Influence of Bulk States on Laterally Confined Surface State Electrons

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Strong scattering by adatoms positioned with the tip of a scanning tunneling microscope (STM) has recently been used to confine surface state electrons to nanoscale structures. We develop a model for confinement by a circular potential on a metal surface, including substrate band structure effects. Scattering into bulk states provides an important broadening mechanism for partially confined states. Contrary to experiment the level width vanishes as the energy approaches the surface state band edge, indicating an additional dominant broadening mechanism for laterally confined surface state levels seen in the STM.

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Recently, Crommie *et al.* [1] have shown how strong scattering by adatoms may be used to laterally confine surface state electrons. Using the tip of a scanning tunneling microscope (STM), individual Fe atoms are positioned with atomic scale precision into corral geometries on the Cu(111) surface. The local density of states (LDOS) of the enclosed electrons, as measured by tunneling spectroscopy, exhibits sharp resonances which lie close to values predicted by a simple "particle-in-a-box" analysis, indicating confinement of the Shockley surface state electrons which occur on the clean Cu surface. An interesting aspect of the results of Crommie *et al.* [1] concerns the linewidth of the measured levels. Possible mechanisms limiting the lifetime of the confined electrons include partial lateral confinement due to leaky corrals (the Fe atoms are separated by 7 Å), and scattering into extended bulk states. The bulk electron states coexist in energy with, but are orthogonal to, the surface state electrons on the clean surface. However, the corral provides a coupling which allows scattering between bulk and surface states. In this Letter we report a study of these broadening mechanisms, for a model system which incorporates the crystal substrate. A proper understanding of these mechanisms may open up the way for improved confinement, through choice of adatom species or substrate material. This is necessary for nanoscale applications, such as imaging "scarred" eigenstates [2] in structures corresponding to classically chaotic systems.

We are led to develop a simplified model by the dimensions of the problem. Typically, the confining structures are built from 50–100 atoms, the enclosed area representing > 1000 substrate atoms–well beyond the capabilities of current *ab initio* techniques. We therefore consider a continuum model where outside the surface, in addition to an uncorrugated vacuum barrier V_B, we include a confining potential V_S. The long wavelength of the surface state electrons makes them insensitive to the barrier thickness which we restrict to a delta-function sheath of radius ϱ_0. In circular-polar coordinates $\boldsymbol{r} = (\varrho, z, \phi) = (\mathbf{x}, \phi)$, with surface normal z,

$$V(\boldsymbol{r}) = V_B(z) + \frac{V_S}{\varrho_0}\delta(\varrho - \varrho_0), \quad z > 0. \tag{1}$$

Increasing V_S increases the degree of confinement. This potential should be viewed as an effective pseudopotential, in principle dependent upon energy and spin, which mimics the scattering by the true confining barrier [3]. For current purposes it is sufficient to take constant V_S. We restrict our attention to $V_S > 0$, so that the extended nature of the confining potential in the $+z$ direction is not significant, since the electron wave function decays exponentially into vacuum [4]. The crystal, unperturbed by the presence of the corral, occupies the half space $z < 0$.

The Green function G for the combined system is found from the separate Green functions G_{I} for the sheath and G_{II} for the bulk crystal. From the matching Green functions method [5] G satisfies the integral equation

$$G = G_{\mathrm{I}} - G_{\mathrm{I}}\Gamma G, \tag{2}$$

where multiplication corresponds to an integral over the matching surface, S, the plane $z = 0$. In deriving (2), G_{I} and G_{II} are assumed to satisfy zero normal-derivative and zero amplitude boundary conditions on S, respectively. Γ, the embedding potential, is

$$\Gamma(\boldsymbol{r}_S, \boldsymbol{r}_S') = -\frac{1}{4}\frac{\partial^2}{\partial n_S\, \partial n_S'} G_{\mathrm{II}}(\boldsymbol{r}_S, \boldsymbol{r}_S'), \quad \boldsymbol{r}_S, \boldsymbol{r}_S' \text{ on } S, \tag{3}$$

with n_S the surface normal to S. Unless otherwise stated, we assume atomic units $e^2 = \hbar = m = 1$.

The important electron states are those in the vicinity of the gap opened near the surface Brillouin zone center, $\bar{\Gamma}$, by the z Fourier component g of the crystal potential, strength V_g. For these we adopt the two-band model, taking free-electron dispersion parallel to the surface [6]:

$$\Gamma(\boldsymbol{r}_S, \boldsymbol{r}_S') = \int \frac{d\mathbf{k}}{(2\pi)^2}\Gamma_k e^{i\mathbf{k}\cdot(\mathbf{r}_S - \mathbf{r}_S')}. \tag{4}$$

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Making the further simplification of the narrow gap approximation, $|V_g| \ll g^2$, and measuring energies relative to the center of the gap at $\bar{\Gamma}$ gives [7]

$$\Gamma_k = g\sqrt{V_g^2 - \varepsilon^2}/4(V_g + \varepsilon), \tag{5}$$

where $\varepsilon = E - k^2/2$. The band gap extends between $\pm V_g$ at $\bar{\Gamma}$, and taking for the vacuum barrier $V_B(z)$ a potential step at $z = 0$, height Δ, a surface state exists for $V_g < 0$, the Shockley condition. In the computations reported here we have used $V_g = -0.1$ and $\Delta = 0.13$, giving a surface state of energy $E_0 = -0.032\,612$ at $\bar{\Gamma}$.

Using symmetry to expand G and G_I as, e.g.,

$$G_I(\boldsymbol{r}, \boldsymbol{r}') = \frac{1}{2\pi}\sum_m e^{im(\phi-\phi')} G_I^m(\mathbf{x}, \mathbf{x}'), \tag{6}$$

we expand the corral Green function G_I^m in terms of the two-dimensional corral eigenstates $|km\rangle$ of the radial Schrödinger equation with the sheath:

$$\langle \varrho | km\rangle = \alpha_k^m \{J_m(k\varrho) + \Theta(\varrho - \varrho_0)\pi V_S J_m(k\varrho_0) \times [J_m(k\varrho_0) N_m(k\varrho) - N_m(k\varrho_0) J_m(k\varrho)]\}, \tag{7}$$

where the normalization constant is

$$\alpha_k^m = \sqrt{k}/|1 + i\pi V_S H_m^1(k\varrho_0) J_m(k\varrho_0)|. \tag{8}$$

Then,

$$G_I^m(\mathbf{x}, \mathbf{x}') = \int dk \langle \varrho | km\rangle g(z, z'; \varepsilon) \langle km | \varrho'\rangle, \tag{9}$$

where $g(z, z'; E)$ is the Green function at energy E for the one-dimensional barrier potential $V_B(z)$, subject to the relevant boundary conditions. Using (9) and (4) in (2) and following through the analysis allows the Green function outside the surface ($z, z' > 0$) to be determined. We find

$$G = G_\infty + G_{2D} + G_3, \tag{10}$$

where G_∞ is the Green function for the potential (1) with an infinite barrier at $z = 0$. This does not contribute to the density for $E < \Delta$. The other terms are

$$G_{2D}^m(\mathbf{x}, \mathbf{x}') = \int dk \langle \varrho | km\rangle f_k \langle km | \varrho'\rangle e^{-\gamma_k(z+z')}, \tag{11}$$

$$G_3^m(\mathbf{x}, \mathbf{x}') = \iint dk dk' \langle \varrho | km\rangle \mathcal{G}_{kk'}^m \langle k'm | \varrho'\rangle e^{-\gamma_k z - \gamma_{k'} z'}, \tag{12}$$

where $\gamma_k = \sqrt{2(\Delta - E) + k^2}$ is the decay constant into vacuum,

$$f_k = 2/(\gamma_k + 2\Gamma_k) \tag{13}$$

and $\mathcal{G}_{kk'}^m$ is found from the integral equation

$$\mathcal{G}_{kk'}^m = -f_k Q_{kk'}^m f_{k'} - f_k \int dk'' Q_{kk''}^m \mathcal{G}_{k''k'}^m \tag{14}$$

with the scattering amplitude Q between corral states given by

$$\langle km | \Gamma | k'm\rangle = \Gamma_k \delta(k - k') + Q_{kk'}^m. \tag{15}$$

The LDOS is $\rho = (1/\pi)\Im G$, and we first consider the contribution from G_{2D},

$$\rho_{2D}(\mathbf{x}) = \frac{1}{\pi}\sum_m |\langle \varrho | k_0 m\rangle|^2 e^{-2\gamma_{k_0} z}/[\gamma_k + 2\Gamma_k]'_{k_0} + \frac{1}{2\pi^2}\sum \int_{k_C}^\infty dk\, |\langle \varrho | km\rangle|^2 \Im[f_k] e^{-2\gamma_k z}, \tag{16}$$

with the prime here denoting d/dk, and E assumed below the vacuum level. The dominant first term comes from the pole in f_k at k_0, where $\gamma_{k_0} + 2\Gamma_{k_0} = 0$—the surface state condition at $E = E_0 + k_0^2/2$. The second term is a relatively unimportant background, coming from the continuum of states which exists for $k \geq k_C = \sqrt{2(E - |V_g|)}$. Apart from the background, ρ_{2D} is *precisely* the LDOS given by a two-dimensional treatment in which the surface state electrons scatter off the corral potential. The role of the crystal is simply to provide the surface state band, with a particular weight outside the surface. This is also the approach used by various authors [8,9] in analyzing other surface state scattering problems.

The contribution ρ_3 to the LDOS from G_3 in (12) is a correction to ρ_{2D} derived from the scattering into bulk states. This term was evaluated by solving the integral equation (14) for $\mathcal{G}^m$ using a Chebyshev polynomial expansion method [10].

In Fig. 1, we show the calculated LDOS ($\rho_{2D} + \rho_3$) at the center of a circular corral, radius 135 a.u.—to which only states with $m = 0$ contribute—in the limit of weak confinement. On the clean surface the surface state band gives rise to a constant LDOS above the band minimum. A nonzero sheath potential introduces a modulation to this band, with peaks appearing roughly at

$$E_n = E_0 + j_{0,n}^2/2\varrho_0^2, \tag{17}$$

where $j_{m,n}$ is the nth zero of the Bessel function J_m. With increasing V_S the amplitude of the oscillations in the LDOS increases, and successive peaks gradually emerge

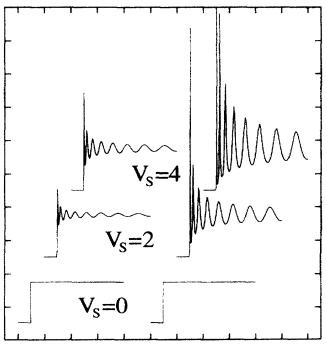

FIG. 1. Development of the LDOS at $\mathbf{x} = (0, 1)$ with increasing sheath potential V_S for a circular corral with $\varrho_0 = 135$. The crystal is modeled as described in the text. Left: full calculation. Right: corresponding result in the two-dimensional approximation. Horizonal divisions of 0.005 a.u. and vertical divisions of 0.01 states/a.u. are shown. Each plot covers the energy range [–0.035,–0.015] and are successively displaced by (0.005,0.020) with increasing V_S.

as well-defined resonances, beginning with those of lowest energies. Also shown in Fig. 1 is the corresponding LDOS from ρ_{2D} alone, i.e., when scattering into bulk states is neglected. The qualitative features are the same, but it is clear that for similar sheath potentials ρ_{2D} greatly overestimates the structure induced by lateral confinement.

This behavior persists for greater values of the confining potential. Figure 2(a) shows the LDOS for $\varrho_0 = 125$ and $V_S = 64$, which gives definite resonances over the whole energy range shown. It is clear from this figure that not only does the inclusion of bulk scattering broaden the very sharp levels of ρ_{2D}, but it also produces energy shifts—if we describe bulk scattering in terms of a self-energy, these are of course the imaginary and real parts, respectively. In fact, the shifts of the peaks from the "ideal" values given by (17) are very small, amounting at most to 0.01 eV for the well defined resonances, and vanish as E approaches the bottom of the surface state band. This means that the measured peaks can be compared directly with the two-dimensional particle-in-a-box result (17) to give information on surface state dispersion. Moreover the smallness of the shifts means that the spin-dependent scattering by the Fe corral atoms is unlikely to contribute significantly to the level widths. Conversely, it is doubtful that any useful information regarding the adatom scattering may be extracted from the level positions.

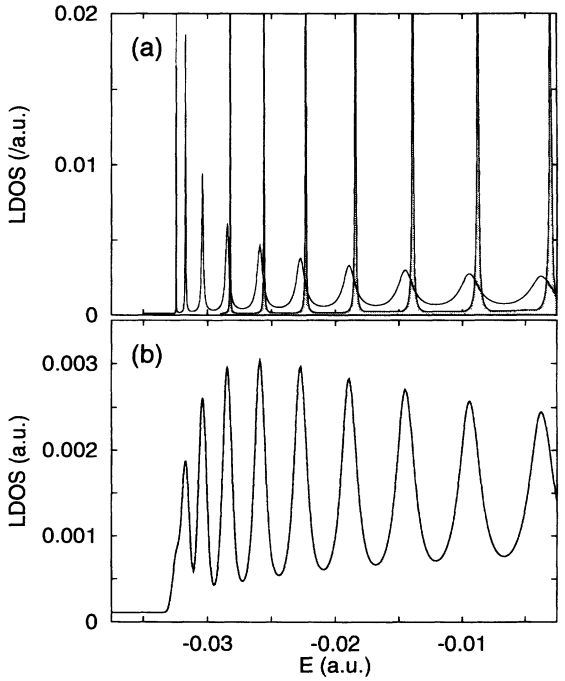

FIG. 2. (a) LDOS at $\mathbf{x} = (0,3)$ for a circular corral, $\varrho_0 = 125$, with $V_S = 64$ (unshaded). The shaded curve is the corresponding result within the two-dimensional approximation and for which the first three peaks have been omitted for clarity. (b) The LDOS in (a) convoluted by a Gaussian of width 0.0004.

The nature of the confinement and the bulk scattering may be traced to the two-dimensional sheath eigenstates. Within the corral $\langle \varrho | km \rangle = \alpha_k^m J_m(k\varrho)$, and as V_S increases this becomes increasingly negligible—and the electron increasingly excluded from the area within the corral—*except* in the vicinity of $k\varrho_0 = j_{m,n}$. In the limit $V_S \to \infty$ only these discrete states exist within the corral (there remains a continuum outside), and the wave functions become $\propto J_m(k_{m,n}\varrho)$: the wave functions within the corral at the allowed energy levels are the clean surface wave functions which do not "see" the confining potential because of the node condition. Consequently, in this limit the scattering amplitudes $Q_{kk'}^m$ vanish, and the levels are infinitely sharp. For finite sheath potential, the scattering into bulk states is a consequence of the modification of the parallel eigenstates from those of the clean surface.

For a quantitative assessment of the importance of bulk scattering we have evaluated the level width of the $m = 0$, $n = 3$ level for various sheath potentials, and also within the two-dimensional approximation (i.e., excluding ρ_3). These are shown in Fig. 3(a), and clearly show the dominant role of scattering into bulk states in limiting the lifetime of confined electrons for all finite V_S. Thus, we can state that more realistic modeling of these systems, including the atomistic nature of the confining structure, *must* include the crystal substrate if quantitative information (e.g., adatom phase shifts) is to be extracted [the variation of level width with V_S shown in Fig. 3(a) suggests this might be possible]. Note that, if anything, our model band structure *underestimates* the importance of scattering into bulk states compared to the real Cu(111) surface, where the surface state lies closer to the lower band edge at $\bar{\Gamma}$ and disperses with a greater effective mass, taking it closer with increasing energy [8,11].

When we compare our results with the experimental spectrum of Ref. [1] there are qualitative discrepancies. The envelope of the peaks in the experimental spectrum reaches a maximum at the third level, while our calcula-

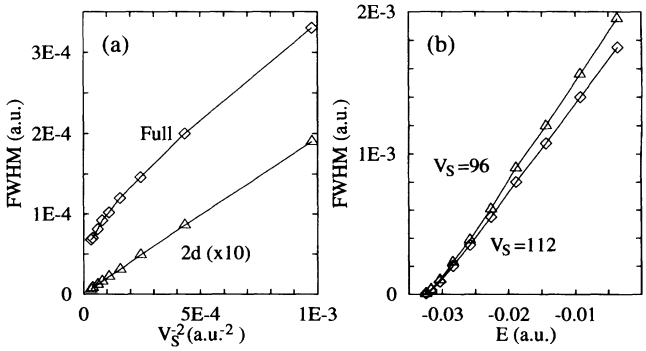

FIG. 3. (a) Calculated width (FWHM) of the $m = 0$, $n = 3$ level in a circular corral, $\varrho_0 = 125$, for different confining potentials, as obtained from a full calculation and within the two-dimensional approximation (scaled by a factor 10). (b) Variation of the level width with level energy, for $m = 0$ states in a corral with $\varrho_0 = 125$.

tions [Fig. 2(a)] show an envelope increasing rapidly as the energy approaches the surface state band minimum. Moreover the calculated level widths go to zero in the same limit [Fig. 3(b), also apparent in Fig. 2(a)], whereas experimentally they decrease to a finite value. The vanishing of the level width as $E \rightarrow E_0^+$ is a general effect which will persist in a more realistic treatment, being due to the effective barrier height of the corral potential behaving like an infinite-strength sheath potential (the reflection coefficient $\rightarrow 1$) as $k \rightarrow 0$. In this limit, as we have seen, the width of the states goes to zero. In order to reproduce the features of the experimental spectra, it is necessary to introduce an *additional* broadening mechanism which dominates for the lowest levels. In Fig. 2(b) we have convoluted the LDOS in Fig. 2(a) with a Gaussian of constant width 0.0004 a.u., comparable with the unconvoluted width of the $n = 5$ level. The resulting spectrum is now qualitatively similar to the experimental dI/dV measurements. Possible origins of this broadening are instrumental or many-body effects, which might be clarified by similar experiments on substrates where E_0 lies closer to the Fermi level [e.g., Ag(111) [12]].

To summarize, we have developed a model, including the crystal substrate, for surface state electrons confined by a circular corral. We have established the important factors governing the positions and widths of the energy levels, and the quantitative information they contain. We find only small shifts in energy levels from ideal positions, which therefore reflect little beyond the surface state dispersion relation. Coupling to bulk states is much more important than partial lateral confinement in determining the level widths, indicating that more attention should be paid to the choice of substrate than adatom species if the lifetime of the confined electrons is to be maximized. We find, also, that the level widths go to zero as the energy approaches the surface state band minimum, revealing that in the spectra seen in the STM there must be a broadening mechanism present in addition to leaking from the corral and scattering into the bulk.

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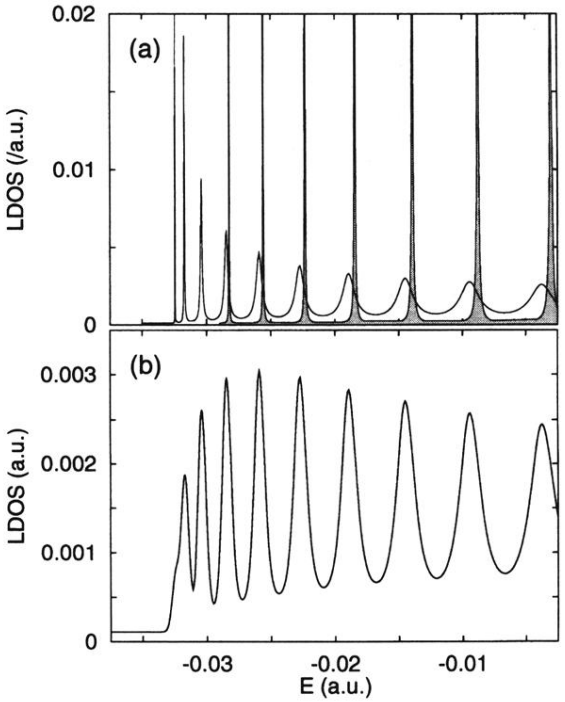

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