Tip orbitals and the atomic corrugation of metal surfaces in scanning tunneling microscopy

William Sacks
Groupe de Physique des Solides, Universités Paris 7 et Paris 6, Unité Mixte de Recherche C.N.R.S. (UMR 75 88), 2 place Jussieu, 75251 Paris Cedex 5, France
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When atomic resolution is achieved, the scanning tunneling microscope (STM) image of a dense metal surface shows a giant amplitude, i.e., between one and two orders of magnitude larger than expected from an *s*-wave tip. To date, no satisfactory explanation has been given. Using our earlier nonperturbative formalism for the tunnel current, we reconsider the corrugation problem with a single atom tip having *s*, *p*, or *d* orbitals, or a combination. Particular emphasis is on the value of the corrugation as a function of the tunnel resistance $\Delta_{l,m}(R)$. Results show that the corrugation, observed over the wide range $(10^5-10^8\Omega)$, is inconsistent by nearly two orders of magnitude with the *s*-orbital theory, and by one order of magnitude with the d_{z^2} one. We also can put aside tip-surface interactions. Tip states, such as p_z and d_{z^2}, give basically *s*-wave behavior in $\Delta_{l,m}(R)$. However, those with axial symmetry, such as $d_{xz}+id_{yz}$ and having a nodal line orthogonal to the surface, give an enhanced corrugation. Finally, in tip states with a nodal plane, such as $d_{x^2-y^2}$, the enhancement effect is much more pronounced. Identical results are obtained by considering separately the nearly free electron model, and a new method of atomic orbital superposition, for the metal surface.

I. INTRODUCTION

The wide impact of STM on the study of surface structures and their local electronic properties is well established. The outstanding atomic scale resolution achieved suggests that the focusing of the tunneling current is due to a small cluster of atoms at the tip, or even just one atom. Early studies of the current very close to (or at) contact between the tip and sample,[1–4] and more recently in Refs. 5,6, lead to the interpretation of a quantum size contact between two infinite reservoirs. The ideal resistance is $R_c=1/\sigma_0 N$ where N is the number of parallel channels, and $\sigma_0=2e^2/h$. One concludes that the STM could be the smallest macroscopically controlled tunneling junction, i.e., a single atom tip and a surface.

Still, an outstanding problem for the last decade has been to explain the anomalously high corrugation observed on compact metal surfaces, where the electrons are very delocalized and the density variation due to the atoms is known to be very small in the vacuum region. On the basis of the *s*-wave tip model of Tersoff and Hamann,[7] it was not expected to resolve the atoms on metal surfaces in comparison to semiconductors or layered semimetals.[8] First observed by Hallmark *et al.*[9] and Winterllin *et al.*,[10,11] atomic resolution on metal surfaces is often achieved under optimal surface and tip conditions, and thus in UHV. Various interesting mechanisms have been proposed to explain the phenomenon.[12–16]

To state the problem in a general way, and for the zero-bias limit, the conductance has the form $\sigma(\mathbf{r}_0)=\sigma_0 T(\mathbf{r}_0)$, where $T(\mathbf{r}_0)$ is usually a complicated transmission coefficient, dependent on the location of the tip $\mathbf{r}_0$ (Fig. 1). In the STM constant current mode, one imposes $\sigma(\mathbf{x}_0,z_0)=1/R$, and the tip follows the constrained path $z_0=\overline{z}+\Delta(\mathbf{x}_0,\overline{z})$, where $\overline{z}$ is the average height, and Δ is the corrugation. The transmission coefficient can be separated into two terms: $T=T_0+\delta T$, where the surface structure leads to a lateral variation $\delta T(\mathbf{x}_0,z_0)$, over the background term, $T_0(z_0)$. Keeping only to linear order, the constraint imposes

$$\Delta(\mathbf{x}_0,\overline{z})=-\frac{\delta T(\mathbf{x}_0,\overline{z})}{dT_0(\overline{z})/dz} \tag{1}$$

$$R=\frac{1}{\sigma_0 T_0(\overline{z})}. \tag{2}$$

In a simple way, these equations express in which direction to look for an enhancement of the corrugation: In addition to the expected δT term in Eq. (1), we see that the background transmission $T_0(\overline{z})$, in particular its slope, could also affect the corrugation. Inversion of Eq. (2) gives the average tip height for a given resistance.

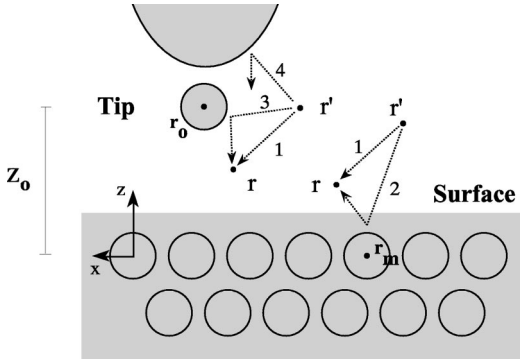

FIG. 1. Schematic of the STM model considered in this work. The Green's functions for the two independent electrodes represent propagation paths of the type 1 and 2, for the surface, and 1, 3, and 4, for the tip. Propagation in the coupled system must include a combination of these (Sec. II). The corrugated surface is treated in both the nearly free electron model (Sec. III) and a new muffin-tin superposition method (Sec. IV).

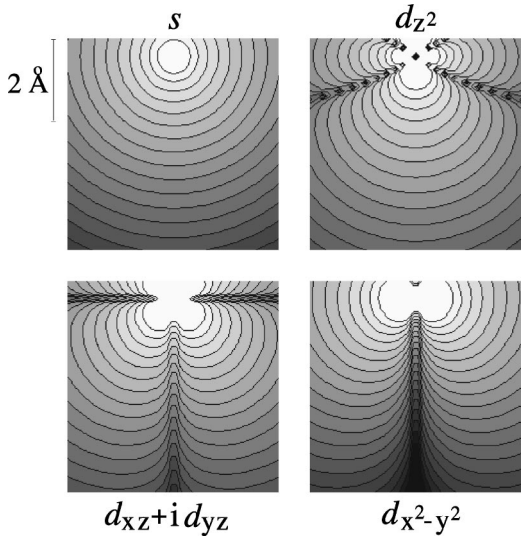

FIG. 2. Isolated tip local density, Im g_{tip}, calculated using the tip Green's function, derived in Sec. II. Plotted in the xz plane, four of the five orbitals considered in the text are compared. Both the grey level, corresponding to a fixed logarithmic scale, and the contours, reveal distinctly the nodal lines for the $m\neq 0$ tip states along the z axis.

Based on the work of Chen,[12,17,18] it is commonly believed that a hypothetical d_{z^2} tip orbital, taking its symmetry axis (z) perpendicular to the sample surface, is at the origin of this atomic resolution. The curious theoretical point is that neither a single atom tip with an s orbital, nor even with the d_{z^2} orbital, can account for the observed data. Indeed, a glance at Fig. 2, showing the orbital density plots in the (x,z) plane, indicates that these two states have a similar asymptotic behavior into the vacuum along the tunneling axis. Moreover, at some distance from the tip (i.e., relevant to the STM situation) the d_{z^2} orbital is not much more ''sharp'' than the s orbital.

Given the complex atomic structure of a real tip, which is possibly unstable, and certainly nonreproducible, there is neither an priori choice of symmetry axis, nor a particular d orbital to favor. The tip state, and in the vicinity of the Fermi level, should be a linear combination of all d orbitals. The final spectral weight is expected to be the result of the local chemical bonding of the tip extreme atom to its nearest neighbors. Even if a d_{z^2} character is dominant, it could indeed be oriented arbitrarily with respect to the surface. Nevertheless, Chen[17,18] considers the effects of $m\neq 0$ tip states, such as those in Fig. 2, and in the geometry shown. These states reveal a nodal line (or nodal plane) oriented orthogonal to the surface, and in this work we consider their possible role in the giant corrugations.

The precise value of the background transmission coefficient, as Eqs. (1) and (2) suggest, may strongly influence the corrugation. Hence, in this work, we shall put the tunneling resistance R back into the picture. Not only is R the experimentally controlled and accurate parameter, but the distance z_0 between tip and sample, defined as in Fig. 1, is unknown. More specifically, we will show that the resistance as a function of $\bar{z}$, or $R(\bar{z})$, is different depending on the tip orbital in question. For example, the lobe of the d_{z^2} orbital, as in Fig. 2, gives a shifted weight towards the surface, compared to the s orbital. Thus for some fixed tip-surface separation, and assuming equal spectral weight, the tunneling current is higher in the case of the d_{z^2} tip. In the orientation proposed in Fig. 2, the $m\neq 0$ states, having a nodal line along the tunneling axis, give a reduced tunneling probability and R is much larger than the d_{z^2} case. Even more care is needed in the case of linear combinations of d states.

As a consequence, if we now take R as the *fixed* parameter, then different tips will be at different relative heights above the surface. Then, it is meaningless to compare theoretical corrugations for different tip orbitals $\Delta_{l,m}(\bar{z})$ for the same value of $\bar{z}$. Yet, this is what is frequently done in the literature.[19] Instead, one should compare corrugations for a given value of the resistance, and compute $\Delta_{l,m}(R)$ by eliminating $\bar{z}$ in Eq. (1) using Eq. (2). This is more difficult, since the same model calculation must be reliable for the background transmission coefficient as well as the corrugation. A closer look at some perturbation methods[7,12,17,18,20] shows that the current is known up to a multiplicative constant. Therefore, in this work we reexamine both the resistance and corrugation problems for s and d orbital tips using a single approach.

The method of Sacks and Noguera[21–23] gives the tunneling current between a quite general surface and a single atom tip analytically, in the low bias and zero temperature limits. The resulting transmission coefficient, for the particular case of the s orbital tip, reads

$$T(\mathbf{r}_0)=4\frac{\mathrm{Im}\,\lambda_{\mathrm{tip}}\{-\mathrm{Im}\,\delta g_s(\mathbf{r}_0,\mathbf{r}_0)\}}{|1+\lambda_{\mathrm{tip}}\delta g_s(\mathbf{r}_0,\mathbf{r}_0)|^2}, \tag{3}$$

where λ_{tip} is the tip reflection amplitude, and $\delta g_s(\mathbf{r},\mathbf{r}')$ is the nonsingular part of the *surface* Green's function. This approach to the tunneling problem is quite different, avoiding perturbative methods such as the Bardeen approximation,[24] and is valid in the thin barrier limit. Indeed, in Ref. 22 we showed how the denominator $(1+\lambda_{\mathrm{tip}}\delta g_s)$ accounts for the tunneling through new states of the coupled tip-surface system. It is tempting to consider these states as a potential source of giant corrugations, a problem we did not pursue further. Here, the main goal is to apply this $T(\mathbf{r}_0)$, and its generalization to higher tip angular momenta.

In the thick barrier limit, the coupling becomes small, and the factor $\lambda_{\mathrm{tip}}\delta g_s\rightarrow 0$. We thus recover qualitatively the result of Tersoff and Hamann (TH): $T(\mathbf{r}_0)\propto \mathrm{Im}\,\delta g_s(\mathbf{r}_0,\mathbf{r}_0)$, which is directly the local density of states (LDOS) of the sample, at the location of the tip:

$$\mathrm{Im}\,\delta g_s(\mathbf{r}_0,\mathbf{r}_0)=-\pi\rho(\mathbf{r}_0,E_F). \tag{4}$$

Thus, in the TH model, the pertinent quantities are the background density ρ_0, and its modulation $\delta\rho$, and their ratio determines the corrugation.

Even in the nearly-free electron model, the calculation of $\delta\rho$ can be quite delicate.[7,12,18,25] More recently, the work of Ref. 26 gives the LDOS for a selection of d band metals. As is well known, the spectral representation

$$\rho(\mathbf{r}_0,E_F)=\sum_\nu |\psi_\nu(\mathbf{r}_0)|^2\delta(E_\nu-E_F) \tag{5}$$

gives the exponential law for the background density $\rho_0 \propto e^{-2\kappa z_0}$ with $\kappa=\sqrt{2m\phi}/\hbar\approx 1$ Å^{-1} the decay constant. Equivalently, the resistance increases by one order of magnitude per Å increase in separation, for a typical work function ϕ. TH and other authors[7,8,25,27,28] also showed that for a corrugation of wavelength $a=2\pi/G$, the decay constant of $\delta\rho$ is $\alpha_{G/2}=\sqrt{(G/2)^2+\kappa^2}$. Thus the ratio (1) gives the asymptotic dependence of the corrugation $\Delta_s(z_0)\propto e^{-2\gamma z_0}=e^{-2(\alpha_{G/2}-\kappa)z_0}$. Evaluating the new decay constant γ for a simple metal surface, one finds one order of magnitude change in Δ_s for a change of ~ 2 Å in separation. Both decays depend quite sensitively on the physical parameters, however.

To show that atomic resolution on metals is an order of magnitude question, consider the original data of Winterllin *et al.*[11] on Al(1,1,1) where a corrugation of $\Delta\approx 0.8$ Å is found for $R\approx 10^6\Omega$. What does the *s*-wave tip model give as an order of magnitude? Taking a limiting value at ''contact,'' and assuming only a single channel, the resistance is $R_c\sim 10^4\Omega$ and the corrugation[7,29] should be smaller than 0.1 Å. Therefore at $10^6\Omega$ the *s* corrugation should be smaller than 0.01 Å. The measurement therefore represents a truly giant corrugation. In a perturbation approach to the tunneling current, and using an asymptotic formula for the corrugation term, Chen[12] concludes that a d_{z^2} tip gives an enhancement factor of about 20, relative to an *s* tip. We find, plotting both hypothetical corrugations as a function of the junction resistance, that the d_{z^2} corrugation is typically less than an order of magnitude higher than the *s* one. Furthermore, our asymptotic expressions show that all $m=0$ states give basically *s* wave behavior, and no giant corrugation is found.

The higher *m* tip states, i.e., those presenting nodal lines orthogonal to the surface, were considered by Chen[18] as a mechanism for image contrast inversion. We do not contest this possibility for some tip configurations. Still, our asymptotic expressions give very different results for both the resistance and the corrugation for these states. In particular, with the approximations used in Refs. 17,18, the author concludes that individual $m\neq 0$ states give both a vanishing conductance, and an unphysical infinite corrugation. Quite to the contrary, our work shows that the strength of the node, depending on the term of the tip multipole expansion, leads to a finite resistance $R(z)\propto(\kappa z)^{m+1}e^{2\kappa z}$. Its influence on the corrugation is to lower the denominator in Eq. (1). The nodal lines, or planes, also have the effect of increasing the modulation term δT in Eq. (1). Thus, we find that higher *m* tip states can give a greatly enhanced corrugation, nearly two orders of magnitude higher than for *s*.

An overview of the paper is as follows. In Sec. II we summarize the model, and describe the quantities relevant to the corrugation on metals. In Sec. III, we develop the arguments above concerning the resistance of the junction for the different tip states. The corrugation is then calculated using first the nearly free electron approximation (Sec. IV) followed by a straightforward muffin-tin atom superposition method (Sec. V). Concluding remarks are in Sec. VI.

II. METHODS AND DEFINITIONS

Our formalism introduced some time ago[21] can account for a single atom tip, or a small cluster, *s*, *p*, or *d* orbitals, and a quite arbitrary surface structure. Its principal aim was to obtain an expression for small tip to surface separations, and thus to include multiple reflections in the barrier omitted in lowest order perturbation theory. A second aim was to verify TH's theory by proceeding in a totally different approach. Here we clarify those quantities entering the expressions of the tunneling current that are relevant to the corrugation problem.

The tip atom, or cluster, is modeled by muffin-tin potentials and the tunneling current is solved analytically in terms of the Green's function $g_s(\mathbf{r},\mathbf{r}')$ of the free surface. In Refs. 21,23 we used a square well tip, however all the results are independent of the particular choice of muffin-tin potential. The current is obtained from the total wave function Ψ of the entire tip-surface system,[30] and in the zero temperature, ohmic limit, reads

$$I=2e^2V\sum_\nu \int d\mathbf{S}\cdot\mathbf{j}_\nu\delta(E_\nu-E_F), \tag{6}$$

where $\mathbf{j}_\nu=(\hbar/m)\mathrm{Im}\{\Psi^*\nabla\Psi\}$ is the current density. Thus at the outset, the method makes no assumption on the coupling strength across the barrier, in contrast to the Bardeen formula.[24] In the following, we describe the surface and the tip as independent electrodes, at equilibrium, prior to treating the coupled system.

A. Surface Green's function

If $\mathbf{r}$ and $\mathbf{r}'$ are two points in the vacuum (Fig. 1), the solution $g_s(\mathbf{r},\mathbf{r}')$ to the one-electron inhomogeneous equation

$$(H_s-E)g_s(\mathbf{r},\mathbf{r}')=-\delta(\mathbf{r}-\mathbf{r}'), \tag{7}$$

is assumed to describe the free surface. We thus maintain the same generality as TH and, for example, the surface LDOS can be immediately found using $\mathrm{Im}\,g_s(\mathbf{r},\mathbf{r})=-\pi\rho(\mathbf{r},E)$. In the vacuum region, one can separate g_s into two terms $g_s=g_0+\delta g_s$, where g_0 is the singular part, and propagates a free particle from the source point $\mathbf{r}'$ to $\mathbf{r}$ (or vice versa):

$$g_0(\mathbf{r},\mathbf{r}')=-\frac{m}{2\pi\hbar^2}\frac{e^{-\kappa|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}$$

$$=\frac{\kappa m}{2\pi\hbar^2}h_0^+(i\kappa|\mathbf{r}-\mathbf{r}'|). \tag{8}$$

Here h_0^+ is the spherical Hankel function and, for E relative to the vacuum energy, $\kappa=(-2mE/\hbar^2)^{1/2}$. Since g_0 has no imaginary part, all LDOS information is only in the surface term δg_s, i.e., precisely the quantity appearing in the tunneling current.

An important example is the asymptotic expression for the Green's function outside a plane free-electron metal used by Hurault.[31] For z and z' much larger than κ^{-1}, he obtains

$$\delta g_s(\mathbf{r},\mathbf{r}') \approx \frac{m}{2\pi\hbar^2} r_s \frac{e^{-\kappa\sqrt{\varrho^2+(z+z')^2}}}{\sqrt{\varrho^2+(z+z')^2}}, \tag{9}$$

where $\varrho = \mathbf{x} - \mathbf{x}'$, and r_s is the reflection amplitude: $r_s = (ik_F+\kappa)/(ik_F-\kappa)$. Here we have put $E = E_F$, i.e., for the case of tunneling at small bias. The quantity δg_s above represents the propagation from $\mathbf{r}'$ to $\mathbf{r}$ but with the further reflection due to the surface (path 2 in Fig. 1). The LDOS for the perfectly plane surface follows:

$$\rho(\mathbf{r},E_F) = -\frac{1}{\pi}\mathrm{Im}\ \delta g_s(\mathbf{r},\mathbf{r}) = \frac{m}{2\pi^2\hbar^2}\frac{k_F\kappa^2}{k_F^2+\kappa^2}\frac{e^{-2\kappa z}}{\kappa z}, \tag{10}$$

provided $\kappa z \gg 1$. Note that the usual barrier exponential decay term has a power law $(\kappa z)^n$ denominator. This additional asymptotic behavior, also found in Ref. 25, plays a significant role in the case of higher tip angular momenta. The correction of this LDOS due to the atomic corrugation is derived in Sec. IV.

B. Tip Green's function

In Ref. 21 we considered the tip wave function, however here we give a derivation using the tip Green's function. It has the advantage of stressing the symmetric aspects of the tip and surface quantities, and giving a more general definition for λ_{tip}. Our formulation can then be connected to a recent propagator-source theory[32] of the STM. Finally, the atom superposition method of Sec. V uses the same relations.

We suppose a single muffin tin is at the position $\mathbf{r}_0$, and similarly write the tip Green's function in the form $g_{\mathrm{tip}} = g_0 + \delta g_{\mathrm{tip}} + \delta g'$, with g_0 the usual vacuum term and δg_{tip} containing reflection terms from the tip extreme atom (path 3, Fig. 1). Then, $\delta g'$ is the term reflected from the remainder of the tip (path 4), whose contribution to the tunneling current will be neglected. The method consists in solving Dyson's equation for g_{tip} analytically:

$$g_{\mathrm{tip}}(\mathbf{r},\mathbf{r}') = g_0(\mathbf{r},\mathbf{r}') + \int_\Omega g_0(\mathbf{r},\mathbf{r}'')V_{\mathrm{tip}}(\mathbf{r}'')g_{\mathrm{tip}}(\mathbf{r}'',\mathbf{r}')d\mathbf{r}'', \tag{11}$$

where V_{tip} is the muffin-tin potential, and Ω its volume.

The problem becomes tractable if both g_0 and g_{tip} are expanded in spherical functions about the tip center, of argument $\mathbf{u} = \mathbf{r} - \mathbf{r}_0$. Then, for fixed $\mathbf{r}'$, $g_0(\mathbf{r},\mathbf{r}')$ has the formal expansion

$$g_0(\mathbf{r},\mathbf{r}') = \sum_{l,m} \mathcal{D}_{l,m} j_l(i\kappa u) \mathrm{Y}_{l,m}(\hat{u}), \tag{12}$$

where j_l is the spherical Bessel function, and the coefficients $\mathcal{D}_{l,m}$ are implicitly dependent on $\mathbf{r}'$. Inversion of this expansion for the set $\mathcal{D}_{l,m}$ is given in Ref. 21. As in Chen's theory,[17] they are determined by a differential operator

$$\hat{\mathcal{D}}_{l,m} = f\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right),$$

TABLE I. Relevant quantities for the calculation of the background density $\rho_{l,m}(z) = Ca_{l,m}(z)e^{-2\kappa z}$ for selected tip orbitals and a metal surface. Columns 2 and 3 show the $\hat{\mathcal{D}}$ operator and the plane-wave eigenvalue squared $|f_{l,m}(\mathbf{k})|^2$, respectively. The latter functions behave as k^{2m} in the $k \to 0$ limit, and as a result the asymptotic form of $a_{l,m}(z)$, final column, is $1/(\kappa z)^{m+1}$.

tip state	$\hat{\mathcal{D}}_{l,m}$	$\lvert f_{l,m}(\mathbf{k})\rvert^2$	$a_{l,m}(z)$
s	$\sqrt{4\pi}$	4π	$\frac{1}{\kappa z}$
d_{z^2}	$-\frac{\sqrt{5\pi}}{\kappa^2}\left(3\frac{\partial^2}{\partial z^2}-\kappa^2\right)$	$\frac{5\pi}{\kappa^4}(3\alpha_k^2-\kappa^2)$	$\frac{5}{\kappa z}$
$d_{xz}+id_{yz}$	$\frac{\sqrt{30\pi}}{\kappa^2}\left(\frac{\partial}{\partial x}-i\frac{\partial}{\partial y}\right)\frac{\partial}{\partial z}$	$\frac{30\pi}{\kappa^4}k^2\alpha_k^2$	$\frac{15}{2}\frac{1}{(\kappa z)^2}$
d_{xy}	$2\frac{\sqrt{15\pi}}{\kappa^2}\frac{\partial^2}{\partial x\partial y}$	$\frac{60\pi}{\kappa^4}k_x^2k_y^2$	$\frac{15}{4}\frac{1}{(\kappa z)^3}$
$d_{x^2-y^2}$	$\frac{\sqrt{15\pi}}{\kappa^2}\left(\frac{\partial^2}{\partial x^2}-\frac{\partial^2}{\partial y^2}\right)$	$\frac{15\pi}{\kappa^4}(k_x^2-k_y^2)^2$	$\frac{15}{4}\frac{1}{(\kappa z)^3}$

leading to a derivative of order l, which acts on the function to be expanded, in this case g_0:

$$\mathcal{D}_{l,m} = \lim_{\mathbf{r}\to\mathbf{r}_0}\{\hat{\mathcal{D}}_{l,m}g_0(\mathbf{r},\mathbf{r}')\} = \hat{\mathcal{D}}_{l,m}g_0(\mathbf{r}_0,\mathbf{r}'). \tag{13}$$

Selected $\hat{\mathcal{D}}_{l,m}$ operators are listed in Table I, noting that the $l=0, m=0$ one is just the identity. Then the first coefficient in the expansion (12) for g_0 is

$$\mathcal{D}_{0,0} = \sqrt{4\pi}g_0(\mathbf{r}_0,\mathbf{r}'),$$

i.e., just a spherical s-wave evaluated at the tip center. Using standard methods, one can show that the $\hat{\mathcal{D}}_{l,m}$ operators acting on g_0 generate the spherical solutions to Schrödinger equation

$$\hat{\mathcal{D}}^*_{l,m}g_0(\mathbf{r},\mathbf{r}_0) = \frac{2\kappa m}{\hbar^2}h_l^+(i\kappa u)\mathrm{Y}_{l,m}(\hat{u}), \tag{14}$$

about the site $\mathbf{r}_0$. We shall use the convention that $\hat{\mathcal{D}}_{l,m}$ and $\hat{\mathcal{D}}^*_{l,m}$ always act on the first and second arguments of $g(\mathbf{r},\mathbf{r}')$, respectively. The real orbitals are obtained using the appropriate linear combination of the $\hat{\mathcal{D}}_{l,m}$ operators, but with a factor $\sqrt{2}$ for normalization.

With these techniques, and after integration, Dyson's equation for the tip gives

$$g_{\mathrm{tip}}(\mathbf{r},\mathbf{r}') = g_0(\mathbf{r},\mathbf{r}') - \sum_{l,m}\lambda_{l,m}\hat{\mathcal{D}}^*_{l,m}g_0(\mathbf{r},\mathbf{r}_0)\hat{\mathcal{D}}_{l,m}g_0(\mathbf{r}_0,\mathbf{r}'). \tag{15}$$

We stress the very convenient ''δ function'' property of V_{tip}, i.e., the above solution contains terms of the form $\hat{\mathcal{D}}g_0$ evaluated at the tip center $\mathbf{r}_0$. However, note that the factor g_{tip} in the integrand of Eq. (11) has also been replaced by $\hat{\mathcal{D}}g_0$. This follows from the matching method in Ref. 21,

where only the *incident* part of the total wave should appear in this term. In the present case, the incident part of $g_{\rm tip}$ is just g_0 (neglecting $\delta g'$).

The functions $\lambda_{l,m}$ are the tip reflection coefficients, which will depend notably on the interaction of the tip atom with its nearest neighbors, and thus on the local electronic structure. For the formal solution of the tunneling current we consider Eq. (15) above as the *defining equation* of λ. This quantity has been explicitly calculated, for example in the case of an adsorbate on a jellium.[22] For an *s* orbital, one finds that λ is approximately

$$\lambda_s = \frac{c_s}{E - E_s - i\Gamma_s}, \tag{16}$$

where c_s and Γ_s give the strength and width of the resonance at E_s. Thus $\mathrm{Im}\,\lambda_{l,m}$ is proportional to the projected DOS onto the orbital l,m of the tip atom. Consulting more realistic tip electronic structure calculations, such as in Ref. 33, this approximation for λ should be adequate.

In principle all angular momenta will participate in the tunnel current, as proved by Eq. (15). At the Fermi level, however, λ is expected to be very small except for the nearest resonance states. For example, if the extreme atom has a single *s* state, the tip Green's function reduces to

$$g_{\rm tip}(\mathbf{r},\mathbf{r}') \approx g_0(\mathbf{r},\mathbf{r}') - 4\pi\lambda_s g_0(\mathbf{r},\mathbf{r}_0) g_0(\mathbf{r}_0,\mathbf{r}'), \tag{17}$$

however Eq. (15) should be used for degenerate orbitals. The above equation also provides the starting point for the muffin-tin superposition method of Sec. V.

C. Coupled tip-surface system

The total wave function Ψ for the coupled system is written in two ways. First, superposition in the barrier region allows one to write $\psi = \psi_i + \psi_r$, where ψ_i and ψ_r are the *total* incident ($e^{+\kappa z}$) and reflected ($e^{-\kappa z}$) waves, respectively. Second, the scattered wave can be expressed in integral form as the Lippman-Schwinger equation

$$\Psi(\mathbf{r}) = \psi_s(\mathbf{r}) + \int g_s(\mathbf{r},\mathbf{r}') V_{\rm tip}(\mathbf{r}') \Psi(\mathbf{r}')\, d\mathbf{r}', \tag{18}$$

where ψ_s is the unperturbed surface wave function. Using the same expansion method, the integration leads to

$$\Psi(\mathbf{r}) = \psi_s(\mathbf{r}) - \sum_{l,m} \lambda_{l,m} \hat{\mathcal{D}}^*_{l,m} g_s(\mathbf{r},\mathbf{r}_0) \hat{\mathcal{D}}_{l,m} \psi_i(\mathbf{r}_0), \tag{19}$$

where the $\hat{\mathcal{D}}_{l,m}$ are the identical operators, but here they act on *surface* quantities. Using this result, the tunnel conductance, $\sigma = I/V$, is found by direct integration over the current density (6):

$$\sigma = 4\pi\sigma_0 \sum_{l,m} \mathrm{Im}\,\lambda_{l,m} \sum_{\nu} |\hat{\mathcal{D}}_{l,m}\psi_i(\mathbf{r}_0)|^2 \delta(E_\nu - E_F). \tag{20}$$

In contrast to either the TH or Chen theories, the current is related to a *modified* LDOS, where the unperturbed surface wave function ψ_s is replaced by the quantity $\hat{\mathcal{D}}\psi_i$, i.e., derivatives of the total incident wave at the tip center. The problem is therefore reduced to finding the unknown components $\hat{\mathcal{D}}_{l,m}\psi_i$ at the position $\mathbf{r}_0$. Taking only the incident part of Eq. (19), and applying $\hat{\mathcal{D}}$ on the left, leads to an infinite set of coupled equations

$$\hat{\mathcal{D}}_{l',m'}\psi_i(\mathbf{r}_0) = \hat{\mathcal{D}}_{l',m'}\psi_s(\mathbf{r}_0) - \sum_{l,m} \lambda_{l,m} \hat{\mathcal{D}}_{l',m'} \hat{\mathcal{D}}^*_{l,m} \delta g_s(\mathbf{r}_0,\mathbf{r}_0) \hat{\mathcal{D}}_{l,m}\psi_i(\mathbf{r}_0), \tag{21}$$

for the components $\hat{\mathcal{D}}\psi_i$. Although quite complex, this set represents the multiple reflections across the barrier, involving all degenerate tip orbitals. Closer inspection reveals that, in addition to ''direct'' terms (with a given $\lambda_{l,m}$), there are also *interference* terms.

In the simplest case, one only needs the solution for a single orbital:

$$\hat{\mathcal{D}}\psi_i = \hat{\mathcal{D}}\psi_s - \lambda\{\hat{\mathcal{D}}\hat{\mathcal{D}}^* \delta g_s\}\hat{\mathcal{D}}\psi_i, \qquad = \frac{\hat{\mathcal{D}}\psi_s}{1 + \lambda \hat{\mathcal{D}}\hat{\mathcal{D}}^* \delta g_s}, \tag{22}$$

with an important ''renormalization'' step, and the conductance reads

$$\sigma(\mathbf{r}_0) = \sigma_0 \frac{4\,\mathrm{Im}\,\lambda\{-\mathrm{Im}\,\hat{\mathcal{D}}\hat{\mathcal{D}}^* \delta g_s(\mathbf{r}_0,\mathbf{r}_0)\}}{|1 + \lambda \hat{\mathcal{D}}\hat{\mathcal{D}}^* \delta g_s(\mathbf{r}_0,\mathbf{r}_0)|^2}. \tag{23}$$

An analytical solution for the three-dimensional tunneling problem can be obtained for a cluster tip, even taking into account degenerate orbitals, but is necessarily more complicated to write. Notice that the final result is a true transmission coefficient, i.e., of the form $\sigma = \sigma_0 T$, where T tends towards unity in the thin barrier limit. An equation having this property was obtained by Ferrer *et al.* in the tight-binding approach.[3]

III. JUNCTION RESISTANCE

The problem for the remainder of this work is to evaluate our general conductance equation (23), specifically applied to the resistance and corrugation equations (1) and (2). In this Section we only discuss the lowest order term for the resistance, $R(z) = 1/\sigma(z)$, which corresponds to a single atom tip and a plane metal surface, leaving the corrugation term for Sec. IV. Even in this case, the conductance (23) depends on the *real part* of δg_s, which is absent in the TH and Chen models. A second point we treat is the role of the $\hat{\mathcal{D}}$ operator, pertinent to each type of orbital. If one ignores multiple reflections in the barrier, which amounts to taking $\hat{\mathcal{D}}\hat{\mathcal{D}}^* \delta g_s \to 0$, the conductance depends asymptotically only on the imaginary part again. Thus the large κz limit should give back Chen's results[12,17,18] for the tunneling current involving higher tip angular momenta, and based on the Bardeen transfer Hamiltonian.[24] This is not the case, as the asymptotic formulas reveal.

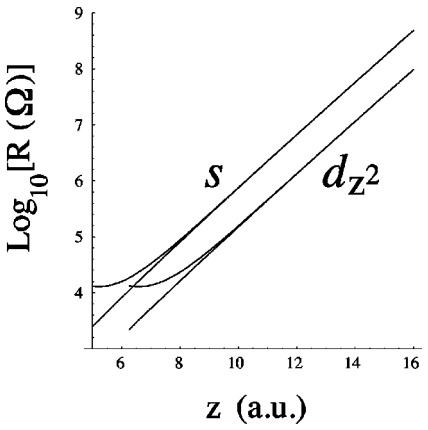

FIG. 3. $R(z)$ curves for the two tip orbitals, s and d_{z^2}, using the ''exact'' conductance equation (23) and assuming equal tip spectral weight. Here z is the distance between the surface and the tip muffin-tin center. The asymptotes, equivalent to the perturbation limit, are shown to be accurate *for both orbitals* for $R>10^5\Omega$. For a fixed resistance the d_{z^2} tip must be further away from the surface than the s tip. This shift has the effect of lowering the expected d_{z^2} corrugation.

A. $R(z)$ for s and d tip orbitals

Although the quantity $\hat{\mathcal{D}}\hat{\mathcal{D}}^*\delta g_s$ has never been considered, δg_s has arisen in the problem of an impurity within a perfectly tunneling planar junction.[31] In the nearly free electron approximation, neglecting the corrugation implies that only the *planar part* of $\delta g_s(\mathbf{r},\mathbf{r}')$ is required. Thus, following Hurault,[31] we write this quantity as

$$\delta g_s(\mathbf{r},\mathbf{r}')=\frac{m}{(2\pi\hbar)^2}\int\frac{1}{\alpha_k}r(\mathbf{k})\psi_0(\mathbf{x},z)\psi_0(\mathbf{x}',z')^*d^2k, \tag{24}$$

where ψ_0 is the plane-wave vacuum solution

$$\psi_0(\mathbf{x},z)=e^{i\mathbf{k}\cdot\mathbf{x}}e^{-\alpha_k z},$$

having the familiar decay constant $\alpha_k=\sqrt{k^2+\kappa^2}$, and $r(\mathbf{k})$ is the surface reflection coefficient. The free-electron case $r(\mathbf{k})=(ik_\perp+\alpha_k)/(ik_\perp-\alpha_k)$, with $k,k_\perp$ the parallel and perpendicular wave vectors, should be a reasonable approximation. Neglecting the k dependence in $r(\mathbf{k})$, i.e., taking $r(\mathbf{k})\approx r(0)=r_s$, leads to a standard k integral and gives approximation (9) to δg_s discussed previously. The subscript denoting the tip position will be dropped.

For the $l\neq 0$ tip states Eq. (24) can be used to compute $\hat{\mathcal{D}}\hat{\mathcal{D}}^*\delta g_s$ directly. While the differential form of $\hat{\mathcal{D}}_{l,m}$ is similar to Chen's,[17] the constant prefactor is not. One can either use the direct formula for $\hat{\mathcal{D}}$ in Ref. 21, or deduce the constant using the identity (14). The orbital coefficient λ_s for the s wave tip was fitted to the sodium/jellium model of Ref. 34 and an equal spectral weight will be assumed for all orbitals. The simple values, $\kappa=0.5$ a.u. and $k_F=1$ a.u. were chosen for the remaining constants.

We compare the resistance as a function of distance first for the two tips s and d_{z^2} in Fig. 3. The asymptotes, essentially equivalent to the perturbation limit, are shown to depart from the true $R(z)$ curves when z gets sufficiently small, i.e., $z<4$ Å for the s tip and $z<5$ Å for the d_{z^2} one. Note that in the former case, the current saturates to $R\approx R_c$ for $z=z_c\approx 2.5$ Å. As evident in the figure, the asymptotes for both tips have the same slope, and thus the same orbital decay into the vacuum. What is equally important is that the $R(z)$ curve for d_{z^2} is shifted with respect to the s curve, towards a larger distance, by nearly a Bohr. This is due to the shifting of the center of gravity of the tip d_{z^2} orbital away from the tip center (visible in Fig. 2), an effect apparently overlooked in Refs. 12,18. In particular, for a barrier thickness of 4 Å the s orbital tip gives a resistance of $10^5\Omega$, while the d_{z^2} tip is close to ''contact.'' Thus the comparison of the corrugations for the two types of tips should clearly not be done at a given value of z, as in Ref. 12, but at a given value of R. Our results show that shifting the d_{z^2} orbital tip away from the surface, to keep the same value for R, has the effect of reducing the corrugation. This puts immediate doubt on its possible origin of the atomic resolution.

A further point is remarkable from Fig. 3. The curved portions for both tips, where the perturbation approximation breaks down, correspond to resistance values less than $10^5\Omega$ in both cases. It is agreed that short range forces are expected when the surface and tip states couple strongly,[3,13,15,16,21,22] i.e., the denominator in the conductance Eq. (23) becomes significant. Figure 3 shows that they can be safely neglected for the common experimental range of $10^5-10^8\Omega$. We therefore expect that the effect of multiple reflections expressed by the complex Eq. (21), should be negligible in the problem of a simple metal surface. This conclusion should not be hastily extended to the non-ohmic situation, or one in which the surface has a more complex structure, such as an adsorbed molecule. We finally note that, based on the exact value of $T(z)$ for the s orbital, it is possible to approximate the asymptote of $R(z)$ as

$$\log\left(\frac{R}{R_o}\right)=2\kappa(\log e)(z-z_o) \tag{25}$$

with $R_o\approx 10^5\Omega$ and $z_o\approx 4$ Å. One cannot replace R_o and z_o by R_c and z_c without making the error of a shifted asymptote.

As described in the Introduction, Chen worked out the tunneling matrix elements for individual d orbital tip states, and in the geometry of Fig. 2. In addition, he suggested that the $m\neq 0$ tip states are the possible cause of image contrast inversion. We propose to show that an $m\neq 0$ tip orbital can give a very large corrugation enhancement, even compared to the usually accepted d_{z^2} one. Note that even a ''pure'' d_{z^2} orbital could be oriented at an arbitrary angle with respect to the surface. Then in the surface coordinate system, it is equivalent to the addition of higher m components.

We therefore examine the additional $d_{xz}+id_{xz}$ orbital, having axial symmetry along z, d_{xy} and $d_{x^2-y^2}$, taking the xy plane parallel to the surface. These are illustrated in Fig. 2 as contour plots of the tip local density, in the xz plane. The lines corresponding to either nodal lines or nodal planes are clearly evident (the orbital $d_{x^2-y^2}+id_{xy}$ has similar behavior as $d_{xz}+id_{xz}$, and will be omitted). The resistance for the case of these other d orbitals, is calculated in an identical way as the d_{z^2} case discussed above, and the results are shown in Fig. 4. In principle, the sum over all d orbitals

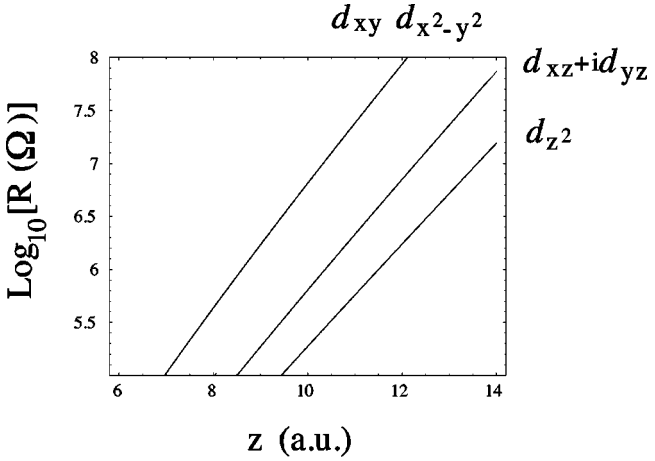

FIG. 4. $R(z)$ curves for each of the tip d orbitals, each having the same spectral weight, and in the nearly free electron model for the surface. These show a quite different asymptotic slope for the d_{z^2} tip state, as compared to the $m\neq 0$ ones. Due to the near axial symmetry of the surface, $R(z)$ is the same for the d_{xy} and $d_{x^2-y^2}$ cases. Analytical expressions are summarized in Table I. It follows that a comparison of the corrugation at a fixed z will be different than at fixed R.

should give back spherical symmetry, assuming equal spectral weight for each. The decay of the tunneling current with tip-surface distance is shown to be quite different for these $m\neq 0$ states. We show below that this is principally due to the axial nodes.

B. Asymptotic formulas

The possible role of nodes in the tip wave functions can best be seen in the asymptotic form of the conductance. Moreover, since multiple reflections can safely be neglected for $R>10^5\Omega$, the $\kappa z\gg 1$ limit should be sufficient for the corrugation equation (1). We therefore focus on the quantity

$$\rho_{l,m}=-\frac{1}{4\pi^2}\mathrm{Im}\,\hat{\mathcal{D}}_{l,m}\hat{\mathcal{D}}^{*}_{l,m}\delta g_s, \tag{26}$$

where the extra factor of 4π assures that the usual LDOS is obtained for the s-wave case. To compare directly with the results of Refs. 12,17,18, and to derive useful asymptotic formulas, we consider the $\mathbf{k}$ representation of $\rho_{l,m}(z)$, which follows immediately using expression (24) for δg_s. It is convenient to call $f_{l,m}(\mathbf{k})$ the eigenvalue of the $\hat{\mathcal{D}}_{l,m}$ operator

$$\hat{\mathcal{D}}_{l,m}\psi_0(\mathbf{r})=f_{l,m}(\mathbf{k})\psi_0(\mathbf{r}),$$

and the calculation proceeds with evaluating:

$$\rho_{l,m}(z)=-\frac{1}{4\pi^2}\frac{m}{(2\pi\hbar)^2}\int\frac{\mathrm{Im}\,r(\mathbf{k})}{\alpha_k}|f_{l,m}(\mathbf{k})|^2e^{-2\alpha_k z}d^2k \tag{27}$$

where the relevant $f_{l,m}(\mathbf{k})$ functions are given in Table I.

Exactly as in the TH theory, due to the exponential factor $e^{-2\alpha_k z}$, the background density is determined mainly from states near the Γ point of the surface Brillouin zone, or the small k limit. In Refs. 12,18 Chen uses this property to take into account *only* those states, i.e., skipping the integral in Eq. (27). This excludes particular cases where a directional gap exists near the Γ point, or other type of singularity. Here we use a method of steepest descent: The exponential argument is expanded about $k=0$, and slowly varying factors, having a finite limit, are assumed constant. Thus one can write

$$\rho_{l,m}(z)\approx Ca_{l,m}(z)e^{-2\kappa z}, \tag{28}$$

where $C=-\kappa m\,\mathrm{Im}\,r_s/(2\pi\hbar)^2$, and the asymptotic form for all l,m is given by the simple dimensionless integral

$$a_{l,m}(z)=\frac{1}{(2\pi\kappa)^2}\int|f_{l,m}(\mathbf{k})|^2e^{-(z/\kappa)k^2}d^2k. \tag{29}$$

Looking at the eigenvalue $f_{l,m}(\mathbf{k})$ for the different states, we first note that only the $l=0$ ones tend to a finite constant in the small k limit. Thus for the s and d_{z^2} states discussed above, the ratio $f_z^2/f_s^2=5(3\alpha_k^2-\kappa^2)^2/4\kappa^4$ is a factor of 5 when $k\to 0$. The k integration then gives the prefactors $a_s(z)=1/(\kappa z)$ and $a_{z^2}(z)=5/(\kappa z)$. One can show that the p_z tip state leads a similar prefactor. The conclusion is that all $m=0$ tip states have the similar asymptotic form $R(z)\propto(\kappa z)e^{2\kappa z}$, for the resistance.

The problem is markedly different for the $m\neq 0$ states. For example, $f_{xz+iyz}\propto k$ and $f_{x^2-y^2}\propto k^2$, i.e., these functions *vanish* as $k\to 0$. In real space, this is due to the nodal line of the tip wave function along the tunneling axis. In fact, we find the power of k in the small k limit of $f_{l,m}(\mathbf{k})$ to reflect the strength of the node, i.e., the degree of shifting of the tip orbital density away from the z axis, and $f_{2,m}\propto k^m$. The corresponding real space factors, summarized in Table I, are then of the form $a_{2,m}(z)=1/(\kappa z)^{m+1}$. These results are reminiscent of the multipole expansion in electrostatics. The resistance asymptote then follows the general form $R(z)\propto(\kappa z)^{m+1}e^{2\kappa z}$, and it would be of interest to check this experimentally.

IV. CORRUGATION

In this section, we consider the asymptotic corrugation for individual tip states

$$\Delta_{l,m}(\mathbf{x},z)\approx-\frac{\delta\rho_{l,m}(\mathbf{x},z)}{d\rho_{l,m}/dz}, \tag{30}$$

which follows immediately from Eq. (1), but we will also treat the case of a superposition of orbitals. The general case is important, since no special axis of symmetry is expected for a real tip. In considering the above equation for the corrugation, one should bear in mind that $R(z)$ is known, and that the main objective is to calculate $\Delta(\mathbf{x},R)$.

The background density $\rho_{l,m}(z)$ can play a more important role in the STM image than is generally thought. For higher m states we have seen that $\rho(z)$ decays faster than the $m=0$ ones. In the analysis of Chen,[12,18] the k integration being ignored, his function $f_{l,m}(\mathbf{k})$ was evaluated only at $k=0$. The conclusions were therefore that $f(0)=0$, hence $\rho_{l,m}(z)=0$, resulting in an *infinite* corrugation in this approximation. This would be true if the tip orbital could be perfectly orthogonal to the surface wave function. As our analysis shows, this is not the case, and the background den-

sity just has a $1/(\kappa z)^m$ prefactor over the usual *s* wave case. Thus, expression (30) must be reconsidered.

A. Nearly free electron approximation

The evaluation of the modulation term, $\delta\rho_{l,m}(\mathbf{r})$, in the nearly free electron approximation is quite well known,[7,8,17,18,25] and will be only briefly sketched here. The arguments we propose are not meant to cover metal surfaces for which the plane-wave approximation is known to break down.[26] However, the problem is still motivated by the wide range of metals, and under a wide range of conditions, that give a giant corrugation. Moreover the results are in good agreement with the simulated images using the muffin-tin surface approach, described in the following section, despite the difference in the treatment of the electronic structure.

Our approach is very similar to Chen and TH in that the modulation term is approximated by a single Bragg reflection. Thus we replace ψ_0 in Eqs. (24) and (26) for $\rho_{l,m}(\mathbf{r})$ by $\psi_0+\psi_1$ where

$$\psi_1 = u_{\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{x}} e^{-\alpha_{\mathbf{k}-\mathbf{G}} z},$$

G being the smallest nonzero reciprocal lattice vector, and the decay constant α_k is the same as previously. We shall consider only the square lattice to get the order of magnitude of the corrugation. The (1,1,1) surface, for example, is treated in Ref. 12.

Introducing the wave function $\psi_0+\psi_1$ in $\rho_{l,m}(\mathbf{r})$, Eq. (26), evidently leads to three terms. The leading term $\propto|\psi_0|^2$ gives the previous background density, and has the decay constant $2\alpha_k$. The cross-term gives the corrugation, i.e., $\propto 2\,\mathrm{Re}\{\psi_0^*\psi_1\}$, having the decay constant $(\alpha_k+\alpha_{\mathbf{k}-\mathbf{G}})$. Consequently, the largest contribution to the corrugation term is for $\mathbf{k}=\mathbf{G}/2$ or the *M* point (or the nearest point to *M* allowed). The last term $\propto|\psi_1|^2$ is a correction to the background density, and will be dropped. We therefore can write

$$\delta\rho_{l,m}(\mathbf{x},\mathbf{z}) = C' e^{-2\alpha z}\sum_n \{u_{\mathbf{G}_n} e^{-i\mathbf{G}_n\cdot\mathbf{x}} b_{l,m}(\mathbf{G}_n,z) + \text{c.c.}\} \tag{31}$$

with, using the abbreviation $\alpha_{G/2}=\alpha$,

$$C' = -\frac{\kappa^2 m\,\mathrm{Im}\,r(G/2)}{\alpha(2\pi\hbar)^2}.$$

In addition to neglecting the *k* dependence of $u_{\mathbf{G}}$, we have approximated perhaps abusively $r(\mathbf{k})\approx r(\mathbf{G}/2)$, which may be a problem for particular electronic structures. The function $b_{l,m}(\mathbf{G},z)$ is defined in dimensionless form, and gives the prefactor of the modulation

$$b_{l,m}(\mathbf{G},z) = \int \frac{d^2q}{(2\pi\kappa)^2} f_{l,m}(\mathbf{q}-\mathbf{G}/2) \times f_{l,m}(\mathbf{q}+\mathbf{G}/2)^* e^{-(\kappa^2 z/\alpha^3)q^2}. \tag{32}$$

While $a_{l,m}(z)$ was defined by approximating *k* near the Γ point, here the exponential argument has been expanded about the *M* point, i.e., $\mathbf{q}=\mathbf{k}-\mathbf{G}/2$. The $b_{l,m}(\mathbf{G},z)$ functions are estimated by the leading term of the integral. Again we note that in Ref. 18, Chen considers only a single **k** point for the asymptotic corrugation. We find that some of the eigenvalues of the $\hat{\mathcal{D}}$ operator $f_{l,m}(\mathbf{k})$ can still vanish even at the *M* point, again due to the tip nodal plane, and thus the explicit integration in Eq. (32) is unavoidable.

To proceed, we assume that the *x* direction of the tip coincides with an atomic row of the surface lattice, for simplicity. As a result of imposing reflection symmetry, and defining

$$\Phi(\mathbf{x}) = \sum_n \cos(\mathbf{G}_n\cdot\mathbf{x}),$$

in our example we have no phase shifts and the modulation reads

$$\delta\rho_{l,m}(\mathbf{x},z) = 2C' b_{l,m}(G,z) u_{\mathbf{G}} e^{-2\alpha z}\Phi(\mathbf{x}). \tag{33}$$

Thus, in the results shown in Table II, $b_{l,m}(G,z)$ depends only on the magnitude of **G**. Also, since we have neglected the band structure near the zone boundary, these should be considered only as an order of magnitude. Similar assumptions are found in the TH and Chen theories.

Examining the modulation $\delta\rho_{l,m}$, it shows the well-known exponential law $\delta\rho\propto e^{-2\alpha z}$, but with the prefactor given by $b_{l,m}(G,z)$. Consequently the d_{xy} modulation decays fastest with $b_{xy}(G,z)\propto 1/(\kappa z)^2$, whereas the $d_{x^2-y^2}$ and $d_{xz}+id_{yz}$ orbitals both give the factor $1/(\kappa z)$. The precise *z* dependence seems to vary according to the orientation of the nodal plane with respect to the crystal axes, i.e., giving a notable difference between the d_{xy} case and $d_{x^2-y^2}$. As the negative sign of $b(G,z)$ indicates, both $d_{xz}+id_{yz}$ and d_{xy} give anti-corrugations, i.e., an inverted image. We find that asymptotically the $d_{x^2-y^2}$ gives a positive corrugation, in sharp disagreement with Ref. 18. A more complete study, taking into account the electronic structure of a selection of *d* metals, shows that even with an *s* wave tip, an anticorrugation can exist.[26] Therefore, in some complex situations involving a *d* orbital tip, it might be difficult to know the true atomic positions from the image.

B. Corrugation enhancement

The difference between our value of the constant current corrugation $\Delta_{l,m}$ and those of other authors[7,8,12,17,18,20,26] is the *z* dependence, as well as the numerical factors combining the constants G,α, and κ (Table II). Using Eqs. (28) for the background density and Eq. (33) for the modulation, the result is

$$\Delta_{l,m}(\mathbf{x},z) = \frac{C' u_{\mathbf{G}}}{\kappa C}\frac{b_{l,m}(G,z)}{a_{l,m}(z)} e^{-2\gamma z}\Phi(\mathbf{x}). \tag{34}$$

Again, we find the usual exponential decay $\Delta_{l,m}\propto e^{-2\gamma z}$, giving about 1 order of magnitude change in the corrugation, per 2 Å change in *z*, i.e., slower than the background density. However, this value does depend sensitively on G/κ, which in our case is 2.75. Note that the ratio of the two constants *C* and C' is in theory

$$\frac{C'}{C} = \frac{\kappa}{\alpha}\frac{\mathrm{Im}\ r(G/2)}{\mathrm{Im}\ r_s},$$

TABLE II. Relevant quantities for the density modulation $\delta\rho_{l,m}=2C'b_{l,m}(G,z)u_{\mathbf{G}}e^{-2\alpha z}\Phi(\mathbf{x})$, in the nearly free electron approximation, where the functions $b_{l,m}(G,z)$, column 2, give the asymptotic form. The corrugation $\Delta_{l,m}(\mathbf{x},z)$ depends critically on the ratio $b_{l,m}(G,z)/a_{l,m}(z)$, and is given in column 3, up to the constant $C'u_{\mathbf{G}}/C$. Finally the ''enhancement'' factor relative to the s orbital tip $A_{l,m}=\Delta_{l,m}/\Delta_s$ is shown in the last column. Note that $A_{l,m}$ is a constant for the d_{z^2} tip, but has a $(\kappa z)^n$ dependence for the $m\neq 0$ states, which is a possible indication of a giant corrugation.

tip state	$b_{l,m}(G,z)$	$\Delta_{l,m}(\mathbf{x},z)$	$A_{l,m}$
s	$\left(\frac{\alpha}{\kappa}\right)^3\frac{1}{\kappa z}$	$\frac{\alpha^3}{\kappa^4}e^{-2\gamma z}\Phi(\mathbf{x})$	1
d_{z^2}	$\frac{5}{4}\left(\frac{\alpha}{\kappa}\right)^3\left(\frac{3\alpha^2}{\kappa^2}-1\right)^2\frac{1}{\kappa z}$	$\frac{\alpha^3}{4\kappa^4}\left(\frac{3\alpha^2}{\kappa^2}-1\right)^2e^{-2\gamma z}\Phi(\mathbf{x})$	$\frac{1}{4}\left(\frac{3\alpha^2}{\kappa^2}-1\right)^2\approx 15$
$d_{xz}+id_{yz}$	$-\frac{15}{8}\frac{G^2\alpha^5}{\kappa^7}\frac{1}{\kappa z}$	$-\frac{G^2\alpha^5}{4\kappa^7}ze^{-2\gamma z}\Phi(\mathbf{x})$	$-\frac{G^2\alpha^2}{4\kappa^3}z\approx -5\kappa z$
d_{xy}	$-\frac{15}{8}\frac{G^2\alpha^6}{\kappa^8}\frac{1}{(\kappa z)^2}$	$-\frac{G^2\alpha^6}{2\kappa^8}ze^{-2\gamma z}\Phi(\mathbf{x})$	$-\frac{G^2\alpha^3}{2\kappa^4}z\approx -18\kappa z$
$d_{x^2-y^2}$	$\frac{15}{64}\frac{G^4\alpha^3}{\kappa^7}\frac{1}{\kappa z}$	$\frac{1}{16}\frac{G^4\alpha^3}{\kappa^6}z^2e^{-2\gamma z}\Phi(\mathbf{x})$	$\frac{1}{16}\frac{G^4\alpha^3}{\kappa^2}z^2\approx 3.5(\kappa z)^2$

but is unknown without selecting a specific band structure. Looking for the possibility of corrugation enhancement, the only candidate is the ratio $b_{l,m}(G,z)/a_{l,m}(z)$, since any giant corrugation must persist in the perturbation limit, i.e., for $R\gg 10^5\Omega$. Moreover, the previous section has shown the denominator to behave in this limit as $a_{l,m}(z)=1/(\kappa z)^{m+1}$, and we can anticipate a possible amplification effect here.

To show this more clearly, the last column of Table II shows the ''enhancement'' factor $A=\Delta_{l,m}/\Delta_s$ relative to the s-wave theory. The d_{z^2} corrugation is found to be ~ 15 times larger, at a given tip surface separation. This is in reasonable agreement with, but smaller than, Chen's value of 19.6. We will show in the following numerical analysis, that this value is still insufficient to explain the experimental data. The enhancement factors for the other $m\neq 0$ states show the important feature of being *dependent on z*, i.e., proportional to $(\kappa z)^n$, an aspect that has been hitherto overlooked. For example, the d_{xy} tip orbital, for a tip-surface separation of 5 Å gives an enhancement over the s-tip by a factor of 100. It seems clear that a very large amplification effect can occur for tip states of higher m.

To compare with the experimental data, we focus only on the order of magnitude of the problem, and no data fitting was considered. Our approach is to select reasonable parameters for the s wave problem, then the d orbital case is known. Aside from the tip coefficient λ_s used for the tunneling resistance in the previous Section, the only free parameter is $C'u_{\mathbf{G}}$ which can be deduced using typical values of the charge density modulation. We then compare in Fig. 5 the corrugation $\Delta_{l,m}$, but as a function of the *junction resistance* for each of the different tip orbitals. The original data of Winterllin *et al.*[11] is shown just for comparison.

What is first striking in Fig. 5 is that the d_{z^2} curve is more than one order of magnitude below the experimental data, and less than an order of magnitude above the s line. The calculation in Ref. 12 manages to fit the d_{z^2} line through these identical data points. Given that both s and d_{z^2} orbitals give similar asymptotic expressions for the density, the latter approach cannot prove that the d_{z^2} orbital is responsible for the giant corrugation. Moreover, the previous section showed that for a given resistance, the d_{z^2} tip is further away from the surface than the s tip (assuming equal tip spectral weight). Plotted as a function of resistance, the corrugation enhancement of d_{z^2} over s is reduced to a factor of 8.

For the tip orbitals of higher angular momentum, the corrugation gains more than an order of magnitude for each

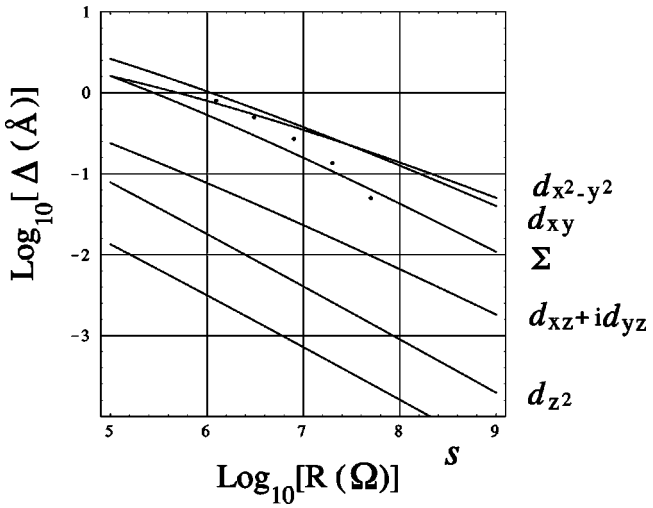

FIG. 5. Magnitude of the corrugation for d orbital tips, over the s wave model, seen here as a function of R. The corrugation $\Delta(R)$, for the d_{z^2} tip is more than one order of magnitude below the data points Ref. 11, and less than one order of magnitude above the s line. The $m\neq 0$ tip states give a corrugation with a very large enhancement over the s tip, which also *increases* with resistance. $\Delta(R)$ shows a gain of more than one order of magnitude, for $d_{xz}+id_{yz}$, or even two orders of magnitude, for the d_{xy} or $d_{x^2-y^2}$ tips. The curve Σ shows the $d_{x^2-y^2}$ corrugation reduced by the superposition of only 2 % d_{z^2}.

increase in m, as Fig. 5 indicates. The previous arguments have shown that this enhancement effect is due to both the faster decay of the background density, and the increase of the modulation term. Furthermore, as Fig. 5 illustrates, the relative enhancement for the $m \neq 0$ tips (as compared to the s tip) *increases* with resistance. It should therefore prove useful to study the behavior of the corrugation as a function of R.

To make contact with experiment, we write approximate formulas that are expected for $\Delta(R)$ on a log-log plot, and for the case of tunneling to a single orbital. Thus using the approximate $R(z)$ equation for the s-wave tip (25), together with the asymptotic formulas for the corrugation, one has

$$\log\left(\frac{\Delta_s(R)}{\Delta_o}\right) \approx -\varepsilon \log\left(\frac{R}{R_o}\right) \tag{35}$$

with $\varepsilon = \gamma/2\kappa \log e$, and Δ_o is the corrugation at $R_o \approx 10^5 \Omega$. Here we neglected the $(\kappa z)^{-1}$ prefactor in the background transmission $T(z)$. The d_{z^2} tip gives the same line but shifted by the additive constant $N_{z^2} \approx 0.8$. For tip states having $m > 0$, we get the general form

$$\log\left(\frac{\Delta(R)}{\Delta_o}\right) \approx N + M \log\left[1 + (\kappa z_o)^{-1} \log\left(\frac{R}{R_o}\right)\right] + \log\left(\frac{\Delta_s(R)}{\Delta_o}\right), \tag{36}$$

where N is a constant shift (as in Fig. 5) and $z_o \approx 4$ Å, defined in the previous section, is a little larger than a lattice constant. Finally the factor M depends on the tip orbital in question, and we find explicitly $M = (1+\gamma), M = (1+2\gamma)$ and $M = 2(1+\gamma)$ for the $d_{xz} + i d_{xz}$, d_{xy}, and $d_{x^2-y^2}$ orbitals, respectively. Thus the first two terms of Eq. (36) combined can give a factor larger than 2, or an enhancement of more than two orders of magnitude above the s-wave case.

The calculations presented so far, involving tunneling to a single orbital tip, can be extended to the case of a linear combination of degenerate d orbitals. We write a new total tip coefficient in terms of the ''individual'' d states as

$$\mathrm{Im}\,\lambda_{\mathrm{tot}} = \sum_i \beta_i \mathrm{Im}\,\lambda_i ,$$

where β_i is the relative weight, which could be deduced from an *ab initio* tip calculation. The total corrugation is *not* the sum of the ''individual'' corrugations, but rather

$$\Delta_{\mathrm{tot}}(\mathbf{x},z) = -\sum_i \beta_i \frac{\delta\rho_i(\mathbf{x},z)}{d\rho_{\mathrm{tot}}/dz}. \tag{37}$$

Thus the correct corrugation $\Delta_{\mathrm{tot}}(R)$ requires both the total junction resistance $R_{\mathrm{tot}}(z)$ and total background density $\rho_{\mathrm{tot}}(z)$. Consequently, we can check how fast the $d_{x^2-y^2}$ amplitude is lowered by adding a d_{z^2} component. The results show (see Fig. 5), that even the small admixture of a few % of $m=0$ reduces significantly the enhancement effect. This is quite as expected, since the d_{z^2} orbital has a lobe towards the surface that easily compensates for the axial node of the $m \neq 0$ states, in the geometry chosen. The further investigation of different tip structures may shed light on which proportion of d orbitals is the most realistic.

V. MUFFIN-TIN SURFACE

The superposition of muffin-tin potentials is also a simple way to implement a surface structure. In previous work we have used the muffin-tin model for an atom on a jellium surface,[22] or a linear chain of atoms.[23] The method outlined below uses the same approach as for writing the Green's function for the tip. Here we calculate the surface Green's function for a finite number of ''atoms'' in a square lattice, and investigate the corrugation for s and d orbital tips.

A. General method

One can transpose the single atom tip argument, leading to Eq. (15), and apply it to the surface. The mathematical trick is to notice that one can solve the Dyson equation (11) or Lippman-Schwinger equation (18) for a given muffin tin with an *arbitrary* external source (what we called the ''incident'' wave in Sec. II). This external wave can thus be the reflected wave from all the other muffin tins of a cluster.

A simple recursion scheme is therefore possible solving the Green's function for *adding* the Mth site, at the new position $\mathbf{r}_M$, in terms of the solution for $M-1$ sites, at the positions $\mathbf{r}_m$. The starting point to implement the method is the s-wave expression found for the single muffin tin

$$g_1(\mathbf{r},\mathbf{r}') = g_0(\mathbf{r},\mathbf{r}') - \lambda_s g_0(\mathbf{r},\mathbf{r}_1) g_0(\mathbf{r}_1,\mathbf{r}'), \tag{38}$$

where $\mathbf{r}_1$ is the position of the first site, and λ_s is approximated by

$$\lambda_s = \frac{c_s}{E - E_s - i\eta}.$$

The propagation implied by Eq. (38) is illustrated in Fig. 1. The nonsingular part of the Green's function is the first ''surface'' term

$$\delta g_1(\mathbf{r},\mathbf{r}') = -\lambda_s g_0(\mathbf{r},\mathbf{r}_1) g_0(\mathbf{r}_1,\mathbf{r}'), \tag{39}$$

and represents propagation from $\mathbf{r}'$ to $\mathbf{r}_1$, followed by $\mathbf{r}_1$ to $\mathbf{r}$. The LDOS is found directly:

$$\rho(\mathbf{r},E) = \frac{1}{\pi} \frac{c_s \eta}{(E-E_s)^2 + \eta^2} g_0(\mathbf{r},\mathbf{r}_1)^2,$$

which is a suitable approximation for a single atomic s state.

The recursive relation we obtain for the Green's function for adding the Mth site to the problem is

$$g_M(\mathbf{r},\mathbf{r}') = g_{M-1}(\mathbf{r},\mathbf{r}') - \beta_M(E) g_{M-1}(\mathbf{r},\mathbf{r}_M) g_{M-1}(\mathbf{r}_M,\mathbf{r}'), \tag{40}$$

with

$$\beta_M(E) = \frac{\lambda_s}{1 + \lambda_s \delta g_{M-1}(\mathbf{r}_M,\mathbf{r}_M)}. \tag{41}$$

Although succinct, this Green's function contains all multiple reflections within the system, i.e., including all neighbors. When expanded in terms of a lower order, say $N < M$, Eq. (40) contains propagation terms, such as: $g_N(\mathbf{r},\mathbf{r}_i)$ or

$g_N(\mathbf{r}_i,\mathbf{r}')$, as well as coupling terms, $g_N(\mathbf{r}_i,\mathbf{r}_j)$. The quantity β_M represents the coupling of the last site to all other sites in the system, an aspect which is very similar to the tight-binding approximation. Restriction to nearest neighbors is therefore very easy to impose.

In order to illustrate simply, consider only 2 sites with $g_1(\mathbf{r},\mathbf{r}')$ as the starting point, while $g_2(\mathbf{r},\mathbf{r}')$ is obtained from the recursion equation

$$g_2(\mathbf{r},\mathbf{r}')=g_1(\mathbf{r},\mathbf{r}')-\beta_2(E)g_1(\mathbf{r},\mathbf{r}_2)g_1(\mathbf{r}_2,\mathbf{r}'). \quad (42)$$

Then the coefficient β_2, with Eq. (39) for δg_1,

$$\beta_2=\frac{\lambda_s}{1-\lambda_s^2 g_0(\mathbf{r}_2,\mathbf{r}_1)^2}$$

is seen to have new possible poles whenever $X=\pm 1$, where

$$X^2=\lambda_s^2 g_0(\mathbf{r}_1,\mathbf{r}_2)^2=1.$$

Neglecting the imaginary part of λ_s, these poles occur at the energies

$$E=E_s\pm c_s|g_0(\mathbf{r}_1,\mathbf{r}_2)|,$$

which are the bonding and anti-bonding states of the ''dimer.'' Looking more closely at the solution (42) for the dimer shows that it contains interference terms, such as $Xg_0(\mathbf{r},\mathbf{r}_1)g_0(\mathbf{r}_2,\mathbf{r}')$, which give rise to the spatial contrast between the bonding and anti-bonding states. In short, Eq. (40) contains a simplified electronic structure of a collection of coupled *s* orbital ''atoms'' and at arbitrary locations. If we neglect all interference terms of Eq. (40), we do get the form of a straight superposition of atomic orbitals

$$g_M(\mathbf{r},\mathbf{r}')\simeq g_0(\mathbf{r},\mathbf{r}')-\beta(E)\sum_{i=1}^{M} g_0(\mathbf{r},\mathbf{r}_i)g_0(\mathbf{r}_i,\mathbf{r}'). \quad (43)$$

However, this is difficult to justify, and the original result (40) is almost as easy to implement.

B. Corrugation for *d* orbital tips

The ''reciprocity principle'' found by Chen[17] for *d* tip states is succinctly demonstrated in the present context. Our tunneling current depends on the quantity $\hat{\mathcal{D}}\hat{\mathcal{D}}^*\delta g_s$, which we have discussed at some length. Thus we can check what an *s*-wave *surface* gives with a *d* tip by directly operating on the nonsingular part of Eq. (43) with $\hat{\mathcal{D}}$:

$$\hat{\mathcal{D}}_{l,m}\hat{\mathcal{D}}^*{}_{l,m}\delta g_s\simeq\beta(E)\sum_{i=1}^{M}\{\hat{\mathcal{D}}_{l,m}g_0(\mathbf{r},\mathbf{r}_i)\}\{\hat{\mathcal{D}}^*_{l,m}g_0(\mathbf{r}_i,\mathbf{r}')\}. \quad (44)$$

Since the source point and field point can be interchanged in the quantity $\hat{\mathcal{D}}_{l,m}g_0(\mathbf{r},\mathbf{r}')$, up to a sign, and furthermore since the $\hat{\mathcal{D}}_{l,m}$ operators generate the spherical solutions (as shown in Sec. II), then Eq. (44) is just the superposition of *d* orbitals with one at each of the surface sites. Thus the reciprocity idea is due to the interchange of field point with the source point.

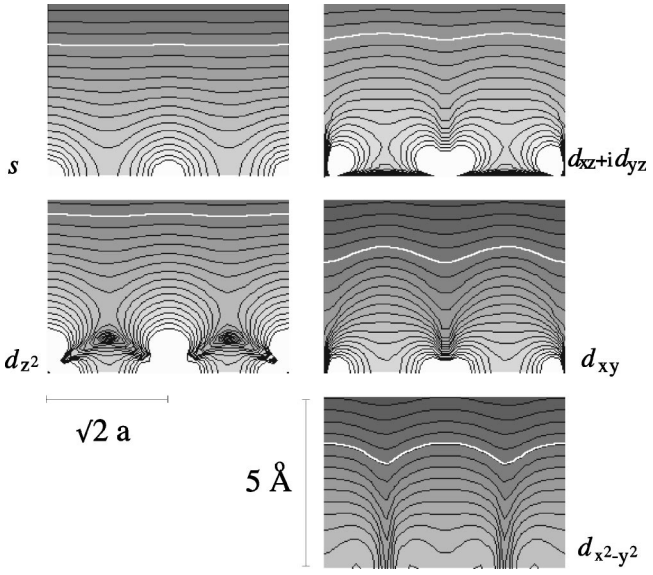

FIG. 6. Grey level representation of the surface LDOS (the quantity $\rho_{l,m}$, defined in the text) in the plane normal to the surface, for the five different tip orbitals, and using the proposed muffin-tin superposition method. The *s* wave case clearly indicates the atom positions, along the diagonal of a square lattice, each atom contributing a single *s* orbital. For the $l\neq 0$ tip states, our $\rho_{l,m}$ verifies Chen's ''reciprocity principle,'' i.e., giving the apparent superposition of a *d* orbital at the surface sites. The contours in white correspond to the same value of the resistance, $R=10^5\Omega$. The corrugation is slightly larger for d_{z^2} but increasingly enhanced for the orbitals of higher *m*, as the strong nodal lines normal to the surface clearly indicate.

It is remarkable that the ''exact'' equation for the muffin-tin surface (40) also verifies this reciprocity. Thus in Fig. 6 we show the STM current profile, for the selection of orbitals discussed in the nearly free electron approximation. More precisely, we compute

$$\rho_{l,m}=-\frac{1}{4\pi^2}\mathrm{Im}\,\hat{\mathcal{D}}_{l,m}\hat{\mathcal{D}}^*_{l,m}\delta g_s,$$

as before. The plane of the figure is along the diagonal of the square unit cell, and the atom positions are clearly seen in the case of the *s* tip. For the *d* orbitals, one notices that Eq. (40) does indeed lead to the superposition of the tip orbital type but on each surface site. The results for the corrugation in each case agree well with the previous Section, even though the electronic structure is treated so differently.

A glance at Fig. 6 may give the impression of a large d_{z^2} corrugation, even compared to those for the $m\neq 0$ tips. However, those contours highlighted in white, corresponding to the fixed resistance of $R=10^5\Omega$, provide a clear illustration of the main point of this article. In particular, the d_{z^2} is seen to have only a slightly larger corrugation than the *s* tip, while the other three cases of interest d_{xz+iyz} d_{xy}, and $d_{x^2-y^2}$ are significantly enhanced. The much weaker decay of the corrugation along the nodal line orthogonal to the surface is quite distinctive. The details of the STM image depends on the orientation of the nodal planes, thus giving a marked difference between the d_{xy} and $d_{x^2-y^2}$ cases. In agreement with the previous asymptotic calculations, the d_{xz+iyz} and

d_{xy} tips give an inverted corrugation, while the $d_{x^2-y^2}$ reveals a positive one. These results are in sharp disagreement with Ref. 18. Finally we note that the simulated STM images, in the case of a d_{xz} or d_{yz} tip, shows a ''striping'' effect, due to a difference in corrugation along two orthogonal directions parallel to the surface. The effect also occurs for some linear combinations of d orbitals.

VI. CONCLUSION

The striking point concerning the large amplitude atomic corrugation on metals is that it occurs for such a wide variety of surfaces, independent of their particular band structure, and for a variety of tunneling conditions. The problem has nevertheless resisted to a simple explanation. In this work we have showed that one needs a theory capable of giving a reliable value of the junction resistance R, as well as the density modulation $\delta\rho$. We applied our somewhat different method of calculating the tunnel current, which has the advantage of giving a suitable transmission coefficient, easily applicable to $l\neq 0$ states of the tip, and being for the most part analytical. We reviewed the asymptotic surface Green's function in the nearly free electron model, and reconsidered the effects of selected d states of the tip.

It transpires that the resistance versus tip-surface separation $R(z)$ depends strongly on the tip electronic structure. In particular, for individual tip d states, we found $R(z) \propto (\kappa z)^{m+1}$, over the usual exponential law, and in strong disagreement with other works. We argued that one cannot compare the corrugation for different tips at a fixed tip-surface separation. Our analysis of the asymptotic corrugation $\Delta_{l,m}(R)$ shows the $m=0$ states (p_z, and d_{z^2}) to have basically the s-wave behavior, with no striking enhancement. The d_{z^2} case is often attributed to the atomic resolution, but it is not much more sharp than a single s orbital tip. Quite to the contrary, the $m\neq 0$ tip states can give a corrugation with a very large enhancement over the s tip. We find in $\Delta_{l,m}(R)$ a gain of more than one order of magnitude, for $d_{xz}+id_{yz}$, or even two orders of magnitude, for the d_{xy} or $d_{x^2-y^2}$. We showed the combined effect of the increased average resistance, and increased current modulation, was due to the nodal lines or nodal planes of these particular tip states.

Among the negative points, we note how easily the effect is masked when a linear combination of degenerate orbitals is considered, in particular putting back a d_{z^2} component. Indeed the enhancement effect due to the tip nodes is very sensitive to the local electronic structure at the tip extremity. On the other hand, it predicts an enhancement for any type of sample metal. We checked our asymptotic calculations with the atom superposition method, which gives a Green's function and LDOS for a system of coupled s orbital atoms, and obtained identical results. This model allows one to visualize the significant effect of the nodal lines directly in the plots of the density (precisely in $\mathrm{Im}\,\hat{D}\hat{D}^*\delta g_s$). This points to the interesting prospect of intentionally preparing tips having this property, either with the intrinsic material, or with a small adsorbed molecule having a high symmetry.

The effect of a node in the *surface* wave function was used by Tersoff to explain giant corrugations on graphite.[20] There he found a singular $\Delta(z)$, again due to the treatment of the asymptotic expressions for the LDOS. Later with Lang,[35] they found that the corrugation was sensitively dependent on the tip electronic states. The giant corrugations on graphite were also attributed to its compressibility under the influence of tip-surface forces.[36] Thus Zheng and Tsong[14] proposed a model of giant corrugations on metals in which the tip extremity is compressible, due to an hypothetical contamination, while the surface remains rigid.

We have considered the possibility of corrugation enhancement due to tunneling through new states induced by the proximity of the tip to the surface. This is provided quite directly via the coupled set of equations (21), derived in Sec. II, which account for multiple reflections across the barrier. We have investigated how this situation of stronger coupling between the electrodes results in significant changes in both the tip and the surface density of states. For example, suppose at large separation we have a pure d_{z^2} orbital, but when the tip is close to the surface a second d-orbital gains spectral weight at the Fermi level, say $d_{xz}+id_{yz}$. Then the tunneling current involves direct d_{z^2}, and $d_{xz}+id_{yz}$ terms, but there are also interference terms, involving both d_{z^2} and $d_{xz}+id_{yz}$. Although of some theoretical interest, our results show that all of the multiple reflection terms are small in the experimental resistance range.

In fact, we have tried to relax the condition of the rigid tip by letting the tip atom position $\mathbf{r}_0$ become a variable, in the spirit of Ref. 14. Then the resonance energy is calculated using the *total* DOS of the tip-surface system. As a consequence, the tip atom moves subject to the total force due to the two remaining electrodes. No giant corrugation is found, principally due to the fact that, beyond $10^5\Omega$, the tip to surface coupling is negligible. In the small resistance case, the corrugation could even be attenuated, i.e. the motion of the tip atom tends to compensate the lateral variation in the density, rather than to amplify it.

In a ''tour de force'' Bracher *et al.*[37] have derived the Green's function for tunneling in an electric field. Thus one can check for a possible enhancement effect which we have totally neglected.[32] The electric field at the tip extremity could be quite large, and we suggest that future calculations of the spectral weight of the tip d orbitals would be even more instructive if the field were taken into account. Another important point we have neglected is self-consistency, and the tip and surface Hamiltonians (H_s and H_{tip}) are considered as independent of each other. Therefore correlations, such as barrier lowering due to the image potential, have not been implemented. This remains true for all the STM models in the one-electron picture.

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