in (9). For completeness, we state here a more general form

which shows the explicit dependence of the current on the rates R_S and R_T :

$$j = \left(\sqrt{R_S/R_T} P_S^{\text{thermal}} - \sqrt{R_T/R_S} P_T^{\text{thermal}} \right) \times \left\{ \sqrt{R_S/R_T} \int_0^\infty dt [\Pi_{SS}(t) - \Pi_{ST}(t)] + \sqrt{R_T/R_S} \int_0^\infty dt [\Pi_{TT}(t) - \Pi_{TS}(t)] \right\}^{-1}. \quad (13)$$

4. Application of the formalism: calculation of STM images

Our scheme for the interpretation of STM images thus consists of eq. (9) or its general form (13) for the current, with propagators calculated as described in section 2. We have applied this scheme to obtain predicted images for given interactions and geometries in simple configurations. While it is straightforward to incorporate considerable detail and complexity into the formalism, we made the following simplifying assumptions. The matrix elements of the Hamiltonian of the STM system were taken to be given by

$$\begin{aligned} H_{mm} &= E_m, \\ H_{mn} &= U_{mn} \exp(-\kappa R_{mn}), \quad \text{for } m \neq n. \end{aligned} \quad (14)$$

Here, κ is the inverse half-decay length which we took to be the same for all pair interactions, viz. $\kappa = \sqrt{2\Phi}$, with $\Phi = 5$ eV, and R_{mn} measures the relevant distance, such as that between the tip and the adsorbate molecule or between the molecule and a part of the substrate. We took the substrate to consist of 10 sites over a length of 20 Å, obeying periodic boundary conditions, and the pre-exponential factor between any two substrate sites to be $U_{SS} = -0.01$ eV. We also took $U_{TS} = -0.01$ eV, the energies $E_T = E_S = 0$ eV, the setpoint current value to be 0.1 nA and the dephasing rate α to be given by a typical value 4×10^{-4} eV. We used the full expression (13) rather than the simplified form (9) for our calculations and took the ratio (R_S/R_T) to be given by $\exp(-V_{\text{tip}}/kT)$ where k is the Boltzmann con-

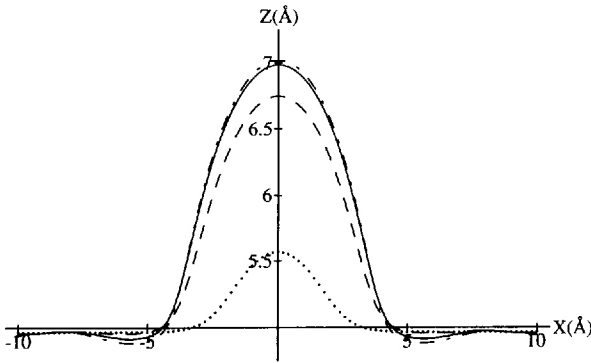


Fig. 1. STM constant-current profile in presence of an adsorbate M at $(0,0,2)$ Å, for different values of the interaction with both the electrodes: $U_{SM} = -0.001$ (dotted), -0.005 (dash-dotted), -0.01 (black), -0.02 (dashed) eV; $U_{TM} = U_{SM}$; $U_{SS} = -0.01$ eV; $U_{TS} = -0.01$ eV; $E_M = 0$, $I = 0.1$ nA; $V_{tip} = 0.02$ V.

stant, T is the temperature, taken to be 298 K, and V_{tip} is assumed to be 0.02 V. This expression for (R_S/R_T) can be justified on the basis of equilibrium arguments.

We have obtained a number of interesting results pertinent to situations involving energy mismatch between the molecule and the tip/substrate system on the basis of our theory. For reasons of space limitation we are unable to present them in this paper. In our illustration here we place a single level with $E_M = 0$ eV at

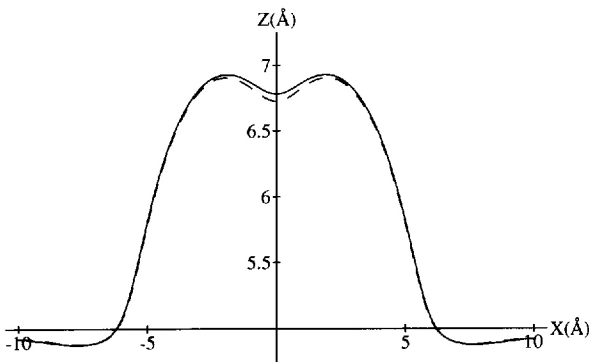


Fig. 2. Effect of the intramolecular interaction on the STM constant-current profile of a homogeneous dimer, lying flat on the substrate: M_1 at $(-2,0,2)$ Å, M_2 at $(2,0,2)$ Å; $U_{M_1M_2} = -0.01$ (black), 0.0 (dashed) eV; $U_{TM_1} = U_{TM_2} = U_{SM_1} = U_{SM_2} = -0.01$ eV; $U_{SS} = -0.01$ eV; $U_{TS} = -0.01$ eV; $E_{M_1} = E_{M_2} = 0$ eV; $I = 0.1$ nA; $V_{tip} = 0.02$ V.

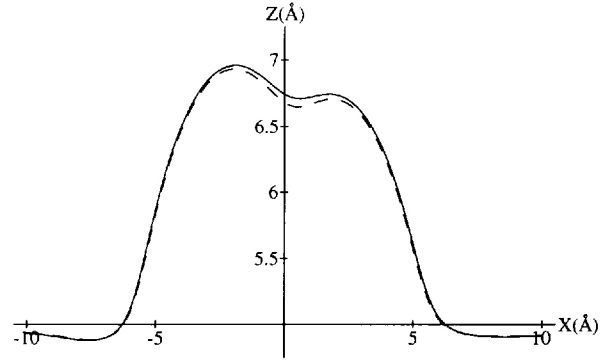


Fig. 3. Effect of the intramolecular interaction on the STM constant-current profile of a heterogeneous dimer, lying flat on the substrate: M_1 at $(-2,0,2)$ Å, M_2 at $(2,0,2)$ Å; $U_{M_1M_2} = -0.01$ (black), 0.0 (dashed) eV; $U_{TM_1} = U_{SM_1} = -0.01$ eV; $U_{TM_2} = U_{SM_2} = -0.005$ eV; $U_{SS} = -0.01$ eV; $U_{TS} = -0.01$ eV; $E_{M_1} = E_{M_2} = 0$ eV; $I = 0.1$ nA; $V_{tip} = 0.02$ V.

$(0,0,2)$ Å with respect to the substrate, and show the image in fig. 1. Each curve corresponds to a different value of $U_{TM} = U_{SM}$, which modulates the strength of the adsorption interaction with both the electrodes. The corrugation increases with the strength of the adsorption, but the maximum tends to an asymptotic finite value at high strength compared with the substrate-to-substrate matrix element. The topographical corrugation appears when $U_{SS} = U_{SM}$. The slight depressions shown to the sides at "strong" adsorption can be attributed to substrate finite-size effects.

In fig. 2 we show the constant-current profile of a homogeneous dimer lying flat on the substrate (call the two molecular states M_1 and M_2). The values of the parameters are $E_{M_1} = E_{M_2} = 0$ eV, M_1 at $(-2,0,2)$ Å and M_2 at $(+2,0,2)$ Å, $U_{SM_1} = U_{SM_2} = U_{TM_1} = U_{TM_2} = -0.01$ eV. The STM image of this configuration resolves the depression in the middle, but no appreciable difference turns out between the case with the interacting adsorbate sites (black line) and the one with non-interacting ones (dashed).

In fig. 3 is shown the constant-current profile of the same configuration as in fig. 2, but with M_2 in this case weakly interacting with the electrodes ($U_{SM_2} = U_{TM_2} = -0.005$ eV). The asymmetry of the heterogeneous dimer is apparent from the right shoulder, and it would be misleading to

attribute it to surface topography, as has been often pointed out in the past [10,17].

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