Fully three-dimensional scattering calculations of standing electron waves in quantum nanostructures: The importance of quasiparticle interactions

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We describe full multiple-scattering calculations of surface-state electrons in quantum nanostructures built from a small number of adatoms. These are structures that have been assembled and studied in recent cryogenic STM experiments. Our calculations confirm the nature of electron confinement deduced from a previous continuum model. We highlight the role of the intrinsic electron lifetime in determining spectral features, arguing that atomic corrals could serve as useful ''nanoscale quantum laboratories'' of many-body processes at surfaces. Results for structures assembled from several different atomic species show remarkable similarities, a specific prediction of our theory.
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Using the tip of a scanning tunneling microscope (STM) it is possible to move atoms on the surface of a metal, and assemble them into ordered nanostructures. This has been beautifully demonstrated by Crommie, Lutz, and Eigler,[1] who have placed Fe atoms on Cu(111) into various geometrical arrangements.[1–3] The adatoms interact strongly with the electrons in surface-state bands, and differential conductance measurements within circular rings of adatoms reveal a series of energy levels, evidencing electron confinement. This has led to the structures being christened ''quantum corrals''.[1] We report the results of a study of these atomic arrays, using full multiple-scattering calculations, in which we focus on the influence of the electron self-energy on the spectrum of confined states. We conclude that through further experiments the quantum corrals could prove useful as nanoscale laboratories of many-body processes at surfaces.

Several theoretical accounts of the experiments have previously been reported.[1,5–9] Alongside the original experiments Crommie, Lutz, and Eigler,[1] were able to explain the *energies* of the states with a two-dimensional particle-in-a-box model. The first insight into the characteristic behavior of the level *widths*, corresponding to the limited lifetime of the confined electrons, came from the work of Heller *et al.*[5,6] who modeled the adatoms as point scatterers in a two-dimensional free-electron gas. These authors found it possible to achieve a consistent account of the experiments using a single complex s-wave phase shift, interpreted as the adatoms scattering about 50% of the incident flux into the bulk. Recently Harbury and Porod[7] have considered a similar model but with finite-radius elastic scatterers for the adatoms, and obtained a similar level of agreement. This suggests a picture in which leakage is dominated by tunneling through the corral walls, with the appearance of a complex phase shift in the work of Heller *et al.* due to the neglect of other scattering channels. In reality the surface state has a cross section of several atomic diameters, so that the problem is intrinsically three dimensional. Crampin, Boon, and Inglesfield[8] developed a three-dimensional continuum model, treating the corral as a finite potential with δ-function width, and quantified the relative importance of these two decay mechanisms. They found that scattering into bulk states is an order of magnitude more important than tunneling through the corral walls in determining the widths of confined levels. However, none of these studies has been able to account for the limiting behavior at low energies, in each case predicting a vanishing of the level width that is contrary to experiment. For completeness we also mention work by Hörmandinger and Pendry[9] on the scattering of surface states by rows of adsorbed adatoms, who identify dense rows of Cu and Fe adatoms as mainly scattering horizontally (leakage into the surface state on other side), but with an enhancement of vertical scattering (into bulk) for sparser adatom arrays, as constructed experimentally,[1–3] due to Bragg diffraction.

In our present work we have performed calculations of the confined surface-state electrons, including a fully atomistic description of both the substrate and the corral. We evaluate the local density of states (LDOS) from the Green function G, determined using multiple scattering theory: $n(\mathbf{r};E)=-(1/\pi)\mathrm{Im}\,G(\mathbf{r},\mathbf{r};E)$. Within this framework, space, including the vacuum barrier region, is partitioned into atomic cells. The scattering properties of the cells, described by individual t matrices, are combined to give the scattering properties of the whole system, described by the full T matrix. From this and the free-space Green function G_0 we have

$$G=G_0+G_0TG_0. \tag{1}$$

We use the scattering-path operator representation for T, so that using standard manipulations[10] we are able to write the Green function formally as

$$G=G_C+G_0\tau_C[(t_C^{-1}-t^{-1})^{-1}-\tau_C]^{-1}\tau_CG_0. \tag{2}$$

G_C is the Green function of the clean surface, in the absence of the corral, and τ_C the scattering path operator for the clean surface. We evaluate the inverse $[\ ]^{-1}$ in Eq. (2) in the site partial wave representation, $|Li\rangle$, the matrix dimension being limited by the number of sites for which the t matrix differs depending upon whether the adatoms are present (t) or not (t_C). The quantity $\langle\mathbf{r}|G_0\tau_C|Li\rangle$ may be identified as the amplitude of the wave with angular momentum L leaving site

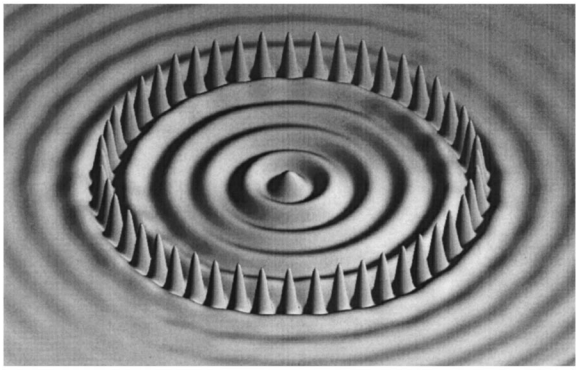

FIG. 1. LDOS at the Fermi energy in and around a 142.8 Å diameter circular corral of 48 Fe atoms on Cu(111).

i due to a point source at $\mathbf{r}$, including full multiple scattering within the clean surface, and $\langle iL|\tau_C G_0|\mathbf{r}\rangle$ relates the amplitude at $\mathbf{r}$ when a partial wave L is incident upon site i of the clean surface, again including full multiple scattering.

We consider circular corrals of 48 adatoms placed at the atomic locations given in Ref. 2. We use the atomic-sphere approximation for the cells, evaluating the cell t matrices from the solutions of the radial Schrödinger equation. We assume that the potentials differ from the clean surface only at the 48 sites directly occupied by the adatoms. The actual potentials used are taken from fully self-consistent calculations of the clean Cu(111) surface, or for the adatom cells from self-consistent calculations of $(\sqrt{3}\times\sqrt{3})$-$R30°$ overlayers. In our studies we have considered corrals built from Fe, Cu, Ag, and Mo adatoms, including partial waves up to $l=3$. For the Brillouin zone integrals we use a special directions method with up to 312 radial sample points heavily weighted near the surface state wave vector and 96 angular sampling points in the full surface Brillouin zone. Decreasing each by a factor of 2 gives barely distinguishable results. Our calculations give a surface-state band edge at $E_0=-0.46$ eV and a surface-state Fermi wavelength of $\lambda_F=29.5$ Å, in good agreement with experiment.[1] We stress that our basic calculations include no adjustable parameters.

In Fig. 1 we illustrate the LDOS in and around the circular corral of 48 Fe atoms, evaluated at the Fermi energy and 5 Å above the surface. This is expected to correspond closely to the experimental constant current scans taken at small voltages.[1] The adatoms are clearly distinguishable as peaks in the LDOS, as found experimentally[1] [this is not trivial, as for other species of adatoms, or at other energies, minima are seen with the STM (Ref. 4)]. Inside the corral we see strong oscillations, corresponding to the confined surface states as described by Crommie, Lutz, and Eigler,[1] and outside the corral there are weaker oscillations. Our results represent the first theory of the atomic corrals, which also reproduces the structure in the LDOS in the immediate vicinity of the adatoms, although we note the STM gives a stronger signal between the adatoms than we find. This may be due to the difference between the LDOS and STM tunnel current, or our single site treatment of the adatom potential.

We now focus on the spectral properties. In Fig. 2 we present results for the LDOS evaluated at the center of the 48 Fe atom corral on Cu(111), and 5 Å above the surface (the results are not sensitive to the precise height, which just

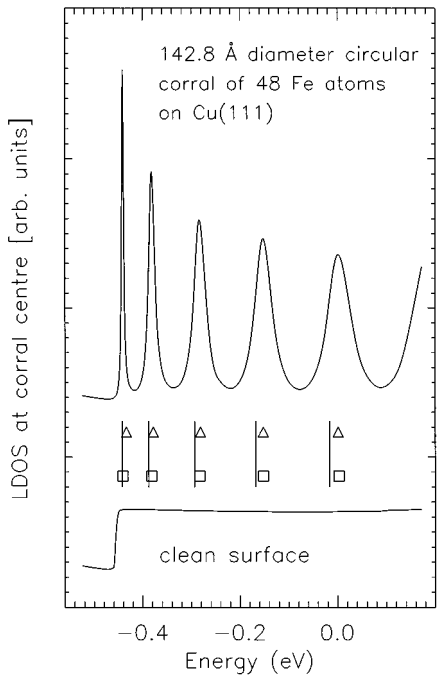

FIG. 2. LDOS at the center of the corral. A linear background due to the energy dependence of the barrier penetration has been removed, so the clean surface gives the characteristic steplike contribution from the surface state (bottom). Within the corral a series of resonant energy levels are seen (top). The peak positions (squares) compare well with experiment (triangles) (from Ref. 1), but differ from the predictions of the hard-wall model using the calculated dispersion (vertical lines).

scales the values). A series of resonant levels are clearly visible, corresponding to the $m=0$ eigenstates of the particle in a box model.[1] This predicts eigenstates $\psi_{nm}(\varrho,\phi) \propto J_m(k_{nm}\varrho/S)\exp(im\phi)$, where S is the corral radius and k_{nm} the nth zero of the Bessel function $[J_m(k_{nm})=0]$, and only states with $m=0$ have amplitude at the origin, $\varrho=0$. It is interesting that the peak positions differ from the predictions of this hard-wall model when we use our calculated dispersion relation $E(k)$ [i.e., the energies $E(k_{nm})$], but agree well with the experimental peak locations.

The resonance widths vary with energy, decreasing as the energy approaches the surface-state band edge. However, and in common with previous results obtained with both two- and three-dimensional models,[5–8] the width actually vanishes in the limit. This is contrary to experiment, where they decrease to a finite value. The calculated behavior was explained by Crampin, Boon, and Inglesfield[8] as a general property originating in the effective strength of the adatom scattering increasing as the lateral momentum of the surface-state electron decreases. Our results show that this effect still holds when the fully atomistic nature of the corral is included. Since the level width Γ corresponds to an inverse lifetime $\hbar/\tau$,[11] this discrepancy implies the existence of an additional decay mechanism that limits the lifetime of the confined electrons. Differences between theory and experiment are also evident in the envelope of the spectrum, with calculated peak heights increasing as the energy decreases. Experimentally they reach a maximum and then fall.[1–3]

To further understand the experiments, and since our cal-

culation includes all elastic scattering processes, we have sought to identify the influence of inelastic scattering by including the effects of Auger decay and electron-phonon scattering. We do this by introducing an electron self-energy, $E \rightarrow E + i\Sigma(E)$. We neglect the wave-vector dependence of Σ, taking a uniform value over the volume of the crystal (and adatom) and putting $\Sigma = 0$ in the vacuum. Theoretical work has shown that Σ vanishes rapidly outside the surface, and our choice of a uniform value is justified as we are focusing our attention on the surface state, which extends over several atomic layers, and which changes only slowly in character over the energy range we are interested in. We do let Σ vary with energy, taking

$$\Sigma(E) = \alpha + \beta(E - E_F)^2. \tag{3}$$

The quadratic term is the contribution from electron-hole pair creation,[12] and we take β to be 0.015 eV^{-1} based upon theoretical estimates.[13] The larger constant contribution originates in electron-phonon scattering and has been discussed elsewhere[14] in the analysis of photoemission linewidths. Based upon that work we take $\alpha = 5$ meV, ignoring the sharp reduction that takes place when $E - E_F$ becomes comparable to excitation energies in the phonon band (recall the experiments are performed at 4 K). At these energies the lifetime of the confined surface state is dominated by scattering into bulk states.

The effects of these interactions are seen in Fig. 3, where we also show results obtained for corrals assembled from Cu, Ag, and Mo atoms. These different species give surprisingly similar results, especially Fe, Cu, and Ag, a prediction of our model as, to our knowledge, all structures assembled have been from Fe atoms. Evidently the differences between the scattering properties of these particular adatoms are much smaller than the difference between each of them and the vacuum region that they substitute. Only for Mo is a greater level width (and correspondingly smaller peak height) especially noticeable. Comparing the Fe spectrum with that calculated without the self-energy, we note the resonances now narrow with energy to a finite value at the surface-state band edge, and, furthermore, the spectrum has developed the characteristic envelope, peaking away from the first level. Including the electron self-energy has led to a marked improvement in the level of agreement with experiment.

Making a more quantitative analysis, we have fitted each of the spectra in Fig. 3 using a series of Lorentzians plus a smooth background. We find that in each case the Lorentzian widths (full width at half maximum) so obtained vary smoothly with energy, and significantly the width of the lowest peak is the same for each species (not so in the subsequent levels). A similar analysis applied to spectra calculated using an arbitrary scaling of Σ gives similar behavior, but the Lorentzian widths converge to a second value. We identify the width of the lowest level as being given, to a good approximation, by

$$\Gamma = 2f\Sigma(E_0), \tag{4}$$

where

$$f = \int_{-\infty}^{0} \psi^* \psi d\mathbf{r} \tag{5}$$

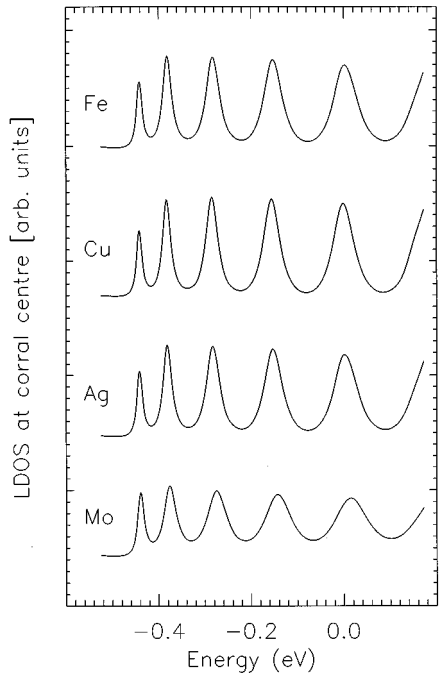

FIG. 3. LDOS at the center of circular corrals made of different species of adatoms. The calculations also include the electron self-energy, as described in the text.

is the fraction of the surface state within the crystal and $\Sigma(E_0)$ the self-energy, both evaluated at the band edge. This is just the result one would obtain including Σ by perturbation theory, valid as $\Sigma \ll E$. The surface-state wave function ψ in Eq. (5) may be taken as that of the clean surface, since although generally this is strongly affected by the corral, the lowest resonance occurs precisely when this has a node at the corral radius and so is barely modified in shape.

Analyzing the experimental spectrum given in Ref. 1, we find similar behavior in the levels widths, but, surprisingly the limiting value is over twice as large, at 35 meV, as that found using the self-energy in Eq. (3), which is based upon current knowledge of inelastic scattering processes. Does this point to a deficiency in our treatment of these effects? It is interesting to note that linewidths measured by angle-resolved photoemission, a well established and widely used probe of surface states, are comparable to the STM measurements.[14] Admittedly the photoemission linewidths have become progressively narrower with time as improved energy and angular resolution have been achieved, and with better surface preparation, but now the remaining differences between theory and experiment are normally attributed to a small residual concentration of defects.[14,15] In the case of the STM corral measurements, defects within the corral would appear to be absent. Certainly there are none on the surface, and subsurface defects would also show up through the interference pattern resulting from their scattering of the surface state.[16,17] We have also established through calculations that disorder in the corral structure that arises when measurements are taken at large bias[1,2] has negligible effect on the lowest level width. As a means of clarifying these issues, which are of some importance,[18] we would encourage further experiments aimed at accurately establishing the level widths, at both Cu and other suitable metal surfaces, along

with calculations including the STM measuring process. If this leads to greater understanding of inelastic scattering processes at surfaces, these corrals may rightly be thought of as nanoscale quantum laboratories.[19]

To summarize, we have made full multiple-scattering calculations on atomic corrals on Cu(111). The level of agreement with experiment over the spectrum of confined surface states is greatly improved when the electron self-energy is included. We find a simple relationship between the self-energy and the lowest level width, but the theoretical width we calculate is considerably smaller than seen in experiment. This is similar to the present message coming from angle-resolved photoemission experiments. Further work on quantum corrals, both experiment and theory, could provide greater insight into many-body processes at surfaces.

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[1] M.C. Crommie, C.P. Lutz, and D.M. Eigler, Science **262**, 218 (1993).

[2] M.C. Crommie, C.P. Lutz, D.M. Eigler, and E.J. Heller, Physica D **83**, 98 (1995).

[3] M.C. Crommie, C.P. Lutz, D.M. Eigler, and E.J. Heller, Surf. Rev. Lett. **2**, 127 (1995); Surf. Sci. **361/362**, 864 (1996); in Electronic Surface and Interface States on Metallic Systems, edited by E. Bertel and M. Donath (World Scientific, Singapore, 1995), p. 203.

[4] M.C. Crommie, C.P. Lutz, and D.M. Eigler, Nature **363**, 524 (1993); Ph. Avouris, I.-W. Lyo, R.E. Walkup, and Y. Hasegawa, J. Vac. Sci. Technol. B **12**, 1447 (1994); Ph. Avouris, I.-W. Lyo, and P. Molinàs-Mata, Chem. Phys. Lett. **240**, 423 (1995).

[5] E.J. Heller, M.F. Crommie, C.P. Lutz, and D.M. Eigler, Nature **369**, 464 (1994).

[6] In the implementation of the model in Ref. 5 (see also Refs. 2 and 3) the energy dependence of the $2/\sqrt{\pi k}$ prefactor in the propagator has been incorrectly omitted [E.J. Heller (private communication)]. This does not affect LDOS scans at fixed energies (beyond a scale factor), or markedly alter the width of the energy levels, but does change the envelope of the spectrum. Correct results with this model (but with different parameters) may be found in: S. Crampin, M.H. Boon, and J.E. Inglesfield, in *Electronic Surface and Interface States on Metallic Systems*, edited by E. Bertel and M. Donath (World Scientific, Singapore, 1995), p. 187.

[7] H.K. Harbury and W. Porod, Phys. Rev. B **53**, 15 445 (1996).

[8] S. Crampin, M.H. Boon, and J.E. Inglesfield, Phys. Rev. Lett. **73**, 1015 (1994).

[9] G. Hörmandinger and J.B. Pendry, Phys. Rev. B **50**, 18607 (1994).

[10] A. Gonis, *Green Functions for Ordered and Disordered Systems* (North-Holland, Amsterdam, 1992).

[11] Not to be confused with the scattering path operator τ_C.

[12] D. Pines and P. Nozières, *The Theory of Quantum Liquids* (Benjamin, New York, 1969).

[13] J.J. Quinn, Phys. Rev. **126**, 1453 (1962).

[14] B.A. McDougall, T. Balasubramanian, and E. Jensen, Phys. Rev. B **51**, 13 891 (1995).

[15] J. Tersoff and S.D. Kevan, Phys. Rev. B **28**, 4267 (1983).

[16] S. Crampin, J. Phys. Condens. Matter **6**, L613 (1994).

[17] C. Nagl *et al.*, Surf. Sci. **321**, 237 (1994).

[18] N.V. Smith, Comments Condens. Matter Phys. **15**, 263 (1992).

[19] G. Hörmandinger, Europhys. News **25**, 147 (1994).