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Generalized expression for the tunneling current in scanning tunneling microscopy

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We present an analytical method for treating the tunneling current between a tip and a sample in scanning tunneling microscopy (STM) that goes beyond the independent-electrode (Bardeen) approximation and is valid for smaller tip-to-surface separations. The extremity of the tip is represented by a single spherical potential well. This well is strongly coupled to neighboring tip atoms, as well as the sample electrode, both of which we leave in a general form. The wave function for the entire system is obtained by a matching procedure, from which the total current is determined. If the current is associated with s-derived tip orbitals, the result is comparable in simplicity with that of J. Tersoff and D. Hamann [Phys. Rev. B **31**, 805 (1985)]. The low-bias tunnel conductance is proportional to the local density of states (LDOS) of the surface, but renormalized to include multiple reflections to all orders: $\sigma \propto \rho_s(\mathbf{r}_0,E_F)/D$, where D depends on both the tip and sample electronic structures and on the tip position $\mathbf{r}_0$. This effect includes the modification of the surface LDOS due to the presence of the tip. A compact expression is also obtained for orbitals of higher angular momenta: p and d states. The current then depends on the gradients of the surface spectral density, and not on the LDOS, and also has a characteristic denominator. We discuss the significance of this effect, both in the interpretation of STM images and related spectroscopies.

I. INTRODUCTION

In view of the established importance of scanning tunneling microscopy (STM) and spectroscopy in surface analysis, there have been a number of theoretical contributions addressing problems related to these techniques. The most widely used theory of STM is that of Tersoff and Hamann,[1] based on Bardeen's approximation[2] for the tunneling current between weakly coupled electrodes and adapted to suit the particular geometry of a metal tip in front of a surface. Their result states that the tunneling conductance at low bias and low temperature is proportional to the Fermi-level local density of states (LDOS) of the sample: $\sigma \propto \rho_t(E_F)\rho_s(\mathbf{r}_0,E_F)$, where t denotes the tip, s the sample, and $\mathbf{r}_0$ the position of the tip. This theory has allowed one to clarify many important questions, such as the resolution of the microscope,[3] the interpretation of STM images,[3-6] and to some degree the tip's influence.[7,8]

Recently, however, some authors have stressed the need to go beyond the independent-electrode approximation in the calculation of the tunneling current in STM.[9-12] One reason for this is straightforward: If the tip-surface distance is small (often the case in practice), a perturbation approach is insufficient. Strong coupling has been fully considered in the past—for example, in the case of metal-insulator-metal (MIM) junctions.[13-15] There have also been a number of differing approaches to calculate the tunnel current between a tip and a sample, in this case.[16-19]

Among the main difficulties in the theory of STM remains its interpretation solely in terms of the unperturbed density of states of either the tip or the sample. It is generally assumed that the barrier thickness is the only relevant parameter ($1/\kappa \sim 1$ Å being the length scale). However, following a formally exact treatment of the tunneling current,[11] Noguera has shown that, quite generally, the reflection coefficients at each surface also play an essential role.[20] Indeed, the Bardeen approximation ceases to be valid under particular circumstances such as at the energies of surface states, impurity states, or other localized states at one of the surfaces, or states associated with the barrier. We have illustrated this point explicitly for simple one-dimensional models,[21] the full three-dimensional case being much more difficult to interpret.[22] Furthermore, while the observation of surface states of semiconductors is very well established,[23,24] this is not the case for metal surfaces.[25] The question that arises is whether or not STM data can be interpreted only in terms of the LDOS.

The achievement of atomic resolution on some compact metal surfaces[26] (such as gold and aluminum) came somewhat as a surprise, as it was not expected on the basis of the corrugation of the LDOS in Tersoff and Hamann's original calculations. Experiments give a typical value for the giant corrugation in the 0.3-Å range, and a number of different mechanisms, beyond the scope of the present work, have been proposed to account for these results.[27] The recent calculation of Doyen *et al.*,[12] however, has failed to account for such a corrugation based on electronic effects alone.

This situation is somewhat unsatisfactory: It would then be very useful to obtain an analytical expression for the tunneling current valid for smaller tip-to-surface distances, while retaining the relative simplicity of Tersoff and Hamann's approach in the weak coupling limit. In an exact treatment, however, the wave function for the electron in the barrier region must be correctly matched at both the tip and the sample surfaces, and they are no longer independent. In the geometry of the STM there is no symmetry whatever to exploit, usually rendering analytical calculations intractable. Even if the free surface has a translational symmetry, the total wave function Ψ_ν in the presence of the tip is not a Bloch function. This is due to the multiple reflected waves at both of the interfaces, whose contribution to the current is ignored in a lowest-order perturbation theory. We therefore propose an approach in which the matching of the total wave function in the barrier to the tip electrode is possible.

We consider the following model depicted in Fig. 1: The extremity of the tip is represented by a single potential well (region III) strongly coupled to the remainder of the tip (region IV), in addition to the sample (I) on the left. We assume that the potential can be taken as constant in the vicinity of the well and that the rest of the tip is not *directly* coupled to the sample surface. These assumptions are not required in principle, but they simplify the mathematics considerably. Our method includes the case of nonplanar surfaces (i.e., steps, adatoms, adsorbates, etc.) as well as a tip with a complex atomic structure (contained in region IV). The wave function Ψ_ν for the entire system is calculated by the matching procedure at the well at the tip extremity, from which the low-bias, low-temperature current can be found.

If E_F lies within an s-derived band of the tip, we find that I takes the simple form:

$$I = \frac{4e^2 V}{\hbar} \frac{\mathrm{Im}\lambda\, \rho_L(\mathbf{r}_0, E_F)}{D} . \tag{1}$$

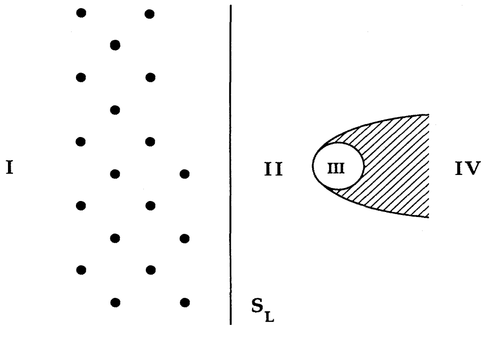

FIG. 1. Schematic of the model for the tip-surface system. The system is divided into the following regions: the sample (I), the barrier region (II), the extremity of the tip electrode (III) consisting of a single spherical potential well, and the remainder of the tip (IV). In our calculation of the tunneling current, regions I and IV are arbitrary. The plane S_L need not be the surface of the sample; it serves merely as a boundary to a region of constant potential (II).

$\rho_L(\mathbf{r}_0, E_F)$ is the Fermi-level LDOS of the surface evaluated at the center of the tip, and λ is proportional to the tip reflection coefficient. D is a denominator representing the renormalization of ρ_L to include multiple reflections between the tip and the sample, to all orders. D depends explicitly on both the tip and sample electronic structures, and also on $\mathbf{r}_0$ (thus also on the barrier thickness). The independent-electrode approximation is equivalent to setting $D = 1$, and one recovers the result of Tersoff and Hamann. In general, we find that D can be greater or smaller than unity, leading to a possible enhancement or reduction of the tunneling current. Its importance depends, however, on the surface electronic states at the tunneling energy. We will also show that this effect can be interpreted as the modification of the surface electronic structure due to the presence of the tip. We expect this to be significant, particularly in those instances described above in which the perturbation expansion is known to be invalid. We are at present considering various examples of surfaces in which the interpretation of their STM images and related spectroscopies may require such considerations.[28]

The content of the paper is as follows: In Sec. II we discuss the method of matching the wave function at the tip. We do this first for an isolated potential well in front of the surface (not connected to the rest of the tip). We then treat the problem of the extended tip. In Sec. III we use these results to obtain the tunneling current and discuss its general characteristics. In this section our method is also applied to tunneling to tip orbitals of higher angular momenta: p and d states. We also compare our results to other approaches and discuss possible extensions of our method.

II. MATCHING PROCEDURE AT THE TIP

A. Single spherical well near a surface

To illustrate our technique of determining Ψ_ν by matching at the tip, it is much simpler to first consider the case of the isolated spherical potential well (radius R and constant depth V_0) centered at $\mathbf{r}_0$ in the vicinity of the surface, as depicted in Fig. 2. Of course, such a system carries no current, but the method we apply for the extended tip is similar, and this case is instructive. Here we match the total wave function Ψ_ν in regions II and III at the radius of the well and, as an example, determine the local density of states at its center.

1. Matching on the well

Let $\psi_{\mathrm{inc}}(\mathbf{r})$ be the *total* incident wave on the sphere from the surface, $\psi_r(\mathbf{r})$ the reflected wave, and $\psi_t(\mathbf{r})$ the transmitted wave (interior solution), shown schematically in Fig. 2. The latter two are easily expressed in terms of spherical functions about the center of the well:

$$\psi_r(\mathbf{r}) = \sum_{l,m} R_{l,m} h_l^+(i\kappa u) Y_l^m(\hat{\mathbf{u}}) , \tag{2a}$$

$$\psi_t(\mathbf{r}) = \sum_{l,m} T_{l,m} j_l(ku) Y_l^m(\hat{\mathbf{u}}) , \tag{2b}$$

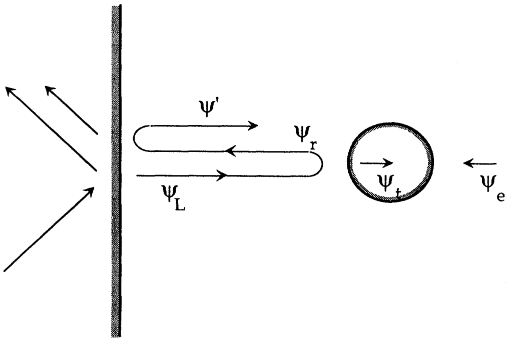

FIG. 2. Simple illustration of the waves present in the tip and sample system: ψ_L is the wave from the surface as if the tip were absent, $\psi_{\rm inc}$ is the sum of right-going waves in region II ($\psi_L+\psi'$), and ψ_r and ψ_t are the reflected and transmitted waves, respectively. The presence of the additional waves ψ_e accounts for the coupling to the remainder of the tip.

where $\kappa=(-2mE/\hbar^2)^{1/2}$,

$$k=[2m(E+V_0)/\hbar^2]^{1/2}\ ,$$

and $\mathbf{u}$ is the difference vector $\mathbf{u}=\mathbf{r}-\mathbf{r}_0$. $R_{l,m}$ and $T_{l,m}$ are, as yet, undetermined coefficients. Here $j_l(z)$, $h_l^+(z)$, and Y_l^m are the spherical Bessel functions, spherical Hankel functions of the first kind, and spherical harmonics, respectively. Due to the presence of the external source (i.e., the surface), angular momentum is not a good quantum number; hence the summation over all l and m in Eq. (2).

The exterior solution can then be written as a superposition of the reflected waves given by (2a) and the waves incident from the surface, which we denote $\psi_{\rm inc}(\mathbf{r})$. These are evanescent waves decaying in the direction perpendicular to the surface. The basis of our new approach is to treat $\psi_{\rm inc}(\mathbf{r})$ expressed in spherical functions about the center of the well, which is essential for matching on the tip:

$$\psi_{\rm inc}(\mathbf{r})=\sum_{l,m}\mathcal{D}_{l,m}j_l(i\kappa u)Y_l^m(\hat{\mathbf{u}})\ . \tag{2c}$$

Notice that $\psi_{\rm inc}(\mathbf{r})$ is the *full* wave incident on the well and is not simply the unperturbed wave function of the surface in the absence of the well [which we term $\psi_L(\mathbf{r})$ hereafter]. This is due to the additional reflected waves at the surface due to the presence of the tip (denoted ψ' in Fig. 2). Indeed, the goal of our matching procedure, rather than a perturbation approach, is to be able to account for such terms.

In Sec. III C and Appendix A, we discuss in detail the determination of the expansion coefficients. However one notices that the $l=0$, $m=0$ coefficient, $\mathcal{D}_{0,0}=\mathcal{D}_0$, is remarkably simple:

$$\mathcal{D}_0=(4\pi)^{1/2}\psi_{\rm inc}(\mathbf{r}_0)\ ; \tag{3}$$

it is proportional to the total incident wave evaluated at the center of the well. This identity already contains the result of Tersoff and Hamann for the tunneling current for the s-wave tip. We shall show below that the tunneling current is proportional to $|\mathcal{D}_0|^2$ if only the $l=0$ waves are retained. Then in the lowest approximation, $\psi_{\rm inc}(\mathbf{r}_0)\approx\psi_L(\mathbf{r}_0)$ and we shall recover their result. However, notice that no approximation has been made here to arrive at Eq. (3).

Using the expansions (2a), (2b), and (2c), we can match interior and exterior solutions in the usual way at the radius R of the well. Valid for all l and m, the coefficients must satisfy

$$R_{l,m}=\mathcal{R}_l\mathcal{D}_{l,m}\ , \tag{4a}$$

$$T_{l,m}=\mathcal{T}_l\mathcal{D}_{l,m}\ , \tag{4b}$$

where we have defined reflection and transmission coefficients $\mathcal{R}_l$ and $\mathcal{T}_l$:

$$\mathcal{R}_l=W\{j_l(i\kappa R),j_l(kR)\}/W\{j_l(kR),h_l^+(i\kappa R)\}\ , \tag{5a}$$

$$\mathcal{T}_l=W\{j_l(i\kappa R),h_l^+(i\kappa R)\}/W\{j_l(kR),h_l^+(i\kappa R)\}\ , \tag{5b}$$

and W is the Wronskian,

$$W\{f,g\}=f\frac{dg}{du}-g\frac{df}{du}\ .$$

The coefficients $\mathcal{T}_l$ and $\mathcal{R}_l$ in (5) diverge precisely at the energies of the bound states of the isolated spherical potential well. Indeed, if the external source vanishes, $\mathcal{D}=0$ in Eq. (4), these are the only allowed energy eigenvalues (depending only on l). With an external source, however, the matching is possible at all energies, and the bound states are broadened into resonances. If E lies near an $l=0$ resonance, for example, the $T_{0,0}$ and $R_{0,0}$ terms are the most significant in the expansions (2a) and (2b) for the transmitted and reflected waves. An analogous argument holds for the $l=1$ case, and so on.

2. *Matching with the surface waves*

So far, the coefficients $T_{l,m}$ and $R_{l,m}$ concerning the well are only formally written in terms of the coefficients $\mathcal{D}_{l,m}$ of the total incident wave. The $\mathcal{D}_{l,m}$ in turn must also be functions of $R_{l,m}$ due to the additional reflection on the sample surface, as depicted in Fig. 2. One therefore requires a further set of independent equations to obtain the complete solution. One method would be to pose a given surface structure for the sample, and again match the wave function explicitly to the solution for the crystal. However, for our purposes this would mean a considerable loss of generality. We have therefore considered a different approach.

For writing the complete solution, let us introduce the Green's function $g_L(\mathbf{r},\mathbf{r}',E)$, corresponding to the Hamiltonian for the surface in the absence of the tip,

$$(H_L-E)g_L(\mathbf{r},\mathbf{r}',E)=-\delta(\mathbf{r}-\mathbf{r}')\ , \tag{6}$$

from which the LDOS is obtained via its imaginary part,

$$\rho_L(\mathbf{r},E)=-\frac{1}{\pi}{\rm Im}\,g_L(\mathbf{r},\mathbf{r},E)\ .$$

This Green's function, as well as the corresponding LDOS, includes the possibility of nonplanar surfaces (such as steps, adatoms, adsorbates, etc.). Our only assumption is that, in the vicinity of the well, the potential is constant.

Now we add the spherical potential well centered at $\mathbf{r}_0$, and the Lippmann-Schwinger (LS) equation for the (total) wave function reads

$$\Psi(\mathbf{r})=\psi_L(\mathbf{r})-V_0\int_\tau d^3r' g_L(\mathbf{r},\mathbf{r}')\Psi(\mathbf{r}') , \tag{7}$$

where $\psi_L(\mathbf{r})$ is the unperturbed wave function of the sample. (We shall throughout suppress the E dependence of g_L). This form for the wave function is particularly convenient: It automatically satisfies the boundary conditions of the problem, and also includes the effects of the surface being nonplanar.

Since the integration in (7) is only over the volume τ of the well, $\Psi(\mathbf{r}')$ in the integrand is exactly the *interior solution* found previously:

$$\psi_t(\mathbf{r})=\sum_{l,m} T_{l,m} j_l(ku) Y_l^m(\hat{\mathbf{u}}) . \tag{2b'}$$

If the Green's function, $g_L(\mathbf{r},\mathbf{r}')$ is also expanded in spherical functions about the center of the well, then the integral over τ can be done analytically. We give the details in Appendix A.

The LS equation can then be solved in terms of quantities related to the unperturbed surface and tip. Retaining only the $l=0$ contribution in the present discussion, the result is

$$\Psi_{\rm II}(\mathbf{r})=\psi_L(\mathbf{r})-\lambda\psi_{\rm inc}(\mathbf{r}_0)\delta g_L(\mathbf{r},\mathbf{r}_0)-\lambda\psi_{\rm inc}(\mathbf{r}_0)g_f(\mathbf{r},\mathbf{r}_0) , \tag{8}$$

with λ related to the well reflection coefficient through $\lambda=-2\pi\hbar^2\mathcal{R}_0/m\kappa$. Here we have written the Green's function as the sum

$$g_L(\mathbf{r},\mathbf{r}')=g_f(\mathbf{r},\mathbf{r}')+\delta g_L(\mathbf{r},\mathbf{r}') .$$

g_f is the free-particle Green's function

$$g_f(\mathbf{r},\mathbf{r}')=-\frac{m}{2\pi\hbar^2}\frac{e^{-\kappa|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} , \tag{9}$$

whose imaginary part vanishes for energies below the vacuum level. The second term δg_L is the contribution only due to the electronic structure of the sample. The wave function in region II can thus be decomposed into these three terms: (i) the unperturbed wave function from the surface, (ii) the reflected waves *off of the surface* whose source is at the point $\mathbf{r}_0$: $\delta g_L(\mathbf{r},\mathbf{r}_0)$, and (iii) the waves reflected by the spherical well $g_f(\mathbf{r},\mathbf{r}_0)$. In Fig. 2 these three terms are labeled ψ_L, ψ', and ψ_r, respectively.

The solution that follows for the total incident wave is then

$$\psi_{\rm inc}(\mathbf{r})=\psi_L(\mathbf{r})-\lambda\psi_{\rm inc}(\mathbf{r}_0)\delta g_L(\mathbf{r},\mathbf{r}_0) . \tag{10}$$

In particular, by taking $\mathbf{r}=\mathbf{r}_0$,

$$\psi_{\rm inc}(\mathbf{r}_0)=\frac{\psi_L(\mathbf{r}_0)}{1+\lambda\delta g_L(\mathbf{r}_0,\mathbf{r}_0)} . \tag{11}$$

We see that the LS equation can be solved in this unique situation. Indeed, $\psi_{\rm inc}(\mathbf{r}_0)$ is written only in terms of quantities of the surface unperturbed by the presence of the well. The electronic structure of the well is only contained in the factor λ. Notice that we have completely avoided mathematical difficulties associated with the divergence of $g_f(\mathbf{r},\mathbf{r}')$ at $\mathbf{r}=\mathbf{r}'$, which is apparently not the case in the method of Ref. 17. [$\delta g_L(\mathbf{r},\mathbf{r}')$ has no such divergence at $\mathbf{r}=\mathbf{r}'$.] In view of Eq. (8), we then have the complete solution for the wave function. Equivalent expressions to (11) for higher angular momentum states (p and d) are derived in Appendix A.

As an example, consider the local density of states at the center of the well,

$$\rho(\mathbf{r}_0,E)=\sum_\nu|\psi_t(\mathbf{r}_0)|^2\delta(E_\nu-E) , \tag{12}$$

which is now straightforward to calculate: Using the interior solution $\psi_t(\mathbf{r}_0)$ in the $l=0$ case, together with the result (11), we obtain

$$\rho(\mathbf{r}_0,E)=|\mathcal{T}_0|^2\frac{\rho_L(\mathbf{r}_0,E)}{|1+\lambda\delta g_L(\mathbf{r}_0,\mathbf{r}_0)|^2} , \tag{13}$$

where $\rho_L(\mathbf{r}_0,E)$ is the unperturbed LDOS of the surface. Equation (13) has the expected resonance behavior near the energy of the bound states, caused by the energy dependence of the denominator. Here, the unperturbed LDOS is renormalized to include multiple reflections between the tip and the sample. Notice that *all orders* must be included to obtain the correct resonance behavior. In Sec. II B we consider the case of the extended tip and find that a similar resonant effect is obtained.

B. Extended tip

The procedure we use for matching the wave function at the extended tip follows very closely the discussion of Sec. II A. We write down the exterior solution in the vicinity of the spherical well, and the corresponding interior solution, with exactly the identical expansions [(2a), (2b), and (2c)]. However, to these we must add the presence of the remainder of the tip. This implies waves incident on the spherical well, as in Fig. 2, of the form

$$\psi_e(\mathbf{r})=\sum_{l,m} D_{l,m} j_l(i\kappa u) Y_l^m(\hat{\mathbf{u}}) , \tag{14}$$

which we add to the external solution and which completely accounts for the coupling to the remainder of the tip. We shall now discuss how both the matching at the tip extremity, and the solution to the *LS* equation, are modified by the presence of ψ_e.

First, since the total incident amplitude on the spherical well is now the sum $\mathcal{D}_{l,m}+D_{l,m}$, the matching conditions at the radius of the well simply become

$$R_{l,m}=\mathcal{R}_l(\mathcal{D}_{l,m}+D_{l,m}) , \tag{15a}$$

$$T_{l,m}=\mathcal{T}_l(\mathcal{D}_{l,m}+D_{l,m}) . \tag{15b}$$

Notice that while the reflection coefficient for the isolated well was $\mathcal{R}_l$, the reflection coefficient for the *entire tip* is found to be

$$\mathcal{R}_{\rm tip}=R_{l,m}/\mathcal{D}_{l,m}=\mathcal{R}_l\left[1+\frac{D_{lm}}{\mathcal{D}_{lm}}\right] . \tag{16}$$

If the extension of the tip is infinite, then $\mathcal{R}_{\rm tip}$ may be complex in some energy ranges. We shall show below that this is the important factor determining whether or not the system carries current.

As an example of these results, consider the special case of the semi-infinite linear chain as the extension of the tip, discussed in detail in Appendix B. In the $l=0$ case, we obtain the factor

$$D_0/\mathcal{D}_0=-1+\exp(ik_Ba)/\chi ,$$

where χ is the coupling between nearest neighbors distant by a lattice constant a: $\chi=\mathcal{R}_0 h_0^+(i\kappa a)$. Here k_B is the Bloch vector related to the energy E of the state via $2\chi\cos(k_Ba)=1$, which defines the s-derived band. χ plays a similar role as the factor $\beta/(E-E_b)$ in a tight-binding approach,[2] β being half the width of a band centered at E_b. The tip reflection coefficient can then be written as

$$\mathcal{R}_{\rm tip}=\mathcal{R}_0\frac{e^{i\kappa_B a}}{\chi} .$$

Since the factor $\mathcal{R}_0$ cancels, $\mathcal{R}_{\rm tip}$ no longer has poles at the energies of the bound states. This is consistent with the broadening of the spectrum into bands: If E lies within a band, the reflection coefficient for the tip does have an imaginary part.

As the matching problem is done, consider then the LS equation for the wave function in region II, which we write symbolically:

$$\Psi_{\rm II}=\psi_L+g_LV\Psi . \tag{17}$$

We then separate the Green's function into two parts, $g_L=g_f+\delta g_L$, and do similarly for the perturbing potential $V=V_{\rm well}+V_e$. The term $V_{\rm well}$ is the spherical potential well, while V_e is the contribution due to the extension of the tip. Assuming no direct coupling between the extension of the tip and the surface, we obtain $\Psi_{\rm II}$ as the sum of four contributions:

$$\Psi_{\rm II}=\psi_L+\delta g_LV_{\rm well}\Psi+g_fV_{\rm well}\Psi+g_fV_e\Psi . \tag{18}$$

The first two terms represent the total incident wave from the surface, which we have previously called $\psi_{\rm inc}(\mathbf{r})$. The third term is the reflected wave from the well on the extremity of the tip ψ_r, while the last term is the reflected wave from the remainder of the tip (which in turn is incident on the spherical well) and is identified with ψ_e. It then suffices to consider only the part of the LS equation concerning the total incident wave:

$$\psi_{\rm inc}=\psi_L+\delta g_LV_{\rm well}\Psi .$$

This equation, however, is *formally identical* to the one solved in Sec. II A for the single potential well, leading to the simple expression for $\psi_{\rm inc}(\mathbf{r}_0)$. However, we obtain a factor λ which is now related to the *total* tip reflection coefficient:

$$\lambda=-\frac{2\pi\hbar^2}{m\kappa}\mathcal{R}_{\rm tip}=-\frac{2\pi\hbar^2}{m\kappa}\mathcal{R}_0\left[1+\frac{D_0}{\mathcal{D}_0}\right] . \tag{19}$$

We thus have the complete solution for the wave function throughout the barrier region II, in the case of the extended tip.

III. TUNNELING CURRENT AND DISCUSSION

The total tunneling current can be calculated by integrating the normal flux density j_z over any plane parallel to S_L and summing over the relevant states:

$$I=2e^2V\sum_\nu\int j_z dS\,\delta(E_\nu-E_F) , \tag{20a}$$

$$j_z=\frac{\hbar}{m}\mathrm{Im}\left[\Psi_\nu^*\frac{\partial\Psi_\nu}{\partial z}\right] . \tag{20b}$$

We use the general expression for $\Psi_{\rm II}(\mathbf{r})$ found in Sec. II, for the $l=0$ case:

$$\Psi_{\rm II}(\mathbf{r})=\psi_L(\mathbf{r})-\lambda\psi_{\rm inc}(\mathbf{r}_0)\delta g_L(\mathbf{r},\mathbf{r}_0)-\lambda\psi_{\rm inc}(\mathbf{r}_0)g_f(\mathbf{r},\mathbf{r}_0)+\psi_e(\mathbf{r}) , \tag{21}$$

with λ given by Eq. (19). Higher-tip angular momenta are considered in Sec. III C. The calculation of I is then relatively straightforward, and we omit the details.

A. Characteristics of the current

We find the following expression for the current:

$$I=\frac{4e^2V}{\hbar}\mathrm{Im}\lambda\sum_\nu|\psi_{\rm inc}(\mathbf{r}_0)|^2\delta(E_\nu-E_F) , \tag{22}$$

where $\psi_{\rm inc}(\mathbf{r}_0)$ is given by (11) above. It presents two major characteristics:

(i) The current is proportional to Imλ, which is also proportional to the imaginary part of the total tip reflection coefficient $\mathcal{R}_{\rm tip}$. We see here that the tip must be infinite in extent (the resulting spectrum must have a continuum). Even a "cluster" tip yields a real value for λ and hence no current can pass through such a system. In the simple case of a semi-infinite linear chain, as calculated in Appendix B, we obtain

$$\mathrm{Im}\lambda=(2\pi\hbar^2/m)ae^{\kappa a}\sin(k_Ba) ,$$

which is also proportional to the group velocity of the electron in the tip. This is in agreement with one-dimensional propagation.

(ii) The second factor implies that the tunneling current is proportional to the local density of states of the surface, but *in the presence of the tip*. More precisely,

$$I=\frac{4e^2V}{\hbar}\mathrm{Im}\lambda\frac{\rho_L(\mathbf{r}_0,E_F)}{|1+\lambda\delta g_L(\mathbf{r}_0,\mathbf{r}_0)|^2} . \tag{23}$$

The latter resembles the result of Tersoff and Hamann,[1] except for the presence of the denominator

$$D=|1+\lambda\delta g_L(\mathbf{r}_0,\mathbf{r}_0)|^2 ,$$

which we shall presently discuss in some detail. Here $\rho_L(\mathbf{r}_0,E_F)$ is the LDOS of the unperturbed surface in the absence of the tip, while $\rho_L(\mathbf{r}_0,E_F)/D$ is the corresponding quantity with the tip present. Then the denominator D can equivalently be interpreted as renormalizing the surface LDOS.

The quantity D involves the waves induced by a source at $\mathbf{r}_0$, reflected by the electrode surface, and detected at $\mathbf{r}_0$. Then $\delta g_L(\mathbf{r}_0,\mathbf{r}_0)$ contains the reflection coefficient at the surface, as well as the usual barrier penetration factor. Furthermore, we have noted that λ is proportional to the tip reflection coefficient; our expression for the tunnel current in (23) is then quite symmetric in the physical quantities related to the tip and sample electrodes.

As an example, for a plane surface in a free-electron (Sommerfeld) model, and taking the potential step U at $z=0$, $\delta g_L(\mathbf{r},\mathbf{r}_0)$ can be written

$$\delta g_L(\mathbf{r},\mathbf{r}_0)=(m/\hbar^2)\int\frac{d^2q}{(2\pi)^2}\frac{1}{\alpha_q}r(\mathbf{q})e^{i\mathbf{q}\cdot\rho}e^{-\alpha_q(z+z_0)}\ , \tag{24}$$

where

$$r(\mathbf{q})=(ik+\alpha_q)/(ik-\alpha_q)$$

and $\rho=\mathbf{x}-\mathbf{x}_0$. Both the normal wave vector k and the decay length $1/\alpha_q$ are q dependent:

$$k=[2m(E+U)/\hbar^2-q^2]^{1/2}\ ,$$

$$\alpha_q=(\kappa^2+q^2)^{1/2}\ .$$

Choosing either z or z_0 sufficiently far from the surface in the barrier, Hurault[29] uses the approximation

$$\delta g_L(\mathbf{r},\mathbf{r}_0)=(m/2\pi\hbar^2)r(\mathbf{0})\frac{\exp[-\kappa\sqrt{\rho^2+(z+z_0)^2}]}{\sqrt{\rho^2+(z+z_0)^2}}\ , \tag{25}$$

which, however, neglects the q dependence in the reflection coefficient but is reasonable for free-electron metals. In this case, $\delta g_L(\mathbf{r},\mathbf{r}_0)$ is a spherical wave whose source appears to be at the *image* of $\mathbf{r}_0$ across the surface. Therefore, for the perfectly planar surface, the quantity $\delta g_L(\mathbf{r}_0,\mathbf{r}_0)$ in our expression for the current goes roughly as $r(\mathbf{0})(e^{-2\kappa z_0}/2z_0)$. Then $\delta g_L\rightarrow 0$ as the barrier thickness increases, and in this limit we obtain complete agreement with an LDOS interpretation for the current, since only the numerator in (23) remains through first order in δg_L. This is not surprising, since in this case no particular electronic effects are encountered, as evidenced in Eq. (25). For example, $r(\mathbf{0})$ is a smooth function of energy near the Fermi level. If the tip is close to the surface, on the other hand, δg_L is not an exponentially small function with z_0, and the denominator must be included in the calculation of the current.

For real surfaces, with a more complex band structure, the general validity of the perturbation expansion involves the condition

$$|\lambda\delta g_L(\mathbf{r}_0,\mathbf{r}_0)|\ll 1\ ,$$

which depends not only on the barrier width (through the argument z_0) but also on both the reflection coefficients at the surface and the tip. Such a condition, then, may not be satisfied for all values of the tunneling energy. This effect could be significant, and we expect even *qualitative* differences predicted by Eq. (23), particularly in those instances described previously in which the perturbation expansion is known to be invalid.[20] The denominator D, being a function of the tip position $\mathbf{r}_0$, may even be necessary to interpret topographic images and the associated corrugations. We also note that the above condition is certainly not satisfied if the tip is close to the surface.

B. Small tip-surface separation

Other authors have treated the coupled states of the tip and sample in the calculation of the tunneling current.[16–18] Here we compare our results to those of Tekman and Ciraci,[9] Ferrer *et al.*,[10] and Doyen *et al.*,[12] all of whom use different methods to treat the tunneling current.

In one approach of Tekman and Ciraci,[9] they first calculate the influence of an additional atom near a graphite surface and interpret its modified electronic structure. This modification, baptized "tip-induced localized states" or TILS, is then included in the matrix elements governing the tunneling process. The authors apparently assume that the TILS for a single atom will be the same as those for an extended tip. The net result of their calculation is an enhancement of the tunneling current, leading also to a larger corrugation. This result depends, however, on a subtle phase relation between the bare sample-tip and the TILS-tip tunneling matrix elements. This must also imply a definite phase relation between the bare sample wave function and the corresponding tip-induced term.

Tip-induced modification of the surface electronic structure is included in our calculation via the total incident wave from the surface $\psi_{\text{inc}}(\mathbf{r})$. Indeed, examining our expression for this quantity (10),

$$\psi_{\text{inc}}(\mathbf{r})=\psi_L(\mathbf{r})-\lambda\psi_{\text{inc}}(\mathbf{r}_0)\delta g_L(\mathbf{r},\mathbf{r}_0)\ ,$$

we note that the second term is precisely the induced wave due to the presence of the tip. In addition, evaluating the above at the center of the tip, $\mathbf{r}=\mathbf{r}_0$, we find the relative amplitude of the induced wave with respect to the bare surface wave to be

$$\frac{-\lambda\delta g_L(\mathbf{r}_0,\mathbf{r}_0)}{1+\lambda\delta g_L(\mathbf{r}_0,\mathbf{r}_0)}\ , \tag{26}$$

the argument of which is the relative phase. Such a phase can take any value depending on the detailed nature of the electronic structures of both the tip and the sample, the position of the tip, and the value of the tunneling energy. Consequently, the relative amplitude given above can lead to an enhancement or a reduction of the tip-induced wave from the surface. In contrast to Tekman and Ciraci's result, the form of this wave is not the same for a single atom tip as for an extended one. It suffices to compare the values of λ, or the reflection coefficients, obtained for the single well and the semi-infinite chain.

In a quite different approach, using a tight-binding formalism, Ferrer *et al.*[10] express the tunneling current in terms of the Green's functions for the surface and the tip multiplied by a tunneling matrix element $|T|^2$. They further neglect the imaginary part of the Green's function compared to its real part, for half-occupied bands. The main goal of their work is to obtain the current for small tip-to-surface separations and to deduce a value for the contact resistance. Within the approximations mentioned above, they find the critical conductance to be exactly $\sigma_c = 2e^2/h$, corresponding to a maximum in the current as a function of distance.

In order to compare with their result, let us select similar conditions, i.e., by taking λ imaginary. For the semi-infinite chain this corresponds to $k_B a = \pi/2$ (E_F lies at the center of the band). Our expression for the tunneling current then becomes

$$I = \frac{4e^2 V}{\pi\hbar} \frac{f}{(1+f)^2 + s^2} , \tag{27}$$

with $f = \pi\,\mathrm{Im}\lambda\rho_L$ and $s = \mathrm{Im}\lambda\,\mathrm{Re}\delta g_L$. If we argue that s, appearing in the denominator, is small compared to f [equivalent to neglecting $\mathrm{Re}(\delta g_L)$ in comparison to $\mathrm{Im}(\delta g_L)$], Eq. (27) is then a function only of f and gives a maximum current for $f = 1$, or a critical value for the conductance of exactly $\sigma_c = 2e^2/h$. However, in general it is difficult to argue that $\mathrm{Re}(\delta g_L)$ is small compared to the imaginary part. Indeed, for the free-electron case described above, it is easy to check that both can be of the same order, and our result gives a lower value for σ_c.

In Fig. 3 we plot the conductance versus tip-surface separation, in the free-electron case, to illustrate this point. The tip was taken to be the semi-infinite chain discussed in Appendix B, while Eq. (24) was used for the surface Green's function. We conclude that the arguments leading to a contact resistance of $h/2e^2$ need to be reconsidered in detail for a given surface: It depends explicitly on the value of $\delta g_L(\mathbf{r}_0, \mathbf{r}_0)$ at the Fermi level, as well as the tip reflection coefficient, and does not appear to take on a universal value. Our results, however, agree qualitatively with those of Ferrer *et al.*, in this example. The denominator plays a key role in the value of the contact resistance.

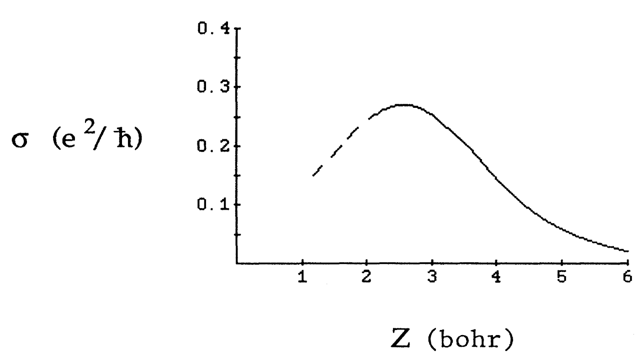

FIG. 3. Plot of tunnel conductance (in units of $e^2/\hbar$) vs tip-surface separation (Bohr) for a free-electron surface, as discussed in the text. The tip is a semi-infinite chain of spherical potential wells, discussed in Appendix B, with a lattice parameter of 4 bohrs. A conductance maximum, slightly less than $2e^2/h$, is encountered when the tip center is 2.6 bohrs from the surface.

Doyen *et al.*[12] have made extensive calculations of the tunneling current between realistic metal surfaces (Al and Pd) and various models for the tip. The principal aim was to account for the observed corrugations on compact metal surfaces. Their calculations include the effect of TILS, which apparently represents a varied contribution to the total current, for the metal surfaces investigated. In agreement with our results, this effect depends on the tip-surface separation, as well as the sample electronic structure: A notable enhancement is obtained for Pd(100), which is not the case for Al. It remains clear, however, that these contributions, which are strongly dependent on the barrier width, should not be calculated using the Bardeen approximation. In addition, these authors have calculated the tunneling current through particular tip orbitals: $6s$, $6p_z$, and $5d_{z^2}$. They find an enhancement effect due to the tungsten d_{z^2} orbital. These results have incited us to use our method to account for higher-tip angular momenta.

C. Tunneling to higher angular momenta tip orbitals

In this paragraph we extend our method in order to give analytical expressions for the tunneling current for p and d orbitals of the tip. If the tip is of tungsten, then s and d states dominate the DOS near the Fermi level, p states being too low in energy. However, p states could arise, for example, if a foreign atom is chemisorbed on the tip. We show that the current can be expressed in terms of the first partial derivatives of $\psi_{\mathrm{inc}}(\mathbf{r}_0)$, for p orbitals, and second-order derivatives of $\psi_{\mathrm{inc}}(\mathbf{r}_0)$ for d orbitals, and so on. The simple relationship between the current and the LDOS at the tip center completely disappears.

For a single arbitrary angular momentum (l,m) of the tip state, one can show that the current is proportional to $|\mathcal{D}_{l,m}|^2$:

$$I \propto \mathrm{Im}\mathcal{R}_{\mathrm{tip}} \sum_{\nu} |\mathcal{D}_{l,m}|^2 \delta(E_\nu - E_F) , \tag{28}$$

where, again, $\mathcal{R}_{\mathrm{tip}}$ is the tip reflection coefficient. If more than a single orbital is involved, then an additional sum over l and m is required. Placing the origin at the center of the tip, the expansion coefficients $\mathcal{D}_{l,m}$ can be written in terms of $\psi_{\mathrm{inc}}(\mathbf{r})$ by taking successive radial derivatives on both sides of Eq. (2c), followed by the limit $\mathbf{r} \to 0$. We find

$$\mathcal{D}_{l,m} = \frac{(2l+1)!!}{l!} (i\kappa)^{-l} \int d\Omega \frac{\partial^l \psi_{\mathrm{inc}}(\mathbf{r}_0)}{\partial r^l} Y_l^m(\hat{\mathbf{r}})^* . \tag{29}$$

This expression shows that the coefficient $\mathcal{D}_{l,m}$ is given by a differential operator of order $l, \hat{\mathcal{D}}_{l,m}$, acting on the total incident wave, and evaluated at the center of the tip:

$$\mathcal{D}_{l,m} = \hat{\mathcal{D}}_{l,m}\psi_{\text{inc}}(\mathbf{r}_0) \; . \tag{30}$$

For example, $\hat{\mathcal{D}}_{1,0}$ is given by

$$\hat{\mathcal{D}}_{1,0} = (12\pi)^{1/2}(i\kappa)^{-1}\frac{\partial}{\partial z} \; , \tag{31}$$

and in Appendix A we list other $\hat{\mathcal{D}}_{l,m}$. Chen[30] has noticed such a "derivative rule" when computing the Bardeen matrix element for the tunneling current. However, it is important to note that our operator $\hat{\mathcal{D}}$ acts on the *total* wave from the surface, which includes the modification due to the presence of the tip, and not on $\psi_L(\mathbf{r}_0)$.

The problem is not complete, however, unless we can express $\hat{\mathcal{D}}\psi_{\text{inc}}$ in terms of the unperturbed quantity $\hat{\mathcal{D}}\psi_L$, as we have done in Sec. II using the Green's-function technique. In Appendix A we show that this is indeed possible, again within the hypothesis of a single tip orbital. In particular, we obtain the following form for $\hat{\mathcal{D}}\psi_{\text{inc}}$:

$$\hat{\mathcal{D}}\psi_{\text{inc}}(\mathbf{r}_0) = \frac{\hat{\mathcal{D}}\psi_L(\mathbf{r}_0)}{1+\lambda\hat{\mathcal{D}}[\hat{\mathcal{D}}']^*\delta g_L(\mathbf{r}_0,\mathbf{r}_0)} \; , \tag{32}$$

where λ is again proportional to the tip reflection coefficient. In the above, $\hat{\mathcal{D}}'$ acts on the surface response function $\delta g_L(\mathbf{r},\mathbf{r}')$ only with respect to its second argument $\mathbf{r}'$.

Returning to the tunneling current, we substitute the solution (32) for the quantity $\hat{\mathcal{D}}\psi_{\text{inc}}(\mathbf{r}_0)$ in Eq. (28) for the current, and obtain the final expression:

$$I \propto \text{Im}\mathcal{R}_{\text{tip}} \frac{\hat{\mathcal{D}}[\hat{\mathcal{D}}']\rho_L(\mathbf{r}_0,\mathbf{r}_0)}{|1+\lambda\hat{\mathcal{D}}[\hat{\mathcal{D}}']^*\delta g_L(\mathbf{r}_0,\mathbf{r}_0)|^2} \; . \tag{33}$$

There is thus a single compact expression for the current to any given orbital of the tip, whether s, p, or d. The latter formula includes tunneling to the $l=0$ orbital, for then $\hat{\mathcal{D}}$ is proportional to the identity operator, and we recover Eq. (23). The tunneling current is written in terms of the *gradients* of the surface response $\delta g_L(\mathbf{r},\mathbf{r}')$, as well as its imaginary part $-\pi\rho_L(\mathbf{r},\mathbf{r}')$, evaluated at the tip center. Our previous discussions apply here: The numerator is the equivalent of the Bardeen approximation, which depends on the surface spectral density with the tip absent, and agrees with the calculations of Chen. Again, we find a denominator, which accounts for tip modification of the surface electronic structure. We have thus derived a convenient analytical form for the tunneling current which accounts for TILS, even in the case of higher-tip angular momenta. To assess its importance, however, means that we must calculate explicitly the quantity $\hat{\mathcal{D}}[\hat{\mathcal{D}}']^*\delta g_L$ for a given surface. Chen has found that the contribution to p_z and d_{z^2} orbitals yields an enhancement of the corrugation, over s states, using the Bardeen approximation. It would then be important to check whether the denominator in (33) plays a significant role, for example, if the tip is close to the surface, or if the sample has a particular electronic structure.

D. Extensions of our work

The expression for the low-bias current could be extended to larger bias following, for example, the discussion by Lang.[31]. We then would obtain a further integration over the energy window from E_F to E_F+eV and the integrand would roughly depend on $\rho_L(\mathbf{r}_0,E)/D(E)$. In the range of investigation of any surface spectroscopy, whether $I(V)$ or dI/dV, if a peak in the density of states is encountered (e.g., an adsorbate level near the sample surface, a defect state, or a surface state), then $D(E)$ may represent an important contribution. Such a peak in the DOS would then appear in both numerator and denominator, which tend to cancel. Furthermore, if the system under investigation (the surface) has a low-dimensional structure, $\rho_L(\mathbf{r}_0,E)$ may have a $E^{-1/2}$ singularity near a band edge in the 1D case, or a logarithmic one in the 2D case. In these instances the independent-electrode approximation may lead to a qualitatively different interpretation. This is important, since many samples in STM are anisotropic, or have low-dimensional electronic structures.

On the other hand, in order to perform tunneling spectroscopy, some investigators prefer to deliberately use blunt tips, while retaining sharp tips for topography, to avoid tip artifacts in the spectra.[8,32] In our calculation, in spite of the general nature of the extended tip, we assume that all the current goes to the well at the tip extremity: It remains essentially a sharp tip. This is also true for the tip in Chen's recent work.[30] Tersoff[7] has suggested a method to interpret the tunneling current for a blunt "incoherent" tip in terms of the solution for a sharp coherent tip (within the local-density-of-states approximation). In the context of our work, a simple remedy for this would be to begin with a number of spherical potential wells arranged in a cluster. These in turn would be coupled to the remainder of the tip, as well as the surface, and one could then apply our method for determining the tunneling current.

IV. CONCLUSION

We have calculated the tunneling current between an arbitrary surface and an extended tip, which terminates in a single spherical potential well. In order to obtain analytical results that go beyond a perturbation approach, we proceeded to solve the matching problem for the total wave function at the tip. It was assumed that only the apex atom of the tip was directly coupled to the surface. The tunneling current was found, in the standard fashion, using the wave function for the system.

The technique used for the matching was the decomposition of the wave function in the barrier in spherical harmonics about the center of the spherical well at the tip extremity. This method may have a much wider application: If more than a single tip atom is strongly coupled to the surface, the decomposition of the surface wave in spherical harmonics about the tip atomic sites could again be exploited.

The tunneling current was expressed in terms of the unperturbed surface and tip electronic structures by solving the Lippmann-Schwinger equation. In particular, we were able to account for the tip-induced wave from the surface, which depends on a part of the sample Green's function: $\delta g_L(\mathbf{r},\mathbf{r}_0)$. This quantity represents the surface response: It involves the waves induced by a point source at $\mathbf{r}_0$, the position of the tip, reflected at the sample surface, and detected again at $\mathbf{r}$. For $l=0$ tip orbitals, we showed that the current is then expressed simply in terms of $\delta g_L(\mathbf{r}_0,\mathbf{r}_0)$. In a symmetric fashion, the current also depends on the tip reflection coefficient. This is expected, since multiple reflections to all orders, between the tip and the sample, are included in our calculation. In this sense, our formula for the tunneling current goes beyond perturbation theory, and is not simply proportional to the LDOS at the surface.

We have also shown that the current can be interpreted in terms of the LDOS of the surface but *in the presence of the tip,* equivalent to the effect of TILS. We discussed in what instances these effects may be important, such as for surfaces where the electronic structure is highly accidented, or if the tip is close to the surface. Furthermore, we can obtain either a reduction or an enhancement of the current, but this depends explicitly on the value of δg_L at the tunneling energy.

We used our method to calculate the tunnel current to orbitals of higher angular momenta: p and d states. A compact expression was obtained that displayed many of the characteristics of the s-wave case. The current is then related to the gradients of the surface spectral density $\rho(\mathbf{r}_0,\mathbf{r}_0)$, but again including the presence of the tip. This, in turn, could be expressed in terms of the gradients of the same quantity δg_L, and again we found a characteristic denominator. For higher-tip angular momenta, the simple relation between current and LDOS is lost.

We have shown the form of δg_L for a free-electron metal, and this quantity should be feasible to calculate for a real surface. This would be necessary, for example, to obtain a better understanding of STM topography, and may provide some insight into the energy dependence of the tunneling current.

APPENDIX A: EVALUATION OF THE LIPPMANN-SCHWINGER EQUATION

We have found a solution to the Lippmann-Schwinger equation for the total wave function, which we detail here for the case of the single spherical potential well near the surface. Following the definitions of Sec. II, if $\psi_L(\mathbf{r})$ is the unperturbed surface wave function, $g_L(\mathbf{r},\mathbf{r}')$ the left Green's function, and $V(\mathbf{u})=-V_0\theta(R-u)$ the perturbing potential, then Ψ_{II} is exactly written

$$\Psi_{\mathrm{II}}(\mathbf{r})=\psi_L(\mathbf{r})-V_0\int_\tau d^3r' g_L(\mathbf{r},\mathbf{r}')\Psi(\mathbf{r}') , \tag{A1}$$

where τ is an integration only over the volume of the well. It is convenient to separate g_L into two terms:

$$g_L(\mathbf{r},\mathbf{r}')=g_f(\mathbf{r},\mathbf{r}')+\delta g_L(\mathbf{r},\mathbf{r}') ,$$

where the former is the free-particle Green's function, defined in Eq. (9), and the latter is the surface term. Furthermore, $\Psi(\mathbf{r}')$ in the integrand is the interior solution $\psi_t(\mathbf{r}')$ to the well (region III); thus we can write

$$\Psi_{\mathrm{II}}(\mathbf{r})=\psi_L(\mathbf{r})-V_0\int_\tau d^3r'\delta g_L(\mathbf{r},\mathbf{r}')\psi_L(\mathbf{r}') \\ -V_0\int_\tau d^3r' g_f(\mathbf{r},\mathbf{r}')\psi_t(\mathbf{r}') . \tag{A2}$$

The third term is simply the reflected wave $\psi_r(\mathbf{r})$, whose expansion in region II is known, and which contains no new information. On the other hand, the first two terms represent the total incident wave from the surface, which we have called $\psi_{\mathrm{inc}}(\mathbf{r})$:

$$\psi_{\mathrm{inc}}(\mathbf{r})=\psi_L(\mathbf{r})-V_0\int_\tau d^3r'\delta g_L(\mathbf{r},\mathbf{r}')\psi_t(\mathbf{r}') . \tag{A3}$$

The integration over τ can be done analytically by using the spherical expansion of ψ_t about the center of the well, used in the matching problem of Sec. II:

$$\psi_t(\mathbf{r})=\sum_{l,m} T_{l,m} j_l(kr) Y_l^m(\hat{\mathbf{r}}) . \tag{A4}$$

Here we have placed the origin at the center of the well. Then we also expand $\delta g_L(\mathbf{r},\mathbf{r}')$ in spherical functions about the center of the well, with respect to its second argument $\mathbf{r}'$. Notice that $\delta g_L(\mathbf{r},\mathbf{r}')$ is a solution to the Schrödinger equation with a constant potential, in the region over which the integration is performed. Its expansion in spherical functions about the center of the well can be written exactly as the one for $\psi_{\mathrm{inc}}(\mathbf{r})$ in Eq. 2(c):

$$\delta g_L(\mathbf{r},\mathbf{r}')=\sum_{l,m}\mathcal{C}_{l,m}(\mathbf{r}) j_l(i\kappa r') Y_l^m(\hat{\mathbf{r}}')^* . \tag{A5}$$

In fact, the coefficients $\mathcal{C}_{l,m}(\mathbf{r})$ can be obtained in much the same fashion as the previous coefficients $\mathcal{D}_{l,m}$. Making these substitutions in the integral of (A3), the integration over the solid angle is straightforward due to the orthogonality of the spherical harmonics. We can also use the matching relation at the radius of the well, $T_{l,m}=\mathcal{T}_l\mathcal{D}_{l,m}$, to eliminate $T_{l,m}$. The expression for the incident wave then becomes

$$\psi_{\mathrm{inc}}(\mathbf{r})=\psi_L(\mathbf{r})-\sum_{l,m}\mathcal{C}_{l,m}(\mathbf{r})\mathcal{D}_{l,m}\lambda_l , \tag{A6}$$

with the final quadrature

$$\lambda_l=V_0\mathcal{T}_l\int_0^R r^2 j_l(i\kappa r) j_l(kr) dr$$

solvable analytically in terms of the spherical Bessel functions evaluated at the radius of the well. (A6) is then the starting point for studying the general case of higher than $l=0$ angular momentum terms.

In the particular instance of an $l=0$ state of the well, we can retain only one term in the expansion. Then using the property that

$$\mathcal{C}_0=(4\pi)^{1/2}\delta g_L(\mathbf{r},\mathbf{r}_0)$$

and analogously, $\mathcal{D}_0=(4\pi)^{1/2}\psi_{\mathrm{inc}}(\mathbf{r}_0)$, (A6) becomes

$$\psi_{\mathrm{inc}}(\mathbf{r})=\psi_L(\mathbf{r})-4\pi\lambda_0\psi_{\mathrm{inc}}(\mathbf{r}_0)\delta g_L(\mathbf{r},\mathbf{r}_0) . \tag{A7}$$

Finally, since

$$4\pi\lambda_0=-2\pi\hbar^2\mathcal{R}_0/m\kappa=\lambda ,$$

we obtain the expression for the total incident wave, Eq. (10), as used in the text including the particular solution

$$\psi_{\rm inc}(\mathbf{r}_0)=\frac{\psi_L(\mathbf{r}_0)}{1+\lambda\delta_L(\mathbf{r}_0,\mathbf{r}_0)} \ . \tag{A8}$$

Let us consider briefly the problem concerning higher angular momentum states of the tip, relevant to the discussion in Sec. III C. Examining the general case (A6) above, we see that if we choose $l=1$, then there are three coupled equations for the $\mathcal{D}_{1,m}$ and five coupled equations for the $\mathcal{D}_{2,m}$, etc. Picking out only a single orbital then uncouples these equations, which we have not yet attempted to justify. For considering tunneling to an individual orbital, it is convenient to rewrite (A6) in terms of the differential operator $\hat{\mathcal{D}}$ [as discussed following Eq. (29)]. Using

$$\mathcal{D}_{l,m}=\hat{\mathcal{D}}\psi_{\rm inc}(\mathbf{r}_0) \ ,$$

$$\mathcal{C}_{l,m}(\mathbf{r})=[\hat{\mathcal{D}}']^*\delta g_L(\mathbf{r},\mathbf{r}_0) \ ,$$

and keeping only one term in the sum, corresponding to a given tip orbital, we obtain

$$\psi_{\rm inc}(\mathbf{r})=\psi_L(\mathbf{r})-\lambda_l\hat{\mathcal{D}}\psi_{\rm inc}(\mathbf{r}_0)[\hat{\mathcal{D}}']^*\delta g_L(\mathbf{r},\mathbf{r}_0) \ . \tag{A9}$$

Then operating once on the entire equation with $\hat{\mathcal{D}}$ (followed by $\mathbf{r}\rightarrow\mathbf{r}_0$), we obtain the desired result:

$$\hat{\mathcal{D}}\psi_{\rm inc}(\mathbf{r}_0)=\frac{\hat{\mathcal{D}}\psi_L(\mathbf{r}_0)}{1+\lambda_l\hat{\mathcal{D}}[\hat{\mathcal{D}}']^*\delta g_L(\mathbf{r}_0,\mathbf{r}_0)} \ , \tag{A10}$$

since the gradients of the total incident wave $\hat{\mathcal{D}}\psi_{\rm inc}$, at the position of the tip, are factored into quantities related only to the unperturbed surface and unperturbed tip electronic structures.

We finally give a short discussion of the operators $\hat{\mathcal{D}}$. Following the general formula (29) for the expansion coefficients $\mathcal{D}_{l,m}$ and then expressing the normal derivative in Cartesian coordinates $x_i=(x,y,z)$, we obtain the useful formula

$$\mathcal{D}_{l,m}=\frac{(2l+1)!!}{l!}(i\kappa)^{-l}\sum_{i,j,\ldots,n}\frac{\partial^l\psi_{\rm inc}(\mathbf{r}_0)}{\partial x_i\partial x_j\ldots\partial x_n} \times\int d\Omega\frac{x_ix_j\ldots x_n}{r^l}Y_l^m(\hat{\mathbf{r}}) \ . \tag{A11}$$

The integral over the solid angle involves only the lth rank Cartesian tensor: $x_ix_j\ldots x_n/r^l$ and the spherical harmonic. For s, p, and d orbitals, with $m=0$, the operator is given by

$$\begin{aligned} &l=0,\quad m=0,\quad \hat{\mathcal{D}}=(4\pi)^{1/2} \\ &l=1,\quad m=0,\quad \hat{\mathcal{D}}=(12\pi)^{1/2}(i\kappa)^{-1}\frac{\partial}{\partial z} \\ &l=2,\quad m=0,\quad \hat{\mathcal{D}}=(20\pi)^{1/2}(i\kappa)^{-2}\left[3\frac{\partial^2}{\partial z^2}-\kappa^2\right] \ . \end{aligned} \tag{A12}$$

We also note that $\hat{\mathcal{D}}_{1,\pm1}$ involves derivatives with respect to the coordinate parallel to the surface:

$$\hat{\mathcal{D}}_{1,\pm1}=\mp(24\pi)^{1/2}(i\kappa)^{-1}\left[\frac{\partial}{\partial x}\mp i\frac{\partial}{\partial y}\right] \ . \tag{A13}$$

APPENDIX B: SEMI-INFINITE LINEAR CHAIN

In this appendix we calculate the total tip reflection coefficient

$$\mathcal{R}_{\rm tip}=\mathcal{R}_l\left[1+\frac{D_{lm}}{\mathcal{D}_{lm}}\right]$$

for a semi-infinite array of spherical potential wells chosen for the *extension* of the tip, following Sec. II. Recall that $\mathcal{D}_{lm}$ and D_{lm} and are the expansion coefficients of the total wave from the surface $\psi_{\rm inc}(\mathbf{r})$ and the remainder of the tip $\psi_e(\mathbf{r})$, respectively. Here we calculate $\mathcal{R}_{\rm tip}$ for the semi-infinite chain, but within the $l=0$ approximation, which is needed for our expression of the tunneling current. We label each well with the index n, with $n=1$ designating the first well to the right of the well on the tip extremity, for which the matching problem has already been solved. Nearest-neighboring wells are separated by a distance a.

The electronic structure of the tip, the form of the wave function, and the tip reflection coefficient can be obtained by solving the matching problem at each well of the remainder of the tip. Consider first the case of the *isolated* semi-infinite chain: The external solution must be a sum of reflected waves from each well:

$$\psi_r(\mathbf{r})=\sum_n\sum_{l,m}R_{l,m}^n h_l^+(i\kappa u_n)Y_l^m(\hat{\mathbf{u}}_n) \ , \tag{B1}$$

with $\mathbf{u}_n$ the vector $\mathbf{u}_n=\mathbf{r}-\mathbf{r}_n$. This must match the interior solution $\psi_t(\mathbf{r})$ at the surface of the nth well:

$$\psi_t(\mathbf{r})=\sum_{l,m}T_{l,m}^{n'}j_l(ku_{n'})Y_l^m(\hat{\mathbf{u}}_{n'}) \ . \tag{B2}$$

The result of this matching gives relations between the coefficients $R_{l,m}^n$ and $T_{l,m}^n$ similar to those obtained for the single sphere with an external source, detailed in Sec. II. One can show that, within the $l=0$ approximation, the reflected amplitudes must satisfy

$$R_0^{n'}=\sum_{n\neq n'}R_0^n\mathcal{R}_0h_0^+(i\kappa|\mathbf{r}_n-\mathbf{r}_{n'}|) \ . \tag{B3}$$

Interestingly, this relation is valid for any configuration of potential wells, and could describe a tip having a more complex structure. For the linear chain, keeping only nearest neighbors, $n=n'\pm1$, and defining the coupling $\chi=\mathcal{R}_0h_0^+(i\kappa a)$ gives the familiar recursion relation

$$R_0^n=\begin{cases}\chi(R_0^{n+1}+R_0^{n-1}), & n>1 \quad \text{(B4a)}\\ \chi R_0^2, & n=1 \ . \quad \text{(B4b)}\end{cases}$$

The solution for R_0^n is then a linear combination of e^{ik_Bna} and e^{-ik_Bna}, where k_B is the reciprocal vector related to the energy E of the state via $2\chi\cos(k_Ba)=1$, defining the s-derived band.

Since the isolated linear chain is solved, we consider the same problem but with an external source: This source is due to the presence of the well at the extremity of the tip, which in turn is coupled to the surface. The presence of this source modifies only Eq. (B4b), to which we add the source term S:

$$R_0^1=\chi R_0^2+S \ . \tag{B5}$$

We then find the particular solution to the recursion relations corresponding to flux transmitted to the right in our system:

$$R_0^n=\frac{Se^{ik_B na}}{\chi} \ . \tag{B6}$$

The latter then gives the form for the total reflected wave from the extension of the tip, using the expansion (B1). In order to calculate the tip reflection coefficient for the $l=0$ case:

$$\mathcal{R}_{\text{tip}}=\mathcal{R}_0\left[1+\frac{D_0}{\mathcal{D}_0}\right] ,$$

we need the relation between the two coefficients D_0 and $\mathcal{D}_0$. The former is straightforward to obtain within the nearest-neighbor approximation: It is the $l=0$ component of the wave reflected from the site $n=1$, and is thus proportional to R_0^1. We obtain

$$D_0=\frac{Se^{ik_B a}}{\chi}h_0^+(i\kappa a) \ . \tag{B7}$$

In addition, one can easily show that the source factor S, above, is related to the reflected amplitude off the well on the extremity of the tip:

$$S=\chi R_0=\chi\mathcal{R}_0(D_0+\mathcal{D}_0) \ . \tag{B8}$$

Combining Eqs. (B7) and (B8), we obtain the desired ratio $D_0/\mathcal{D}_0=e^{2ik_B a}$. Then the total tip reflection coefficient for the linear chain can be determined:

$$\mathcal{R}_{\text{tip}}=\frac{\mathcal{R}_0 e^{ik_B a}}{\chi}=\frac{e^{ik_B a}}{h_0^+(i\kappa a)} \ . \tag{B9}$$

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