Theoretical approach to the scanning tunneling microscope

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Within a one-electron approach, based on a Green's-function formalism, a nonperturbative expression for the tunneling current is obtained and used to discuss which spectroscopic information may be deduced from a scanning-tunneling-microscope experiment. It is shown up to which limits the voltage dependence of the tunneling current reproduces the local density of states at the surface, and how the reflection coefficients of the electronic waves at the surface may modify it.

I. INTRODUCTION

During the past few years, it has become obvious that the scanning tunneling microscope (STM) is a very powerful tool to obtain local structural information on metallic or semiconducting surfaces. Moreover its "spectroscopic mode," in which the tunneling current J is recorded as a function of the applied bias V, gives information on the local electronic structure of surfaces. It is widely accepted that the dJ/dV versus V curves reproduce roughly the local density of states of the surface in the neighborhood of the Fermi level. This equivalence was demonstrated theoretically by a perturbative method[1,2] based on the transfer Hamiltonian approach,[3] and experimentally[4] by comparing the spectroscopic data of a Si(111) (7×7) structure with a photoemission spectrum. It is obviously highly desirable to understand whether such correspondence is quantitatively correct or whether it just represents a qualitative guide. In the second hypothesis, care will be required in the analysis of STM spectroscopic data to extract reliable detailed information upon the surface (discrimination between different kinds of atoms, discrimination between neighboring models of surface structure, etc.).

It is the purpose of this paper to present a method of calculation of the tunneling current which goes beyond the perturbation approximation. This method relies on only two assumptions: (a) it is possible to find a satisfactory effective one-electron potential describing the behavior of tunneling electrons, and (b) the system may be shared into three regions, such that the left and the right regions are unchanged compared to the free-electrode configurations (see Fig. 1 below). Aside from these two points, the method, developed in Sec. II, is exact. It yields an expression for the tunneling current (Sec. III) in terms of two quantities which characterize the free electrodes (contrary to other related approaches[5-7]) and in terms of a transmission coefficient through the vacuum barrier. This latter contains all multiple events in the barrier and, consequently, remains valid both in the limit of vanishing barrier width, and in the Fowler-Nordheim regime. The quantities which characterize the free electrodes are studied in Sec. IV and we discuss in detail the relationship between them and the local density of states at the surface. The calculation details can be found in Appendices A–D. Various outcomes of this work have already been published: in Ref. 8 we have used this method to explore several one-dimensional models; Ref. 9 was devoted to the question of the observability of surface states in the STM spectroscopic mode; in Ref. 10 we showed how it is possible to rederive the transfer Hamiltonian approach from the Green's-function formalism, thanks to a perturbation approximation. Compared to these papers, the present manuscript gives for the first time the steps of the calculation; it discusses the transmission through the vacuum barrier; the expression for the Logarithmic derivative of the Green's function X in one dimension given in Sec. IV is an analytic generalization of the work of Ref. 8 and is precisely compared to the surface density of states. Finally, we present a possible way for calculating X in a realistic three-dimensional case.

II. DESCRIPTION OF THE METHOD

We present in this section the application of a Green's-function formalism to the calculation of the tunneling current. This formalism, although heavy to handle, has several advantages compared to a direct manipulation of the wave functions: first, quantities of physical interest such as the electronic current, or the density of states, are easily expressed, and, second, it presents a good starting point for later introduction of many-body effects.

To calculate a current, we need two kinds of Green's functions: first the advanced or retarded Green's functions are required, which in terms of stationary states ψ_ν of energy E_ν read

$$g^{a,r}(\mathbf{x},\mathbf{x}')=\sum_\nu \psi_\nu(\mathbf{x})\psi_\nu^*(\mathbf{x}')/(\omega-E_\nu\pm i\eta) \tag{1}$$

(the + and − signs refer, respectively, to the superscripts a and r); second, we need the g^+ Green's function discussed by Keldysh[11] for out-of-equilibrium situations and which, here, contains information on the occupied states of the system:

$$g^+(\mathbf{x},\mathbf{x}')=2i\pi\sum_{\nu_{\rm occ}} \psi_\nu(\mathbf{x})\psi_\nu^*(\mathbf{x}')\delta(\omega-E_\nu)\ . \tag{2}$$

In both expression and throughout this paper we use Green's functions which are Fourier transformed with respect to time variables.

Our aim is to calculate the G^+ Green's function of the system (electrodes plus vacuum barrier) in a STM configuration (capital letters refer to the whole system) from which the current density may be derived:

$$\mathbf{J}(\mathbf{x})=\int d\omega \,\mathrm{Re}\nabla_x G^+(\mathbf{x},\mathbf{x}')\Big|_{\mathbf{x}'\to\mathbf{x}} . \tag{3}$$

$J(\mathbf{x})$ depends in a complex way upon various physical quantities such as the electronic structure of both electrodes, the applied bias, the thickness of the vacuum barrier, etc. In order to disentangle the different contributions, we divide the system into three regions, which, from left to right, describe the electrode I (region L), the vacuum barrier in the presence of the electric field (region M), and the electrode II (region R). The location of the surface S_1 and S_2 which limit these regions [see Fig. 1(a)] presents some difficulty. Actually, we wish that, on the left (right) of S_1 (S_2) the electrons experience the same potential as in the free electrode (we call free electrode or free surface, an electrode in contact with a semi-infinite vacuum medium). This is easily obtained if an abrupt potential discontinuity exists between the inner potential and the outside, but it is known that exchange and correlation effects soften the discontinuity, which makes the partitioning not so simple; for example, this latter might even become impossible if the electrodes come in close contact. It is clear that, in that last situation, our requirement is not fulfilled. Yet, we will discard these limiting cases, because they represent situations in which the electrodes are so much perturbed by each other that there is no hope to deduce information on the free electrodes from an STM measurement.

We introduce the three Green's functions g_{I}^a, g_{I}^r, g_{I}^+ of the free left electrode [associated with the potential depicted in Fig. 1(b)] and similar quantities with indexes II and III, respectively, for an infinite vacuum medium with the applied electric field, and for the free right electrode depicted in Fig. 1(c). In all the following we assume that these functions are known and we use them to evaluate the Green's functions G^a, G^r, G^+ of the whole STM system, and the tunneling current.

To do so, one recognizes that the behaviors of $G^{a,r}$ and $g_{\mathrm{I}}^{a,r}$ in region L are governed by the same differential equation (this was precisely our goal when we defined S_1): only the boundary conditions differ. The same can be said for $G^{a,r}$ and $g_{\mathrm{II}}^{a,r}$ in region M and for $G^{a,r}$ and $g_{\mathrm{III}}^{a,r}$ in region R, and the same remark applies to the g^+ Green's functions. Consequently, in perfect analogy with optics, the propagation of an electron in a given region can be analyzed as due to a primary source (δ function on the right-hand side of the Green's-function differential equation) plus secondary sources on the boundary surface(s). The mathematical transcription of this property leads to the matching equations. They may be found in Ref. 12 in the case of one boundary and in the Appendix A for the STM geometry. The matching equations present a different structure for advanced (or retarded) Green's functions and for the g^+ ones. We derived these latter from Keldysh's work.[11] Just to exemplify the procedure, we present here the equations for $G^u(\mathbf{x},\mathbf{x}')$ and $G^+(\mathbf{x},\mathbf{x}')$ when both x and x' belong to L ($u=a,r$) (atomic Rydberg units are used throughout):

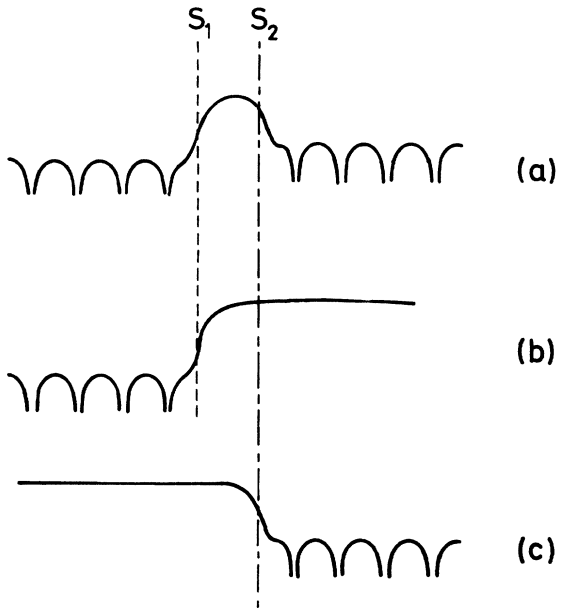

FIG. 1. Schematic representation of the electronic potential in the electrodes and the barrier: (a) STM configuration (called *whole* system in the text); (b) free left-electrode configuration. The boundary surface S_1 is chosen in such a way that for each point located on its left, the potentials in (a) and (b) are equal. On the right of S_1 for the free electrode, the vacuum extends to infinite. (c) Free right-electrode configuration; same considerations as in (b) with a mere interchange of left and right.

$$G^u(\mathbf{x},\mathbf{x}')=g_{\mathrm{I}}^u(\mathbf{x},\mathbf{x}')-\int_{S_1} d\mathbf{S}_1[\nabla g_{\mathrm{I}}^u(\mathbf{x}^-,\mathbf{x}_1)G^u(\mathbf{x}_1,\mathbf{x}')-g_{\mathrm{I}}^u(\mathbf{x},\mathbf{x}_1)\nabla G^u(\mathbf{x}_1,\mathbf{x}'^-)] , \tag{4}$$

$$G^+(\mathbf{x},\mathbf{x}')=g_{\mathrm{I}}^+(\mathbf{x},\mathbf{x}')-\int_{S_1} d\mathbf{S}_1[\nabla g_{\mathrm{I}}^a(\mathbf{x}^-,\mathbf{x}_1)G^+(\mathbf{x}_1,\mathbf{x}')-g_{\mathrm{I}}^a(\mathbf{x},\mathbf{x}_1)\nabla G^+(\mathbf{x}_1,\mathbf{x}')]$$
$$+\int_{S_1} d\mathbf{S}_1[g_{\mathrm{I}}^+(\mathbf{x},\mathbf{x}_1)\nabla G^r(\mathbf{x}_1,\mathbf{x}'^-)-G^r(\mathbf{x}_1,\mathbf{x}')\nabla g_{\mathrm{I}}^+(\mathbf{x},\mathbf{x}_1)] . \tag{5}$$

Unless otherwise specified, the gradients refer to the coordinate on which the integration is performed, and we have specified the positions of $\mathbf{x}$ and $\mathbf{x}'$ relative to the matching surface by a superscript: $-$ for left and $+$ for right. This stems for the existence of a discontinuity of the gradient of the advanced and retarded Green's functions when $\mathbf{x}'\to\mathbf{x}$, arising from the presence of the source term $\delta(\mathbf{x}-\mathbf{x}')$ on the right-hand side of their differential equation. It is unnecessary in Eq. (5) since no source term exists for g^+.

The second system, Eq. (5), may be written under a more tractable form, by taking advantage of the relationships (n =I,III)

$$g_n^+(\mathbf{x},\mathbf{x}')=[g_n^r(\mathbf{x},\mathbf{x}')-g_n^a(\mathbf{x},\mathbf{x}')]\Theta(\mu_n-\omega) \ . \tag{6}$$

$\mu_{\rm I}$ and $\mu_{\rm III}$ represent the Fermi levels of the systems I and III in the presence of the applied bias V, and the Heaviside function Θ [$\Theta(x)=0$ if $x<0$; $\Theta(x)=1$ if $x>0$] tells that empty states of energies ω larger than μ do not contribute to g^+ at zero temperature. Consequently ($x\in L, x'\in L$)

$$G^+(\mathbf{x},\mathbf{x}')+\int_{S_1} d\mathbf{S}_1[G^+(\mathbf{x}_1,\mathbf{x}')\nabla g_{\rm I}^a(\mathbf{x}^-,\mathbf{x}_1)-g_{\rm I}^a(\mathbf{x},\mathbf{x}_1)\nabla G^+(\mathbf{x}_1,\mathbf{x}')]$$
$$=-2i\Theta(\mu_{\rm I}-\omega)\left[\mathrm{Im}g_{\rm I}^a(\mathbf{x},\mathbf{x}')+\int_{S_1} d\mathbf{S}_1[\mathrm{Im}g_{\rm I}^a(\mathbf{x},\mathbf{x}_1)\nabla G^r(\mathbf{x}_1,\mathbf{x}'^-)-G^r(\mathbf{x}_1,\mathbf{x}')\mathrm{Im}\nabla g_{\rm I}^a(\mathbf{x},\mathbf{x}_1)]\right] . \tag{7}$$

The resulting system is quite general and, up to now, we have only assumed that (i) there exists a one-electron differential equation governing the behavior of the system, and (ii) it is possible to define the boundary surfaces S_1 and S_2. In addition, in the following, we will restrict ourselves to situations where there are no occupied states in region M so that $g_{\rm II}^+(\mathbf{x},\mathbf{x}')$ is identically equal to zero. We thus exclude from the present study the case of resonant tunneling.

The simultaneous resolution of the two sets of matching equations is given in Appendix B. We found it convenient to introduce an operator form of the Green's functions:

$$\langle x|G|x'\rangle=G(\mathbf{x},\mathbf{x}') \ ,$$

together with a symbolic notation for the integration on surfaces S_1 and S_2:

$$|1\rangle\langle 1|=\int_{S_1} d\mathbf{S}|x\rangle\langle x| \ ,$$
$$|2\rangle\langle 2|=\int_{S_2} d\mathbf{S}|x\rangle\langle x| \ . \tag{8}$$

We discuss the resulting expression for the tunneling current in the next section.

III. EXPRESSION OF THE TUNNELING CURRENT

In the absence of occupied states in the barrier, the total tunneling current reads

$$J=\int_{\mu_{\rm I}}^{\mu_{\rm III}} d\omega \mathrm{Tr}\langle 1|\mathrm{Im}X_{\rm I}^a|1'\rangle\langle 1'|G^a|2\rangle \times\langle 2|\mathrm{Im}X_{\rm III}^a|2'\rangle\langle 2'|G^r|1\rangle \ . \tag{9}$$

It involves an integration on energies, limited by the two Fermi levels of the electrodes (in the presence of the applied bias) and two integrations on each boundary. The interesting output of this approach is the natural factorization of the current into three parts, characterizing, respectively, (i) the left electrode in contact with the vacuum, (ii) the right electrode in contact with the vacuum, and (iii) the propagation through the barrier in the presence of the electrodes. We discuss now these different factors.

A. Logarithmic derivative of the Green's function

The electronic structure of the left (respectively right) free electrode appears in the tunneling current through the operator $X_{\rm I}^a$ ($X_{\rm III}^a$). In order to understand the meaning of this operator, we turn back to the matching equation (4) ($x\in L, x'\in L$):

$$\langle x|I+\nabla_2 g_{\rm I}|1\rangle\langle 1|G|x'\rangle=\langle x|g_{\rm I}|1\rangle\langle 1|I+\nabla_1 G|x'\rangle \ . \tag{10}$$

[We have suppressed the superscripts a or r, which should be the same for all Green's functions. I is the identity $\langle x|I|x'\rangle=\delta(\mathbf{x}-\mathbf{x}')$. We have added a subscript 1 or 2 to the gradients to specify relative to which coordinate the gradient should be performed, and we recall that the gradients are projected upon the normal to the boundary surface at the point under consideration.] We now introduce an "inverse" operator $\tilde{G}$ (relative to the integration on S_1) such that

$$\langle x|G|1\rangle\langle 1|\tilde{G}|x'\rangle=\delta(\mathbf{x}-\mathbf{x}') \tag{11}$$

for all $x\in S_1$ and $x'\in S_1$. Since

$$\langle x|I+\nabla_1 G|1\rangle\langle 1|\tilde{G}|x'\rangle=\langle x|\tilde{G}|1\rangle\langle 1|I+\nabla_2 G|x'\rangle \ , \tag{12}$$

we find that Eq. (4) has the form of a conservation relationship:

$$\langle x|\tilde{g}_{\rm I}|1\rangle\langle 1|I+\nabla_2 g_{\rm I}|x'\rangle=\langle x|\tilde{G}|1\rangle\langle 1|I+\nabla_2 G|x'\rangle \ . \tag{13}$$

The operators

$$X_{\rm I}=\tilde{g}_{\rm I}|1\rangle\langle 1|(I+\nabla_2 g_{\rm I}) \tag{14}$$

and

$$X=\tilde{G}|1\rangle\langle 1|(I+\nabla_2 G) \tag{15}$$

have the same matrix elements on S_1. They can be called "logarithmic derivatives of the Green's function" because in one dimension (S_1 being defined by x_1)

$$\langle x_1|X_{\rm I}|x_1\rangle=\frac{\left[1+\frac{dg_{\rm I}}{d2}(x_1^- x_1)\right]}{g_{\rm I}(x_1 x_1)}=\frac{\frac{dg_{\rm I}}{d2}(x_1^+ x_1)}{g_{\rm I}(x_1 x_1)} \ . \tag{16}$$

Equation (13) thus tells that the logarithmic derivative of a Green's function is conserved during a matching procedure, just as we know that the logarithmic derivative of a wave function is continuous at an interface. Further-

more, it is clear from our derivation that the operator X_I is independent on the value of the potential on the right of S_1. We could as well have introduced the Green's function g'_I for an electrode bound by infinite barrier on the right of S_1. A matching equation of the type of Eq. (4) would have then told us that $X_I \equiv X'_I$ on S_1. This property will be used in the discussion in Sec. IV.

To sum it up, we find that the operator X_I [Eq. (14)] contains all the information on the electronic structure of the left electrode relevant for the tunneling current. In Sec. IV, we will examine which states contribute to X_I, how it is related to the local density of states on S_1, etc.

B. Transmission through the vacuum barrier

The transmission through the vacuum barrier appears in the expression of the current through the matrix elements $\langle 1'|G^a|2\rangle\langle 2'|G^r|1\rangle$ in which G^a and G^r are the advanced and retarded Green's function of the whole system. They are obtained by resolution of the first set of matching equations in Appendix C. When one considers their matrix elements of the type $\langle 1|G|2\rangle$, it is possible to write them under the following form:

$$G=(I-T-U)^{-1}g_{II} , \tag{17}$$

with

$$T=(\nabla_2 g_{II}-g_{II}|1'\rangle\langle 1'|X_I)|1\rangle\langle 1| , \tag{18}$$

$$U=(-\nabla_2 g_{II}-g_{II}|2'\rangle\langle 2'|X_{III})|2\rangle\langle 2| . \tag{19}$$

By generalizing the results of the one-dimensional case obtained in Appendix C, we find that (i) G is a complicate quantity which depends not only on g_{II} but also on the electronic properties of the electrodes. Yet these latter appear only through the operators X_I and X_{III} described above. (ii) T and U possess only two kinds of matrix elements and one can assign a physical meaning to each of them: $\langle 1|I-T|1'\rangle$ or $\langle 2|I-U|2'\rangle$ represent the inverse effective reflection coefficients of the electronic waves at the surfaces S_1 and S_2. Their vanishing is associated with anomalous conditions of matching which may reveal the presence of surface states. The off-diagonal terms $\langle 2|T|1\rangle$ and $\langle 1|U|2\rangle$ depict effective propagation coefficients through the barrier. In one dimension they vary with the barrier thickness D as $e^{-\kappa D}$ (κ is the imaginary wave vector at the energy under consideration). (iii) The development of G to all orders in T and U gives two kinds of effects: at the lowest order in $e^{-\kappa D}$, it modifies the bare propagator g_{II} to account for multiple scattering events in the left and right electrodes thanks to the matrix elements $\langle 1|I-T|1'\rangle$ and $\langle 2|I-U|2'\rangle$ (in terms of the many-body diagrammatic language, this is a vertex correction). The second consequence is the inclusion of all multiple propagation events in the barrier, due to the off-diagonal matrix elements; in one dimension each additional path contributes by a quantity $U_{21}T_{12}/(1-T_{11})(1-U_{22})$, the product of two propagation factors (varying each as $e^{-\kappa D}$) weighted by the reflection coefficients $(1-T_{11})^{-1}$ and $(1-U_{22})^{-1}$ on the electrodes. This proves that our approach is valid whatever the value of the barrier thickness; in principle it is able to reproduce the tunneling conductance in the limit of vanishing barrier width,[5,7,13] but we should keep in mind that the result would be questionable because of the uncertainty in the determination of S_1 and S_2. (iv) The Green's function in Eq. (17) may also describe the Fowler-Nordheim regime. The barrier states associated with current oscillations appear in our formalism as zeros of the off-diagonal matrix elements of $(I-T-U)$. (v) In one dimension, the leading dependence of $\langle x_1|G|x_2\rangle$ as a function of the barrier thickness is in most cases $e^{-\kappa D}$. Yet this dependence becomes anomalous (in $e^{\kappa D}$) for energies close to a surface state: $1=T_{11}$ or $1=U_{22}$.

We conclude this section in stressing that, although not very easily tractable, the expression for the tunneling current given in Eq. (9) contains all the relevant physics met in the context of the scanning tunneling microscopy. Thanks to the natural factorization that it involves, it allows a discussion of the separate roles of the transmission through the barrier and of the electronic structure of the electrodes. We have shown elsewhere how to use such an expression in various one-dimensional models[8] and that it is a good starting to derive Bardeen's result[3] by a use of perturbation developments.[10]

IV. SPECTROSCOPIC INFORMATION INCLUDED IN THE TUNNELING CURRENT

We examine in this section which features of the electronic structure of the free electrodes may be extracted from the tunneling current. For this purpose, we first analyze in Sec. IV A the one-dimensional case for which there exists an exact expression of X and we compare it to the local density of states at the surface of the electrode. This step represents a generalization of the calculations in Refs. 8 and 9. The same study is not possible in three dimensions at the present time: it would require the elaboration of a numerical code, which does not exist, to our knowledge, and this is beyond the scope of this paper. We thus simply propose in Sec. IV B an indirect way to achieve this goal.

A. One-dimensional case

In one dimension, several equivalent analytical expressions for X may be derived, depending upon the choice of the wave-function basis. We first express it in terms of the bulk Bloch states of the electrode. Then we compare it to the local density of states at the surface.

(1) To express X as a function of Bloch states of an infinite crystal, we make use of the property stressed in Sec. III: X does not depend upon the value of the potential on the right of S_1 (for X_I). It is thus legitimate to calculate it by assuming that the periodic potential of the electrode extends to infinity on the right. We call ψ_k and ψ_{-k} ($=\psi_k^*$) the Bloch states of energy E_k and we develop $G(xx')$ on this basis:

$$G(xx')=\sum_k \frac{\psi_k(x)\psi_{-k}(x')}{E-E_k+i\eta} . \tag{20}$$

If k_0 represents the Bloch wave propagating towards the right ($x>0$) at the energy E ($E=E_{k_0}$ and $k_0>0$), the integration in k space yields

$$G(xx')=-\frac{2i\pi n(k)}{dE_k/dk|_{k=k_0}}\psi_{k_0}(x_>)\psi_{-k_0}(x_<) . \quad (21)$$

[$x_>=\max(x,x')$; $x_<=\min(x,x')$, and $n(k)$ is the density of states in the reciprocal space in one dimension: $n(k)=L/\pi$.] There is another way of expressing $G(x,x')$, which makes use of the Wronskian $\mathcal{W}(k_0)$ of ψ_{k_0} and ψ_{-k_0}:

$$\mathcal{W}(k_0)=\frac{d}{dx}\psi_0(x)\psi_{-k_0}(x)-\psi_{k_0}(x)\frac{d}{dx}\psi_{-k_0}(x) . \quad (22)$$

Since ψ_{k_0} and ψ_{-k_0} are solutions of the same Schrödinger equation at the same energy, $\mathcal{W}_{k_0}$ is independent of x, and $G(xx')$ reads

$$G(xx')=-\frac{1}{\mathcal{W}_{k_0}}\psi_{k_0}(x_>)\psi_{-k_0}(x_<) . \quad (23)$$

This expression obviously satisfies all requirements for $G(xx')$ including the discontinuity of its derivative at $x=x'$. Comparison of Eqs. (21) and (23) establishes the relationship:

$$\mathcal{W}_{k_0}=\frac{1}{2i\pi n(k)}\frac{dE_k}{dk}\bigg|_{k=k_0} . \quad (24)$$

The logarithmic derivative of the Green's function at the position x is then written

$$X(x)=\frac{\frac{\partial}{\partial x}G(xx^+)}{G(xx)}=\frac{\frac{d}{dx}\psi_{k_0}(x)\psi_{-k_0}(x)}{\psi_{k_0}(x)\psi_{-k_0}(x)} . \quad (25)$$

The elimination of ψ_{-k_0} would show that X is equal to the logarithmic derivative of ψ_{k_0}, but we prefer to keep Eq. (25) under this form to calculate $\mathrm{Im}X(x)$, which, thanks to the property of the infinite periodic system $\psi_{-k_0}=\psi^*_{k_0}$, reads

$$\mathrm{Im}X(x)=\frac{\mathcal{W}_{k_0}}{2i|\psi_{k_0}(x)|^2} . \quad (26)$$

Finally, making use of (24), and of $n(E)dE=n(k)dk$, we find

$$\mathrm{Im}X(x)=\frac{-1}{4\pi n(k)}\frac{1}{|\psi_{k_0}(x)|^2}\frac{dE(k_0)}{dk}$$

$$\equiv-\frac{1}{4\pi n(E)}\frac{1}{|\psi_{k_0}(x)|^2} . \quad (27)$$

Several comments can be made. (i) Since X can be calculated entirely as a function of the bulk wave functions and energies, one should not expect to extract any specific characteristics of the surface. (ii) $\mathrm{Im}X$ is actually inversely proportional to the bulk local density of states at the position x [$\propto n(E)|\psi_k(x)|^2$]. (iii) $\mathrm{Im}X$ is proportional to the group velocity of the electrons at the energy under consideration; this seems a reasonable step in the calculation of a current. Moreover, through this quantity, the different kinds of atomic orbitals contribute differently to the current: d orbitals, which are more localized, give rise to narrow bands and thus to small group velocities; they contribute to the current less than s-p orbitals, as noted earlier with a different approach.[1,2] (iv) In our derivation [from Eq. (21)] we have explicitly assumed that the electrode has propagating states at the energy E. If E lies in a gap, it is obvious that $\mathrm{Im}X=0$.

(2) We now turn to the evaluation of the local density of states at the surface of the free electrode; for this, one writes matching equations similar to (A1) with only one boundary and one introduces the vacuum Green's function g_0.[12] Denoting X and X_0 the logarithmic derivatives of the Green's function g_I and g_0 on S_1 (X_0 is real in the energy range of interest), we find

$$g_I(x_1x_1)=\frac{1}{(X_I+X_0)} , \quad (28)$$

so that the local density of states $N_s(x_1)$ at the surface x_1, which is proportional to $-(1/\pi)\mathrm{Im}g_I(x_1x_1)$, reads

$$N_s(x_1)=\frac{1}{\pi}\frac{\mathrm{Im}X_I}{|X_I+X_0|^2} . \quad (29)$$

Actually this expression is correct when E lies in the bulk bands ($\mathrm{Im}X_I\neq0$), but $N_s(x_1)$ also possesses nonzero values at discrete energies such that $\mathrm{Im}X_I=0$ and $X_I+X_0=0$. We already discussed in Sec. III these surface states associated with an anomalous matching ($X_I+X_0=0$) and an infinite reflection coefficient [$(X_I+X_0)^{-1}\to\infty$]. Keeping this in mind, and provided that $X_I+X_0\neq0$, we can invert Eq. (29):

$$\mathrm{Im}X_I=\pi N_s(x_1)|X_I+X_0|^2 , \quad (30)$$

and say that *there exists a rough proportionality between* $\mathrm{Im}X_I$ and $N_s(x_1)$, if the factor $|X_I+X_0|^2$ is smooth as a function of energy, *but this is only true at the energies of bulk bands. At the energy of surface states,* although $N_s(x_1)$ is nonzero, $\mathrm{Im}X_I=0$, *and there is no tunneling current* (within the one-electron approximation).

The limitations of the transfer Hamiltonian approach, which predicts that there is a tunneling current each time that $N_s(x_1)\neq0$, have been made explicit in Ref. 10. In addition, since it was also shown[5] that the tunneling current could be expressed under a form similar to ours, with $\mathrm{Im}X$ replaced by $\mathrm{Im}g'_1(x_Ax_A)$ (x_A close to x_1), we clarify the equivalence between the two results in Appendix D; we stress that both are compatible, since $\mathrm{Im}g'_1(x_Ax_A)$ is not the local density of states at the surface of the *free* electrode.

B. Three-dimensional case

In three dimensions, there is no such simple means of calculating $\mathrm{Im}X$ as in the one-dimensional case, for several reasons. First, it depends on the actual shape of the surfaces S_1 and S_2, which should be carefully studied case by case. Second, it involves an "inversion" of the

Green's operator on the boundary. To our knowledge, there exist several numerical codes for evaluating a Green's operator, but not a 2D-inverse Green's operator. It will thus be impossible to carry out a serious discussion on X without an important numerical effort. We are, at the present time, exploring a possible path: as demonstrated in Appendix D in one dimension, but obvious in 3D from Ref. 14, the imaginary part of the X_{I} operator is proportional to the imaginary part of the Green's operator g_{I}' of an unphysical system having the potential of the left electrode on the left of S_1 and an infinite barrier on its right, provided that g_{I}' can be evaluated at an (infinitely) small distance ϵ from the surface. As a consequence, if we apply one of the existing codes to such an unphysical system, we will get a quantity proportional to the ImX of the actual free electrode. That may represent a way to quantitatively measure how much the spectroscopic information included in ImX differs from the surface density of states of the electrodes. At the present time, the only thing which remains obvious, without any calculation, is that the surface-specific features of the electronic structure, which depend upon the work function (position of the vacuum level with respect to the inner Fermi level) will never be present in X, because, as we stressed several times in this paper, X is independent of the value of the potential outside the electrodes (on the right of S_1 for the electrode I or left of S_2 for the electrode II).

V. CONCLUSION

This paper presents a calculation of the tunneling current which makes use of a Green's function formalism. The two assumptions on which it relies are (i) a one-electron approximation, and (ii) the possibility of defining two boundaries S_1 and S_2 on the outside of which the potential experienced by the electrons is equal to that of the free electrodes. We also supposed that there were no occupied states in the barrier to write down all our results, but this hypothesis is not akin to the method. We showed that the current is expressed as the trace of a product of four operators: there is a natural factorization of quantities which characterize the electrodes and the barrier. The transmission through the barrier displays all multiple reflection paths, which are important when the barrier width decreases or in the Fowler-Nordheim regime. It generally varies as $\sim e^{-2\kappa D}$ with the barrier width D but the dependence may become anomalous in $\sim e^{2\kappa D}$ close to surface-state energies. For the first time the tunneling current is written in terms of quantities X characterizing the *free* electrodes. We show that X depends upon the surface orbitals present at the given energy, that the group velocity of the electrons plays an important role, but that all surface features related to the value of the work function (e.g., the surface states) are absent because X is independent of the value of the potential outside the electrode. The expression of X in three dimensions is quite involved and we have not found any easy way to evaluate it in a realistic case. Yet, due to the proportionality which exists between ImX and the imaginary part of the Green's function of a fictitious electrode bound by an infinite potential, some hope of progress in the future remains.

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APPENDIX A: MATCHING EQUATIONS

Following the method described in the text, we write down the matching equations which allow us to calculate the advanced or retarded Green's functions $G^u(\mathbf{x},\mathbf{x}')$ as a function of g_{I}^u, g_{II}^u, g_{III}^u and then similar equations for $G^+(\mathbf{x},\mathbf{x}')(u=a,r)$. Since we are interested in calculating the total current or the density of current in the barrier, we locate the "source" x' of the Green's functions in region M. The gradients always refer to the variable on which the integration is performed—we will, nevertheless, keep the subscripts 1 or 2 according to whether it is the first or the second argument of the Green's function:

$$G^u(\mathbf{x},\mathbf{x}')=-\int_{S_1} d\mathbf{S}_1[\nabla_2 g_{\mathrm{I}}^u(\mathbf{x}^-,\mathbf{x}_1)G^u(\mathbf{x}_1,\mathbf{x}')-g_{\mathrm{I}}^u(\mathbf{x},\mathbf{x}_1)\nabla_1 G^u(\mathbf{x}_1,\mathbf{x}'^+)] \quad \text{if } x\in L\ , \tag{A1a}$$

$$G^u(\mathbf{x},\mathbf{x}')=g_{\mathrm{II}}^u(\mathbf{x},\mathbf{x}')+\int_{S_1} d\mathbf{S}_1[\nabla_2 g_{\mathrm{II}}^u(\mathbf{x}^+,\mathbf{x}_1)G^u(\mathbf{x}_1,\mathbf{x}')-g_{\mathrm{II}}^u(\mathbf{x},\mathbf{x}_1)\nabla_1 G^u(\mathbf{x}_1,\mathbf{x}'^+)]$$
$$-\int_{S_2} d\mathbf{S}_2[\nabla_2 g_{\mathrm{II}}^u(\mathbf{x}^-,\mathbf{x}_2)G^u(\mathbf{x}_2,\mathbf{x}')-g_{\mathrm{II}}^u(\mathbf{x},\mathbf{x}_2)\nabla_1 G^u(\mathbf{x}_2,\mathbf{x}'^+)] \quad \text{if } x\in M\ , \tag{A1b}$$

$$G^u(\mathbf{x},\mathbf{x}')=\int_{S_2} d\mathbf{S}_2[\nabla_2 g_{\mathrm{III}}^u(\mathbf{x}^+,\mathbf{x}_2)G^u(\mathbf{x}_2,\mathbf{x}')-g_{\mathrm{III}}^u(\mathbf{x},\mathbf{x}_2)\nabla_1 G^u(\mathbf{x}_2,\mathbf{x}'^-)] \quad \text{if } x\in R\ , \tag{A1c}$$

$$G^+(\mathbf{x},\mathbf{x}')=-\int_{S_1} d\mathbf{S}_1[\nabla_2 g_{\mathrm{I}}^a(\mathbf{x}^-,\mathbf{x}_1)G^+(\mathbf{x}_1,\mathbf{x}')-g_{\mathrm{I}}^a(\mathbf{x},\mathbf{x}_1)\nabla_1 G^+(\mathbf{x}_1,\mathbf{x}')]$$
$$+\int_{S_1} d\mathbf{S}_1[g_{\mathrm{I}}^+(\mathbf{x},\mathbf{x}_1)\nabla_1 G^r(\mathbf{x}_1,\mathbf{x}'^+)-\nabla_2 g_{\mathrm{I}}^+(\mathbf{x},\mathbf{x}_1)G^r(\mathbf{x}_1,\mathbf{x}')] \quad \text{if } x\in L\ , \tag{A2}$$

$$
\begin{aligned}
G^+(\mathbf{x},\mathbf{x}')=&\int_{S_1} d\mathbf{S}_1[\nabla_2 g^a_{\mathrm{II}}(\mathbf{x}^+,\mathbf{x}_1)G^+(\mathbf{x}_1,\mathbf{x}')-g^a_{\mathrm{II}}(\mathbf{x},\mathbf{x}_1)\nabla_1 G^+(\mathbf{x}_1,\mathbf{x}')]\\
&-\int_{S_2} d\mathbf{S}_2[\nabla_2 g^a_{\mathrm{II}}(\mathbf{x}^-,\mathbf{x}_2)G^+(\mathbf{x}_2,\mathbf{x}')-g^a_{\mathrm{II}}(\mathbf{x},\mathbf{x}_2)\nabla_1 G^+(\mathbf{x}_2,\mathbf{x}')]\\
&+g^+_{\mathrm{II}}(\mathbf{x},\mathbf{x}')-\int_{S_1} d\mathbf{S}_1[g^+_{\mathrm{II}}(\mathbf{x},\mathbf{x}_1)\nabla_1 G^r(\mathbf{x}_1,\mathbf{x}'^+)-\nabla_2 g^+_{\mathrm{II}}(\mathbf{x},\mathbf{x}_1)G^r(\mathbf{x}_1,\mathbf{x}')]\\
&+\int_{S_2} d\mathbf{S}_2[g^+_{\mathrm{II}}(\mathbf{x},\mathbf{x}_2)\nabla_1 G^r(\mathbf{x}_2,\mathbf{x}'^-)-\nabla_2 g^+_{\mathrm{II}}(\mathbf{x},\mathbf{x}_2)G^r(\mathbf{x}_2,\mathbf{x}')] \quad \text{if } x\in M\ ,\\
G^+(\mathbf{x},\mathbf{x}')=&\int_{S_2} d\mathbf{S}_2[\nabla_2 g^a_{\mathrm{III}}(\mathbf{x}^+,\mathbf{x}_2)G^+(\mathbf{x}_2,\mathbf{x}')-g^a_{\mathrm{III}}(\mathbf{x},\mathbf{x}_2)\nabla_1 G^+(\mathbf{x}_2,\mathbf{x}')]\\
&-\int_{S_2} d\mathbf{S}_2[g^+_{\mathrm{III}}(\mathbf{x},\mathbf{x}_2)\nabla_1 G^r(\mathbf{x}_2,\mathbf{x}'^-)-\nabla_2 g^+_{\mathrm{III}}(\mathbf{x},\mathbf{x}_2)G^r(\mathbf{x}_2,\mathbf{x}')] \quad \text{if } x\in R\ .
\end{aligned}
$$

The second system of equations may be written under a simplified form by expressing g^+_{I} and g^+_{III} as a function of g^u_{I} and g^u_{III} ($u=a,r$), and assuming that there are no available occupied states in the barrier ($g^+_{\mathrm{II}}=0$):

$$
\begin{aligned}
G^+(\mathbf{x},\mathbf{x}')=&-\int_{S_1} d\mathbf{S}_1[\nabla_2 g^a_{\mathrm{I}}(\mathbf{x}^-,\mathbf{x}_1)G^+(\mathbf{x}_1,\mathbf{x}')-g^a_{\mathrm{I}}(\mathbf{x},\mathbf{x}_1)\nabla_1 G^+(\mathbf{x}_1,\mathbf{x}')]\\
&-2i\Theta(\mu_{\mathrm{I}}-\omega)\left[\mathrm{Im}G^a(\mathbf{x},\mathbf{x}')+\int_{S_1} d\mathbf{S}_1[\nabla_2 g^a_{\mathrm{I}}(\mathbf{x}^+,\mathbf{x}_1)\mathrm{Im}G^a(\mathbf{x}_1,\mathbf{x}')-g^a_{\mathrm{II}}(\mathbf{x},\mathbf{x}_1)\mathrm{Im}\nabla_1 G^a(\mathbf{x}_1,\mathbf{x}'^+)]\right] \quad \text{if } x\in L\ ,\\
G^+(\mathbf{x},\mathbf{x}')=&-\int_{S_1} d\mathbf{S}_1[\nabla_2 g^a_{\mathrm{II}}(\mathbf{x}^+,\mathbf{x}_1)G^+(\mathbf{x}_1,\mathbf{x}')-g^a_{\mathrm{II}}(\mathbf{x},\mathbf{x}_1)\nabla_1 G^+(\mathbf{x}_1,\mathbf{x}')]\\
&-\int_{S_2} d\mathbf{S}_2[\nabla_2 g^a_{\mathrm{II}}(\mathbf{x}^-,\mathbf{x}_2)G^+(\mathbf{x}_2,\mathbf{x}')-g^a_{\mathrm{II}}(\mathbf{x},\mathbf{x}_2)\nabla_1 G^+(\mathbf{x}_2,\mathbf{x}')] \quad \text{if } x\in M\ ,\\
G^+(\mathbf{x},\mathbf{x}')=&\int d\mathbf{S}_2[\nabla_2 g^a_{\mathrm{III}}(\mathbf{x}^+,\mathbf{x}_2)G^+(\mathbf{x}_2,\mathbf{x}')-g^a_{\mathrm{III}}(\mathbf{x},\mathbf{x}_2)\nabla_1 G^+(\mathbf{x}_2,\mathbf{x}')]\\
&+2i\Theta(\mu_{\mathrm{III}}-\omega)\left[\mathrm{Im}G^a(\mathbf{x},\mathbf{x}')-\int_{S_2} d\mathbf{S}_2[\nabla_2 g^a_{\mathrm{III}}(\mathbf{x}^+,\mathbf{x}_2)\mathrm{Im}G^a(\mathbf{x}_2,\mathbf{x}')-g^a_{\mathrm{III}}(\mathbf{x},\mathbf{x}_2)\mathrm{Im}\nabla_1 G^a(\mathbf{x}_2,\mathbf{x}'^-)]\right] \quad \text{if } x\in R\ .
\end{aligned}
\tag{A3}
$$

Θ is the Heavyside function [$\Theta(x)=0$ if $x<0$; $\Theta(x)=1$ if $x>0$], and μ_{I} and μ_{III} are the Fermi levels of the electrodes in the presence of the applied bias.

APPENDIX B: CALCULATION OF THE TUNNELING CURRENT

In this appendix we give the steps which lead to the evaluation of the quantity $\mathrm{Re}\nabla_1 G^+(\mathbf{x},\mathbf{x})$ from which the tunneling current is straightforwardly obtained [Eq. (3)].

First we use Eq. (A1a) and (A1c) to express the gradients of G^u as a function of G^u and we introduce the operators X^u_{I} and X^u_{III} such that

$$\langle x_1|X^u_{\mathrm{I}}|x'_1\rangle=\langle x_1|\tilde{g}^u_{\mathrm{I}}|1\rangle\langle 1^-|I+\nabla_2 g^u_{\mathrm{I}}|x'_1\rangle\ , \tag{B1}$$

$$\langle x_2|X^u_{\mathrm{III}}|x'_2\rangle=\langle x_2|\tilde{g}^u_{\mathrm{III}}|2\rangle\langle 2^+|I-\nabla_2 g^u_{\mathrm{III}}|x'_2\rangle\ . \tag{B2}$$

(The superscripts tell how the gradients have to be taken. The difference in sign between X^u_{I} and X^u_{III} comes from the choice of the gradients; these expressions are defined when $\mathbf{x}_1$ and $\mathbf{x}'_1$ lie on S_1, and when $\mathbf{x}_2$ and $\mathbf{x}'_2$ lie on S_2.) We find that

$$\langle x_1|\nabla_1 G^u|x'^+\rangle=\langle x_1|X^u_{\mathrm{I}}|1\rangle\langle 1|G^u|x'\rangle,\quad x_1\in S_1,\quad x'\in M \tag{B3}$$

$$\langle x_2|\nabla_1 G^u|x'^-\rangle=-\langle x_2|X^u_{\mathrm{III}}|2\rangle\langle 2|G^u|x'\rangle,\quad x_2\in S_2,\quad x'\in M\ . \tag{B4}$$

These equations are used to get relationships between G^+ and its gradients from Eqs. (A3a) and (A3c) ($x'\in M$):

$$\langle 1'|X^a_{\mathrm{I}}|1\rangle\langle 1|G^+|x'\rangle-\langle 1'|\nabla_1 G^+|\mathbf{x}'\rangle=2i\Theta(\mu_{\mathrm{I}}-\omega)\langle 1'|\mathrm{Im}X^a_{\mathrm{I}}|1\rangle\langle 1|G^r|x'\rangle\ , \tag{B5}$$

$$\langle 2'|X^a_{\mathrm{III}}|2\rangle\langle 2|G^+|x'\rangle+\langle 2'|\nabla_1 G^+|\mathbf{x}'\rangle=-2i\Theta(\mu_{\mathrm{III}}-\omega)\langle 2'|\mathrm{Im}X^a_{\mathrm{III}}|2\rangle\langle 2|G^r|x'\rangle\ . \tag{B6}$$

Introducing (B3), (B4), (B5), and (B6) in (A1b) and (A3b), we obtain

$$\langle x|Z^u_{\mathrm{I}}|1\rangle\langle 1|G^u|x'\rangle+\langle x|Z^u_{\mathrm{III}}|2\rangle\langle 2|G^u|x'\rangle=\langle x|g^u_{\mathrm{II}}|x'\rangle\ , \tag{B7}$$

$$\begin{aligned}
\langle x|Z^a_{\mathrm{I}}|1\rangle\langle 1|G^+|x'\rangle+\langle x|Z^a_{\mathrm{III}}|2\rangle\langle 2|G^+|x'\rangle=&2i\Theta(\mu_{\mathrm{I}}-\omega)\langle x|g^a_{\mathrm{II}}|1'\rangle\langle 1'|\mathrm{Im}X^a_{\mathrm{I}}|1\rangle\langle 1|G^r|x'\rangle\\
&-2i\Theta(\mu_{\mathrm{III}}-\omega)\langle x|g^a_{\mathrm{II}}|2'\rangle\langle 2'|\mathrm{Im}X^a_{\mathrm{III}}|2\rangle\langle 2|G^r|x'\rangle\ ,
\end{aligned}
\tag{B8}$$

with

$$\langle x|Z_{\rm I}^{u}|1\rangle=\langle x|I-\nabla_2 g_{\rm II}^{u}|1\rangle+\langle x|g_{\rm II}^{u}|1'\rangle\langle 1'|X_{\rm I}^{u}|1\rangle \tag{B9}$$

$$\langle x|Z_{\rm III}^{u}|2\rangle=\langle x|I+\nabla_2 g_{\rm II}^{u}|2\rangle+\langle x|g_{\rm II}^{u}|2'\rangle\langle 2'|X_{\rm III}^{u}|2\rangle\ . \tag{B10}$$

(B7) and (B8) show that there is a relationship between G^{+} and G^{a} which reads

$$\langle 1|G^{+}|x'\rangle=2i\Theta(\mu_{\rm I}-\omega)\langle 1|G^{a}|1'\rangle\langle 1'|{\rm Im}X_{\rm I}^{a}|1\rangle\langle 1|G^{r}|x'\rangle-2i\Theta(\mu_{\rm III}-\omega)\langle 1|G^{a}|2'\rangle\langle 2'|{\rm Im}X_{\rm III}^{a}|2\rangle\langle 2|G^{r}|x'\rangle\ , \tag{B11}$$

$$\langle 2|G^{+}|x'\rangle=2i\Theta(\mu_{\rm I}-\omega)\langle 2|G^{a}|1'\rangle\langle 1'|{\rm Im}X_{\rm I}^{a}|1\rangle\langle 1|G^{r}|x'\rangle-2i\Theta(\mu_{\rm III}-\omega)\langle 2|G^{a}|2'\rangle\langle 2'|{\rm Im}X_{\rm III}^{a}|2\rangle\langle 2|G^{r}|x'\rangle\ . \tag{B12}$$

The total current is related to either ${\rm Tr}_1{\rm Re}\langle 1|\nabla G^{+}|1\rangle$ or ${\rm Tr}_2{\rm Re}\langle 2|\nabla G^{+}|2\rangle$ which are obtained from (B5) and (B6) with the help of (B11) and (B12):

$$\begin{aligned}{\rm Tr}_1{\rm Re}\langle 1|\nabla G^{+}|1\rangle&={\rm Tr}_2{\rm Re}\langle 2|\nabla G^{+}|2\rangle\\&=[\Theta(\mu_{\rm I}-\omega)-\Theta(\mu_{\rm III}-\omega)]{\rm Tr}_1\langle 1|{\rm Im}X_{\rm I}^{a}|1'\rangle\langle 1'|G^{a}|2\rangle\langle 2|{\rm Im}X_{\rm III}^{a}|2'\rangle\langle 2'|G^{r}|1\rangle\ .\end{aligned} \tag{B13}$$

The density of current in the barrier could in principle be derived with our approach, but no compact expression for it could be found.

APPENDIX C: TRANSMISSION THROUGH THE VACUUM BARRIER

In this appendix we solve the set of matching equation (A1a)–(A1c) in order to obtain the matrix element $\langle 1|G^{a}|2\rangle$ ($|1\rangle\in S_1$, $|2\rangle\in S_2$) which characterizes the transmission of electrons through the vacuum barrier. The steps of the calculation are the following: from (A1a) and (A1c) we deduce ($x_1\in S_1$, $x'\in M$, $x_2\in S_2$):

$$\langle x_1|\nabla_1 G|\mathbf{x}'\rangle=\langle x_1|X_{\rm I}|1\rangle\langle 1|G|x'\rangle\ , \tag{C1}$$

$$\langle x_2|\nabla_1 G|\mathbf{x}'\rangle=-\langle x_2|X_{\rm III}|2\rangle\langle 2|G|x'\rangle\ . \tag{C2}$$

We introduce these expressions in (A1b):

$$\begin{aligned}G=&g_{\rm II}+(\nabla_2 g_{\rm II}-g_{\rm II}|1'\rangle\langle 1'|X_{\rm I})|1\rangle\langle 1|G\\&+(-\nabla_2 g_{\rm II}-g_{\rm II}|2'\rangle\langle 2'|X_{\rm III})|2\rangle\langle 2|G\ .\end{aligned} \tag{C3}$$

Just for simplifying the notation, we call

$$T=(\nabla_2 g_{\rm II}-g_{\rm II}|1'\rangle\langle 1'|X_{\rm I})|1\rangle\langle 1|\ , \tag{C4}$$

$$U=(-\nabla_2 g_{\rm II}-g_{\rm II}|2'\rangle\langle 2'|X_{\rm III})|2\rangle\langle 2|\ . \tag{C5}$$

Formally it is thus possible to write

$$G=(I-T-U)^{-1}g_{\rm II}\ , \tag{C6}$$

which is equivalent to

$$G=g_{\rm II}+(T+U)g_{\rm II}+(T+U)^2 g_{\rm II}+\cdots\ . \tag{C7}$$

Equations (C6) and (C7) represent the most general form of G that we may use to calculate $\langle 1|G|2\rangle$.

We give in the following its explicit expression in one dimension when the surfaces S_1 and S_2 are reduced to x_1 and x_2. T and U have, in that case only two matrix elements:

$$\begin{aligned}&T_{21}=\langle x_2|T|x_1\rangle,\quad T_{11}=\langle x_1|T|x_1\rangle\ ,\\&U_{12}=\langle x_1|U|x_2\rangle,\quad U_{22}=\langle x_2|U|x_2\rangle\ .\end{aligned} \tag{C8}$$

Inverting the operator I-T-U stems to inverting a 2×2 matrix. The final form of $\langle x_1|G|x_2\rangle$ is

$$\langle x_1|G|x_2\rangle=\frac{\mathcal{A}}{\mathcal{B}}\ , \tag{C9}$$

$$\begin{aligned}\mathcal{A}=&\langle x_1|g_{\rm II}|x_2\rangle(1+\langle x_2|\nabla_2 g_{\rm II}|x_2\rangle)\\&-\langle x_1|\nabla_2 g_{\rm II}|x_2\rangle\langle x_2|g_{\rm II}|x_1\rangle\ ,\\\mathcal{B}=&(1+\langle x_2|\nabla_2 g_{\rm II}|x_2\rangle+\langle x_2|g_{\rm II}|x_2\rangle X_{\rm III})\\&\times(1-\langle x_1|\nabla_2 g_{\rm II}|x_1\rangle+\langle x_1|g_{\rm II}|x_1\rangle X_{\rm I})\\&-(\langle x_1|\nabla_2 g_{\rm II}|x_2\rangle+\langle x_1|g_{\rm II}|x_2\rangle X_{\rm III})\\&\times(\langle x_2|\nabla_2 g_{\rm II}|x_1\rangle-\langle x_2|g_{\rm II}|x_1\rangle X_{\rm I})\ .\end{aligned}$$

The numerator $\mathcal{A}$ varies as $e^{-\kappa D}$, where $D=x_2-x_1$ is the barrier thickness and $i\kappa$ the imaginary wave vector at the energy under consideration. The denominator $\mathcal{B}$ is the difference between two terms, the first of which is independent upon D and the second varies as $e^{-2\kappa D}$. The electronic structure of the electrodes appears only through $X_{\rm I}$ and $X_{\rm III}$, the logarithmic derivatives of the Green's function at the positions x_1 and x_2 of the boundaries.

APPENDIX D: CONNECTION WITH GREEN'S-FUNCTION FORMALISM USING DIFFERENT BOUNDARY CONDITIONS

The method that we have followed is closely related to the one used by Caroli *et al.*[5,6] and Feuchtwang[7] in the context of planar tunneling junctions. These authors have similarly applied a Green's-function formalism together with a matching procedure at the boundaries. Yet, their boundary conditions were different. For example, Caroli *et al.* developed their result on a basis made of wave functions which vanish on S_1 and S_2. In Fig. 1(b), this would correspond to the choice of an infinite barrier on the right of S_1. Let us call $g_{\rm I}'$ the Green's functions of such a system. The tunneling current was shown[5] to take a form similar to ours in Eq. (9), with ${\rm Im}X_{\rm I}$ replaced by a quantity proportional to ${\rm Im}g_{\rm I}'(x_A,x_A)$. x_A represents the position of the last atom in a tight-binding approach[5] or a point at a distance ϵ from the surface in a continuous approach.[14] Since we know that on the boundary surface S_1, ${\rm Im}X_{\rm I}(x_1)={\rm Im}X_{\rm I}'(x_1)$, the equivalence between our result and that of Ref. (5) will be proved if we show that

$$\mathrm{Im}g_1'(x_A,x_A) \propto \mathrm{Im}X_1'(x_1) \ . \tag{D1}$$

For this it would be convenient to make some kind of Taylor development of $g_1'(x_A,x_A)$ when x_A is close to x_1, and use the property that $g_1'(x_1,x_1)=0$ due to the vanishing of the wave functions on S_1. Yet care must be taken, since g_1' has a discontinuity of its derivatives when $x=x'$; the first-order term actually takes the special form $-\min[(x-x_1),(x'-x_1)]$:

$$g_1'(x,x') \simeq -\min[(x-x_1),(x'-x_1)] + (x-x_1)(x'-x_1)\frac{\partial 2 g_1'}{\partial 1 \partial 2}(x_1,x_1)+\cdots \ . \tag{D2}$$

From this we deduce three relationships:

$$\mathrm{Im}\frac{\partial g_1'}{\partial 1}(x,x') \sim (x'-x_1)\mathrm{Im}\frac{\partial^2 g_1'}{\partial 1 \partial 2}(x_1x_1) \ , \tag{D3}$$

$$\mathrm{Re}g_1'(x,x') \sim -(x'-x_1) \quad \text{if } x'<x \ , \tag{D4}$$

$$\mathrm{Im}g_1'(x,x) \simeq (x-x_1)^2\mathrm{Im}\frac{\partial^2 g_1'}{\partial 1 \partial 2}(x_1x_1) \ , \tag{D5}$$

valid to lowest orders in $(x-x_1)$ and $(x'-x_1)$. $\mathrm{Im}X_1'$ is directly obtained from (D3) and (D4):

$$\mathrm{Im}X_1'(x_1x_1) = -\mathrm{Im}\frac{\partial^2 g_1'}{\partial 1 \partial 2}(x_1x_1) \ . \tag{D6}$$

The local density of states at $x=x_1$ associated with g_1' reads

$$\mathrm{Im}g_1'(x_A,x_A) = (x_A-x_1)^2\mathrm{Im}\frac{\partial^2 g_1'}{\partial 1 \partial 2}(x_1x_1) \ , \tag{D7}$$

so that

$$\mathrm{Im}g_1'(x_A,x_A) = (x_A-x_1)^2\mathrm{Im}X_1'(x_1x_1) \ , \tag{D8}$$

which proves the complete agreement between approaches using different boundary conditions, as it should.

It is worth noting, in conclusion, that the mathematics associated with g_1' are much simpler than what we did. But the expression of the tunneling current which results involves the local density of states of an unphysical system (electrode in contact with an infinite barrier instead of the free electrode). We have nevertheless completely developed this demonstration because it is used in Sec. IV B to propose an evaluation of $\mathrm{Im}X_1'$ in a realistic three-dimensional situation.

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