Time-independent tunneling current of a tip-sample system in scanning tunneling spectroscopy

Fredy R. Zypman
Department of Physics and Electronics, University of Puerto Rico, Humacao, Puerto Rico 00791

Luis F. Fonseca
Department of Physics, University of Puerto Rico, Rio Piedras, Puerto Rico 00931
(Received 24 August 1994)

When analyzing data from scanning tunneling spectroscopy (STS) it is generally assumed that the density of states and local density of states (LDOS) are simply related with the current-voltage (I-V) curves. This assumption has been derived phenomenologically within the framework of theories developed for a variety of situations. We continue here with the development of a theory of STS with concrete applications for semiconducting samples, going beyond the traditional Bardeen approximation. As in previous works, our present model provides a current that is a sum over tip states of semiconductor local density of states modulated by tip-dependent coefficients. For a tungsten tip and silicon sample, we find that these coefficients are nonzero only for energies close to the Fermi energy. This makes the I-V curve closely follow the LDOS. On the other hand, we have found that the conductance-voltage curves present features derived from the Van Hove singularities of the semiconductor.

I. INTRODUCTION

In scanning tunneling spectroscopy (STS), the current-voltage (I-V) and conductance-voltage (σ-V) curves of a tip-sample system are used to extract information about the sample density of states (DOS) and local density of states (LDOS). This has been done experimentally on semiconductors,[1-3] superconductors,[4] and metals.[5] Today, after many theoretical studies have appeared in the literature,[6-14] there is yet no agreement on what is the exact relationship between I-V or/and σ-V, and the densities of states. For low voltages, the Tersoff and Hamann theory[6] has proved to be successful in explaining experimental data. Lang,[15] Selloni *et al*,[16] and Tsukada *et al.*[17] have extended the calculations to finite voltages. On the other hand, there have been models to describe specifically scanning tunneling microscopy (STM) on metals[18-20] and on semiconductors.[21] A common feature of most of these approaches is the use of Bardeen approximation[22,23] to evaluate the electron transition probability from tip to sample. This approximation is so popular because it is simple and gives results which are consistent with experimental observations at certain tip-sample distances. However, the range of validity of the approximation requires clarification, and alternative approaches are required for ranges where the Bardeen approximation fails. Basically Bardeen's formula provides the interaction Hamiltonian between two, somewhat distant, systems. From the Hamiltonian, one can calculate the tunneling transition rate between the systems. This is basically a time-dependent calculation. Since the typical tip-sample distances are of a few Å, we are dealing with a clearly quantum system and, therefore, it is not unreasonable to expect the formation of states that extend into both tip and sample which will make the electron transfer from tip to sample a steady-state one. Under these conditions, we can still talk of tunneling because the tip and the sample are two clearly defined and distinct systems (this does not necessarily mean that the Bardeen approximation applies though). In fact, the issue of resonant tunneling versus sequential tunneling to explain the mechanism of tunneling through quantum wells has been a subject of debate. From a fundamental standpoint, it is correct to solve the appropriate steady-state problem for the tunneling between the tip and the sample. In this paper, we introduce a theoretical framework that makes no use of Bardeen approximation and within which it is possible to compare characteristic curves and densities of states. There are two main reasons to follow this path. First, following our previous discussion, in typical STM and STS conditions (tip-sample voltage of few volts and tip-sample distance of 1–5 Å) it is expected that global tip-sample effects are of importance and thus, the behavior of the electron wave function between tip and sample does not have to be that of an evanescent exponential but could have some richer structure. Second, since the Bardeen approximation has been successful in certain cases, it would be of use of gauge its range of validity. We model the tip-sample system as two cubes, one for the tip and one for the sample, linked by an atom (c atom, for channel atom) of the same chemical nature as the tip. Microscopically, we assume that the cubes have simple cubic cell structure (different from each other). Then, we find the energies and wave function in the tight-binding (TB) approach. With suitable boundary conditions, we consider only those Bloch functions that come from far away within the tip. By choosing appropriate TB parameters, we can account for a metallic tip and a semiconductor sample. In the next section, we present the general theory for this model and in the following section, we present concrete results for the case of a tungsten tip and a silicon sample.

Our results show that I-V follows closely the LDOS of the sample at the Fermi energy at the position of the c

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atom. This resemblance is better as the tip-sample distance increases, which is in accordance with calculations based on the Bardeen approximation. The σ-V curve presents characteristics that are borrowed from the van Hove singularities of the DOS of the sample.

II. THEORY

In order to calculate the tunneling current, we start by obtaining the proper energies and wave functions. Consider the system (Fig. 1) to be the union of a semiconductor with simple cubic structure with N_S Wigner-Seitz cells on a side, a metal with simple cubic structure and N_T Wigner-Seitz cells on a side and, inlaid between them, a c atom that serves as the channel for current between metal and semiconductor. Its energy states are considered in the near-neighbor TB approach[24] with an s-type basis function (cubium model[25]). This type of approach has been used in the past to study chemisorption on surfaces[25–27] and DOS of surface states.[28] In this context, the global wave function has the following expression at the tip and sample locations:[29]

$$\Psi_{\mathbf{k}}^{T}=\sum_{\mathbf{m}=\text{tip sites}} C_{\mathbf{m},\kappa}\Phi_{\mathbf{m}} , \tag{1}$$

$$\Psi_{\mathbf{k}}^{S}=\sum_{\mathbf{m}=\text{sample sites}} C_{\mathbf{m},\kappa}\Phi_{\mathbf{m}} , \tag{2}$$

where $\mathbf{k}$ is the tip electron crystal momentum, κ the sample crystal momentum, $\Phi_{\mathbf{m}}$ are s-type atomic orbitals, and $C_{\mathbf{k},\mathbf{m}}$ and $C_{\kappa,\mathbf{m}}$ are the expansion coefficients. The vector index $\mathbf{m}$ tags both tip and sample atomic sites, and can take $N_T^3+N_S^3+1$ different values. We impose, as the first boundary condition, that the wave function, far away from the c atom, be a Bloch wave;

$$C_{\theta,\mathbf{m}} \propto e^{\pm i\mathbf{m}\theta} \quad \text{for } |\mathbf{m}-\mathbf{m}_{c-\text{atom}}| \geq m_0 , \tag{3}$$

where m_0 is a number that gives an idea of the extent of the tunneling region. One expects it to be a single-digit number, because bulk properties are present a few atoms away from a perturbation to the perfect-crystal structure. In Eq. (3), θ is defined in the tip as $\mathbf{k}$ times the tip lattice constant, and in the sample as κ times the sample lattice constant. Concretely, in that far-away region, we take for the tip the sum of an electron wave function with amplitude $|A|^2$ that comes from far away in the bulk, plus an electron wave function with amplitude $|B|^2$ that moves away from the tunneling region, and into the bulk,

$$C^T=e^{i(m_x\theta_x^T+m_y\theta_y^T)}(Ae^{im_z\theta_z^T}+Be^{-im_z\theta_z^T}) . \tag{4}$$

For the sample, we consider an electron that moves away from the tunneling region, towards the sample bulk region with unit amplitude,

$$C^S=e^{i(m_x\theta_x^S+m_y\theta_y^S)}e^{im_z\theta_z^S} . \tag{5}$$

With these assumptions, total reflection corresponds to the case $A=\pm\infty$, and, in general, the transmission probability is given by $|A|^{-2}$. Strictly speaking, the electron tunneling involves a scattering process in which Bloch waves move away from the c atom in all directions in both tip and sample. We, however, wrote down a simpler form in which the total scattered wave is concentrated in a forwardly transmitted and a specularly reflected electron. This assumption is correct in the far-away region (where we set our boundary conditions) as can be inferred from previous calculations.[7] In the tunneling region, where the previous assumption does not necessarily hold, our results contain the full scattered wave.

The energy of the whole system is parametrized like in bulk as

$$\begin{aligned} E&=\alpha^T+2\beta^T(\cos\theta_x^T+\cos\theta_y^T+\cos\theta_z^T)\\ &=eV+\alpha^S+2\beta^S(\cos\theta_x^S+\cos\theta_y^S+\cos\theta_z^S) , \end{aligned} \tag{6}$$

where V is the voltage applied between the tip and the sample and e is the charge of the electron. α is the Coulomb integral and β the resonance integral.

By using TB, we can calculate all the coefficients in the tunneling region and A and B. Thus, we can calculate the total current between tip and sample,

$$I=\frac{1}{(2\pi)^3}\int_{E<E_F} d\theta^T \frac{1}{|A|^2}(-e)n^T\Omega v_z^T , \tag{7}$$

where n^T is the electronic density of the tip, Ω is the tip transverse area in the bulk region, and v_z^T is the electron velocity in the tip along the tunneling direction, and can be explicitly calculated as

$$v_z^T=\frac{1}{\hbar}\frac{\partial E}{\partial k_z}=\frac{1}{\hbar a^T}\frac{\partial E}{\partial \theta_z}=-\frac{2\beta^T}{\hbar a^T}\sin\theta_z^T , \tag{8}$$

where a^T is the tip lattice constant and the definition of θ was used. Finally, the current takes the form

$$I=\frac{en^T\Omega\beta^T}{4\pi^3\hbar a^T}\int_{E<E_F} d\theta^T\frac{\sin\theta_z^T}{|A|^2} , \tag{9}$$

which is the form we used to evaluate the results of the next section. The main result of this paper is the method we proposed for the evaluation of A in Eq. (9).

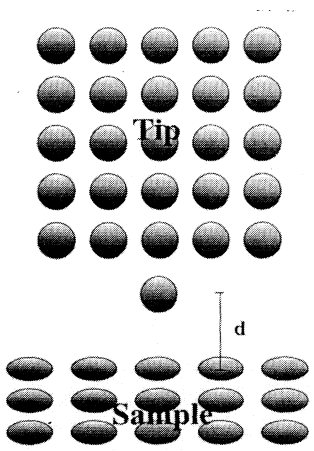

FIG. 1. Tip-sample system.

III. APPLICATION TO A W TIP AND Si SAMPLE

In this section, we apply the general results obtained in Sec. II, to the particular and common case in which a tungsten tip is used to investigate a silicon sample. In order to obtain the proper bulk energy band gap for the Si, and Fermi energy for W, we take $\alpha_s = -9$ eV, $\beta_s = 0.67$ eV, $E_F = -13.5$ eV, the minimum energy of the tip is located at -19.5 eV. In the tunneling region, we assume that the c atom interacts with tip and sample through the proper resonance integrals as $\beta_{c\text{-}T} = 3.5$eV, $\beta_{c\text{-}S} = 41537.63 d^4 e^{-5.358d}$, where d is the separation between the c atom and the sample surface, and β is in eV and d in Å (Refs. 30–32) (the decay lengths of tip and sample are 0.4 and 0.35 Å, respectively). With these parameters, we investigated various features of the system. First, we want to know to what extent does $I(V)$ follow the sample LDOS. Figure 2 shows I-V and LDOS for tip-sample separations of 1, 3, and 5 Å. We can see that, as the separation is increased, the two curves have a closer resemblance and, therefore, the STM measures the LDOS roughly for separations of 3 Å and up. This result is in agreement with work on metals,[3,33] at low voltages, in general,[6] and with similar works.[34,35]

The source of the disagreement at small separations, comes from the fact that the tip substantially affects the sample wave function and the sample loses its identity. It is interesting to note that at large distances, the well known Bardeen approximation is valid and predicts that $I(V)$ is proportional to the LDOS. So we find that approximation breaks down at small separations, where it is not possible to describe the tip and sample wave functions as exponentially decaying in vacuum. An experimental check of the break down of Bardeen approximation at small distances would be the detection of resonant tunneling instead of sequential tunneling.[36]

A second question we address here is as follows: what are the states that contribute most to the current? For that purpose, in Fig. 3 we plot together (for $d = 1$, 3, and 5 Å), the I-V due to all states, and the I-V produced by a narrow band (less than 2.5 eV) below E_F. We see that both curves agree very well and, therefore, the current is coming mostly from states with energies close to E_F. Figure 4(a) shows a $\theta_z^T = f(\theta_x^T, \theta_y^T)$ contour plot of the tip Fermi sphere, and 3(b) the sample Fermi surface for various voltages. From this figure, it is seen that the maximum overlap between the volumes within these surfaces occurs at $V \approx 2$ V, which coincides with the position of the $I(V)$ peak. We see that $(\theta_x^T, \theta_y^Y) \approx (\pm\pi, \pm\pi)$. For the W parameters, $\sin(\theta_z^T) \approx 1$ and, therefore, in Eq. (9) the sine term should not affect the current. To recheck this, in Fig. 5, we plot the current again, as calculated from

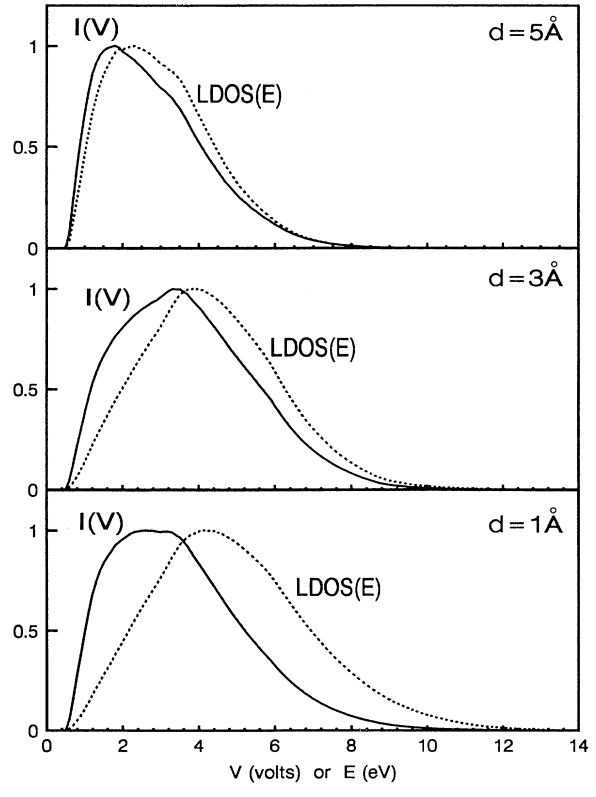

FIG. 2. Normalized tunneling current (continuous curve) and LDOS (dashed) as a function of voltage or energy, respectively, for the following tip-sample separations: (a) 5 Å, (b) 3 Å, (c) 1 Å.

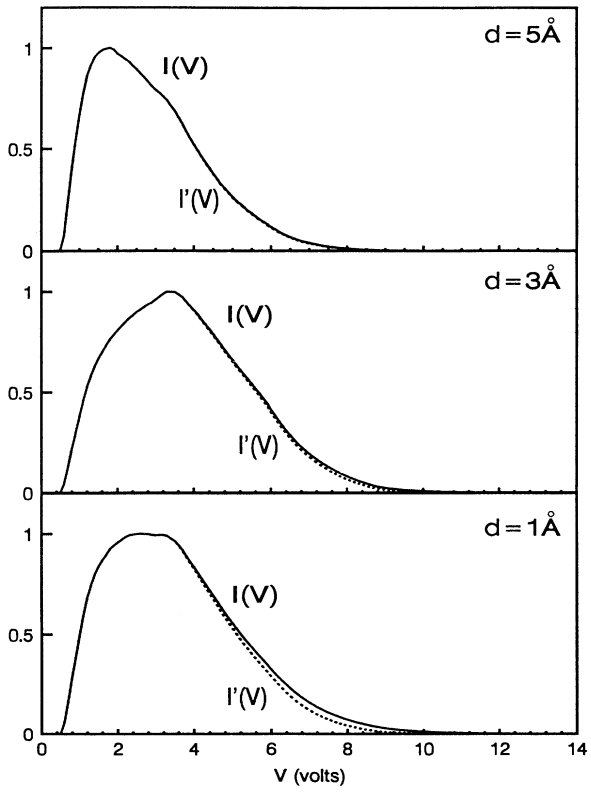

FIG. 3. The continuous line shows the normalized tunneling current as a function of voltage as in Fig. 2. Also shown (dashed) are the tunneling currents produced by states whose energies are close to E_F.

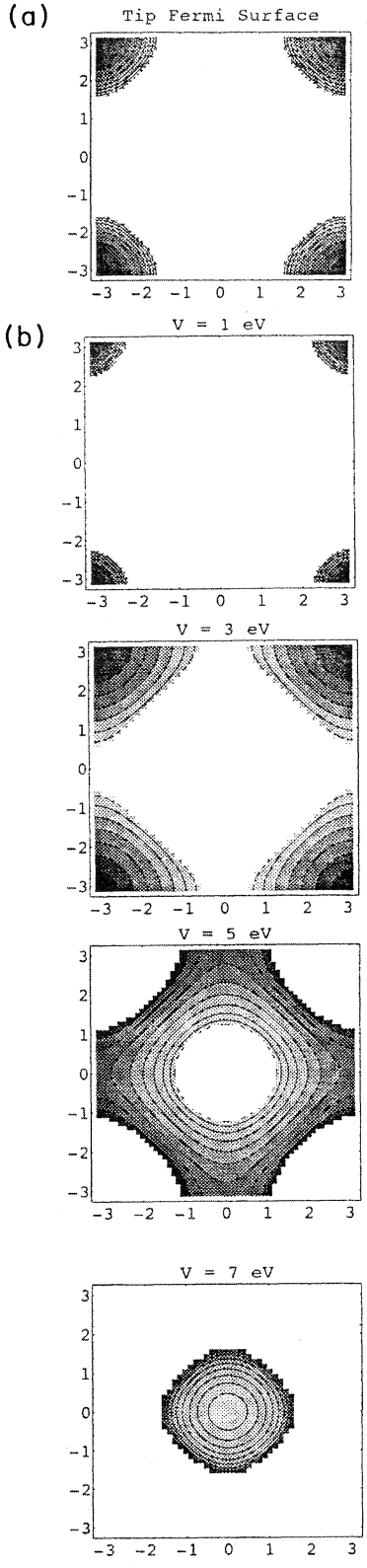

FIG. 4. (a) Fermi sphere for the bulk states of the tip. (b) Fermi surfaces for the bulk states of the sample for various tip-sample voltages. The horizontal axis represents θ_x and the vertical axis θ_y, both in radians.

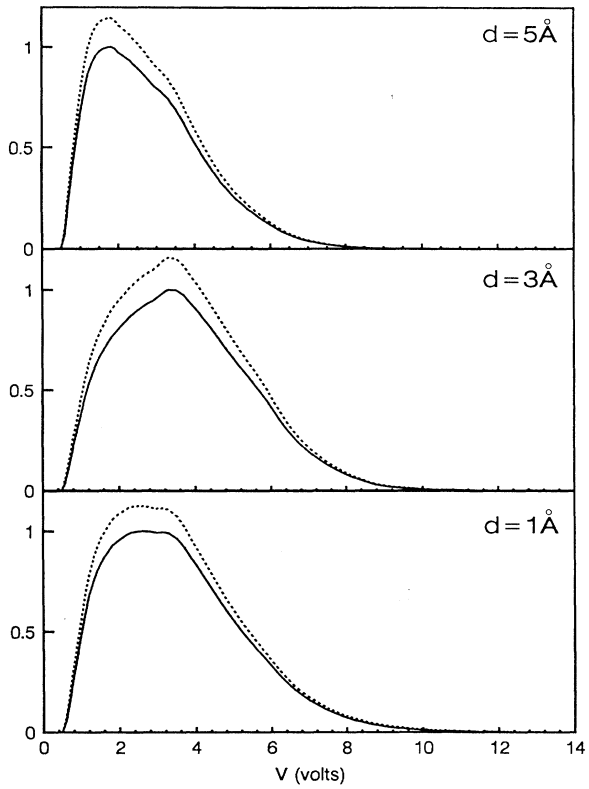

FIG. 5. Comparison between normalized tunneling current (continuous curve) and current with the velocity in Eq. (9) taken to be constant equal to V_F (dashed).

Eq. (9) and also calculated without the sine term. We see that both curves agree at any of the distances considered.

Finally, we use our model to study the relationship between density of states and dI/dV. This is important since it has been argued that is this quantity, and not I-V which is relevant.[37] Figure 6 shows a dI/dV curve for a

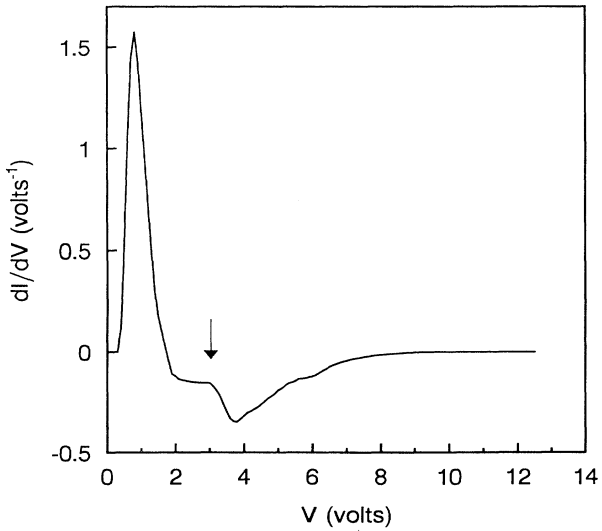

FIG. 6. dI/dV vs voltage for 5-Å tip-sample separation. A jump in the function can be seen at about 3.5 eV, which corresponds to the first Van Hove singularity of the sample.

tip-sample separation of 5 Å. The more interesting feature is that is presents nondifferentiable points which correspond to the Von Hove singularities of the DOS of the sample. Concretely, we see a jump of dI/dV at 3.5 V, which comes from the Van Hove singularity of Si. The jump is not extremely sharp because as the voltage varies, a few tip states close to E_F contribute to the current.

IV. CONCLUSIONS

We have presented a method for calculating steady-state tunneling current in STM by using running Bloch functions. We have used the method to study the common experimental situation of a tungsten tip and a silicon sample. Results show that I-V curves follow the sample LDOS unless the tip-sample distance becomes too small. At small distances tip and sample are indistinguishable and the concept for sample LDOS is meaningless.

We have found that, at distances below 3 Å, Bardeen approximation stops to provide good results. Our model provides a good tool to investigate resonant tunneling that is more important in the small distances regime. Our results also prove that most of the tunneling current comes from states with enegies close to the Fermi energy.

In agreement with previous work,[21] we found that dI/dV present nondifferentiable points that come from the Van Hove singularities of the sample. Last, from an experimental point of view, we provide a framework within which alternative experimental results can be interpreted. Although working with the STM in regimes in which the particular shape of the tip and/or sample wave functions is relevant would make it difficult to extract microscopic information, that is not to say that people would not like to investigate those regimes. In fact, a lot of new important science may be obtained there.

ACKNOWLEDGMENTS

This work was supported by Grant No. NSF EHR-9108775 (L.F.) and Nos. NIH CA60041-01 and NASA NAG8-1003 (F.Z.).

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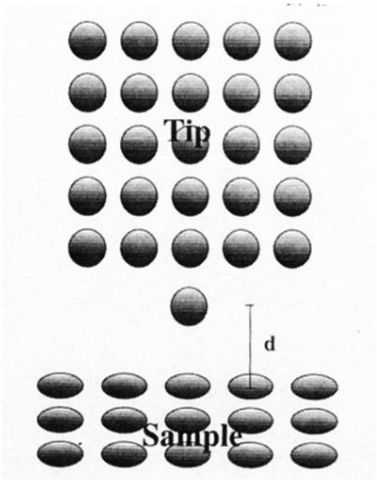

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