Quantization of the electron wave vector in nanostructures: Counting *k*-states

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Low-temperature scanning tunneling spectroscopy and *ab initio* based theory reveal electron wave-vector quantization due to electron confinement in a nanostructure. A Fourier transformation of the spatial modulation pattern of the local density of states (LDOS) indicates quantization of the electron wave vector within the nanostructure, which gives rise to a discontinuous, staircaselike dispersion relation. Our results show that each step of the dispersion relation corresponds to an extremum of the LDOS and it identifes an eigenstate. The sequence of steps reveals the complete eigenstate spectrum, where states are enumerated and classified according to their even-odd parity.

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Since early work on quantum interference on metal surfaces by scanning tunneling microscope (STM),[1,2] many STM studies have been devoted to the analysis of the electron local density of states (LDOS) in nanostructures. Fascinating maps of the spatial modulation of the LDOS have been obtained by STM and scanning tunneling spectroscopy (STS).[3] The LDOS modulation patterns reflect the electron confinement in the nanostructures, which is due to electron scattering at the border of the nanostructures.

Important electronic properties such as the electron eigenstates of a confined system have been extracted for a variety of nanostructures such as nanometer-sized islands of adatoms[4–6] and also for vacancy islands.[7,8] The energy width of these eigenstates has been discussed with respect to electron lifetime, and estimates regarding relevant electron-scattering mechanisms which determine the electron lifetime have been presented.[7]

In contrast to the two-dimensional LDOS modulation pattern which characterizes electron eigenstates of spatially extended nanostructures, experimentally the energy positions of electron eigenstates have been determined mainly from single-point STS. The differential conductance dI/dU (I, tunneling current; U, gap voltage U_{gap}) is usually measured at a high-symmetry point within the nanostructure,[4,7,9–12] and peak positions of dI/dU spectra have been identified with energy eigenvalues. This previously established procedure rests on an energy analysis of dI/dU spectra and it stringently requires supporting models to identify the assignment between a peak position of the dI/dU spectra and the respective energy eigenvalues.[3,9] The resulting spectrum of eigenstates is incomplete, and this has been exploited in previous studies to explore states which fulfill certain symmetry constraints. Following the common quantum mechanics approach for the classification of eigenstates of symmetric systems, we show here that all eigenstates with even and odd parities can be determined in our analysis, whereas the previous study has only identified states of even parity.[9,10]

Here, we analyze the complete map of the spatial modulation of the LDOS of the whole nanostructure. The striking result of our experiments and calculations is that we observe and quantitatively analyze quantization of the electron wave vector k, and this analysis opens the way to completely describe and count electron eigenstates in a nanostructure.

We performed *ab initio* based calculation of the LDOS within the nanostructure to check the validity of our approach. Both experiment and theory reveal the k quantization. A noncontinuous staircaselike electron-dispersion relation is measured and calculated, where only discrete values of k are observed. These discrete k values identify all eigenstates of the system, as evidenced by the combined analysis of our experimental and theoretical results. Our analysis

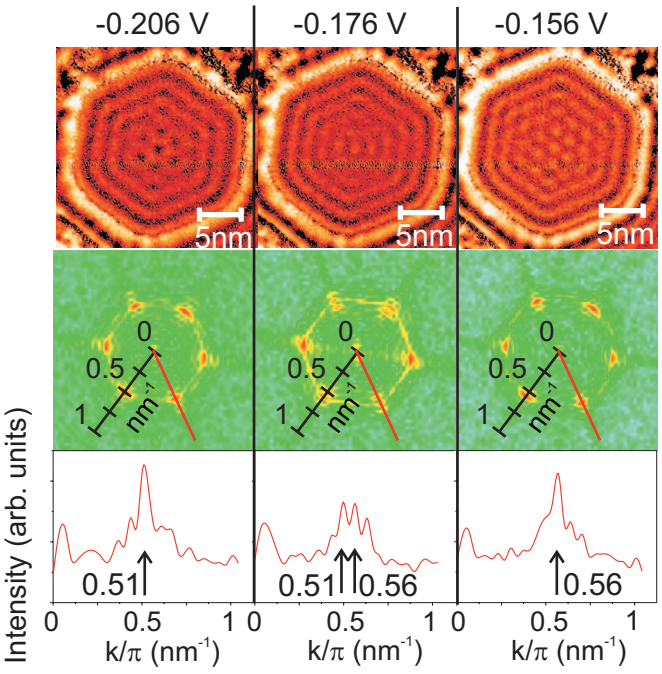

FIG. 1. (Color) Spatial modulation of the LDOS in a hexagonal crater of 20.5 nm size, measured by STS at the indicated gap voltage (I=1 nA). The LDOS patterns at −0.206 and −0.156 V show the eigenstates n=10 and n=11 (see text). The center one is a superposition of these states. Center row: map of the Fourier transformation (FT) of the top LDOS patterns (red, high intensity; green, low intensity). Bottom row: Linescans through the FT maps along the red line. The linescan at the intermediate gap voltage −0.176 V shows the simultaneous presence of the two wave numbers k (0.51 nm^{-1}, 0.56 nm^{-1}) which characterize two eigenstates at −0.206 and −0.156 V, respectively.

avoids a shortcoming of the previous measurements which, due to their local nature, identified just a subset of states, namely, even eigenstates with maxima at the nanostructure center.

We use hexagonal craters (vacancy islands) on Cu (111) to study electron confinement in nanostructures.[8] These monolayer deep (0.21 nm) depressions are often of almost perfect hexagonal shape. STM topography measurements reveal a size between a few nanometers and 25 nm, which is given by the distance between opposite edges at half depth. The hexagonal craters form in a self-assembled manner on Cu(111) upon deposition of submonolayer quantities of Co at 300 K. The Cu(111) crystal is cleaned prior to Co deposition by cycles of ion bombardment (Ar^+, 1 keV, 1 μA) and subsequent annealing at 700 K (15 min) in an ultrahigh vacuum chamber ($<5\times10^{-11}$ mbar). Morphology and LDOS of the hexagonal craters are investigated by low-temperature STM and STS at 7 K. STS data are collected by modulating U_{gap} (defined as the sample voltage) with an ac signal of 5 mV amplitude at 4.8 kHz and detecting the resulting modulation of the tunnel current with a lock-in amplifier. Thus, dI/dU maps and dI/dU spectra are recorded, and the data reflect maps of the LDOS and local LDOS spectra, respectively.[13]

To extract the energy dependence of the LDOS, we have measured STS maps of hexagonal craters of different sizes at gap voltages $U_{gap}=-0.44$ to $+0.5$ V, in steps of 10 mV. Figure 1 shows three maps of the dI/dU signal, taken at a 20.5 nm size hexagonal crater, at the indicated gap voltages. The dI/dU maps indicate a pronounced spatial modulation of the LDOS due to electron scattering at the rim of the crater.[8] The images clearly reveal a change of the LDOS pattern with energy; e.g., from -0.206 to -0.156 V, the center intensity changes from a minimum to a maximum. These two patterns correspond to eigenstates at energies of -0.206 and -0.156 eV with odd and even parities, respectively. The pattern at -0.176 V is ascribed to a superposition of the two neighboring eigenstates shown in Fig. 1.

We perform a Fourier transformation (FT) of the LDOS pattern inside the hexagonal crater to extract the wave vector k of the LDOS spatial modulation.[14,15] The result of the FT is shown in the center row of Fig. 1. The map of the FT is centrosymmetric and reflects the hexagonal symmetry of the LDOS pattern. Clear maxima of the FT intensity are observed, which are separated by 60° along the azimuthal direction. These maxima identify wave vectors which cause the spatial modulation of the original LDOS pattern. In the following, we analyze the variation of the intensity and the peak position of one of these maxima. Thus, we analyze the confinement along one direction of the hexagon, i.e., between two opposite straight sides, as indicated by the red line in Fig. 1. The same analysis made for other directions gives equivalent results, which depend on the distance between opposite sides, as will be shown below.

The plots at the bottom line of Fig. 1 show linescans through the FT maps along the direction indicated by red lines. At -0.206 and -0.156 V, we deduce from the linescan pronounced maxima at 0.51 and 0.56 nm^{-1}, respectively. However, at the intermediate value -0.176 V, the linescan indicates two peaks at 0.51 and 0.56 nm^{-1}, but no peak at the intermediate value, as one might have expected for a continuous variation of k with energy. Further, peaks of the linescans identify other eigenstates, and these peaks reach their maximum amplitude at different energies.

We calculate the LDOS within the nanostructure by our previously established approach, which reproduces essential aspects of electron confinement in a nanostructure such as spatial modulation of the LDOS and peak position and width of the LDOS in close agreement with experimental data.[8] In short, our calculations are based on density-functional theory and the Korringa-Kohn-Rostoker Green's-function method, which we recently developed for quantum resonators on metal surfaces.[8,16]

The FT analysis of the measured and calculated LDOS patterns gives the correlation between k and the electron energy eU_{gap}. Thus, we obtain the complete dispersion relation $E(k)$. Figure 2 summarizes our results, which we measured at a step edge and at craters with sizes of 20.5 and 13.5 nm. The dispersion relation of the step edge gives a continuous parabola [see inset of Fig. 2(a)], as expected for surface-state electrons. A parabolic fit of this curve gives the surface-state band edge $E_0=-0.43\pm0.01$ eV and the electron effective mass $m^*/m_e=0.39\pm0.01$, where m_e is the electron mass. These values are in very good agreement with previous studies on the dispersion relation of surface-state electrons of Cu(111).[1] We have also analyzed the LDOS pattern by fitting Bessel functions,[1,17] and we obtain the same result, proving the validity of our FT analysis.

Figures 2(a) and 2(b) reveal that in contrast to the dispersion relation obtained at a step edge, the dispersion relation of the confined system is a discontinuous curve. Although measurements and calculations are performed in steps of 10 mV, we observe the absence of k values within certain k ranges. Experimental and theoretical data points are always clustered around discrete, quantized k values. An indication of a noncontinuous dispersion relation has been displayed, without further analysis, for Co islands.[18,19] Our results show that the quantization of k is determined by the lateral size of the crater. The larger the crater, the denser the spacing between the observed k values. This finding follows from the data for the 20.5 nm crater in (a), as compared to the 13.5 nm crater in (b).

The inset of Fig. 2(b) shows that the observed sequence of k values can be described by the quantization rule $k_n=n\pi/d$, where n is an integer and d is the crater size. The slope of the curve is π/d in each case, and it gives the crater sizes of 20.1 and 12.8 nm, respectively, in very good agreement with our topological STM measurements. This quantization rule allows one to number every state. An even (odd) index n identifies an odd (even) state with a minimum (maximum) of the LDOS at the vacancy symmetry center.

This quantization rule reflects the boundary conditions of a particle confined to a one-dimensional potential step of extension d with inversion symmetry. This strikingly simple result comes as a surprise, as it does not seem to reflect the two-dimensional nature of the problem explicitly. Our results suggest that the confinement can be properly ascribed to parallel straight edges of the crater at a distance d. At first glance, our system seems to exhibit inversion symmetry, and therefore, it follows the classification scheme of the eigenstates in terms of even and odd parities. Based on our results,

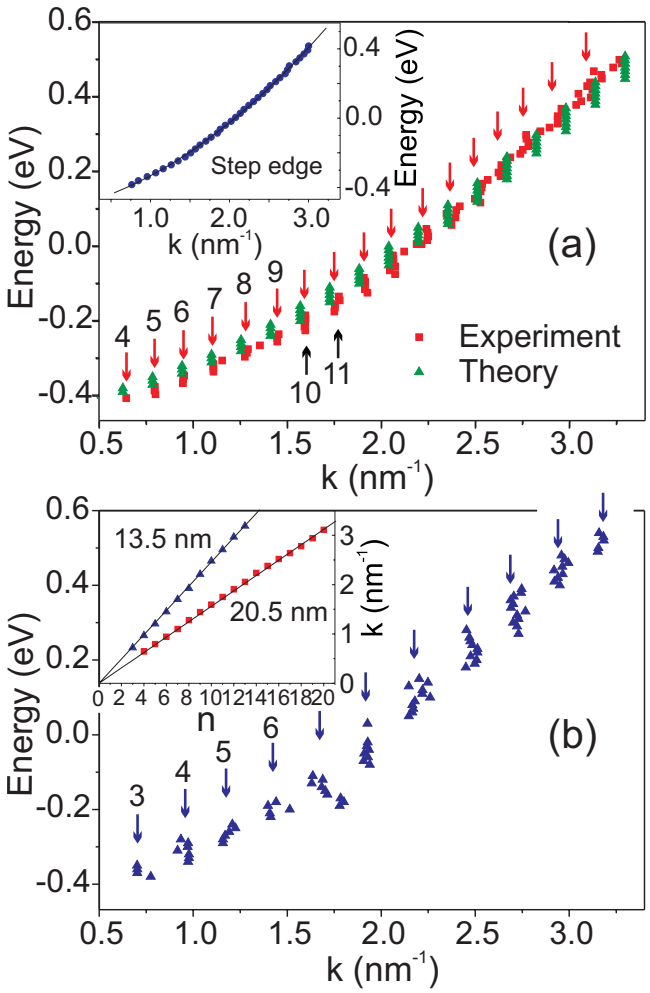

FIG. 2. (Color) (a) Dispersion relation obtained by the FT analysis of the LDOS of a 20.5 nm crater. Experiment, red square; theory, green triangle. (b) Experimental results of a 13.5 nm crater. Note the discontinuous curves, where just discrete k values are observed. The inset in (a) shows the continuous dispersion curve of electrons scattered, measured at a step edge. The horizontal error bars increase with wave vector: ± 0.04 nm^{-1} around 1 nm^{-1} and ± 0.12 nm^{-1} around 3 nm^{-1}. The black arrows show the two states corresponding to the STS maps of Fig. 1. The inset of (b) reflects the quantization rule $k_n = n\pi/d$. The first eigenstates in (a) and (b) are enumerated according to this rule.

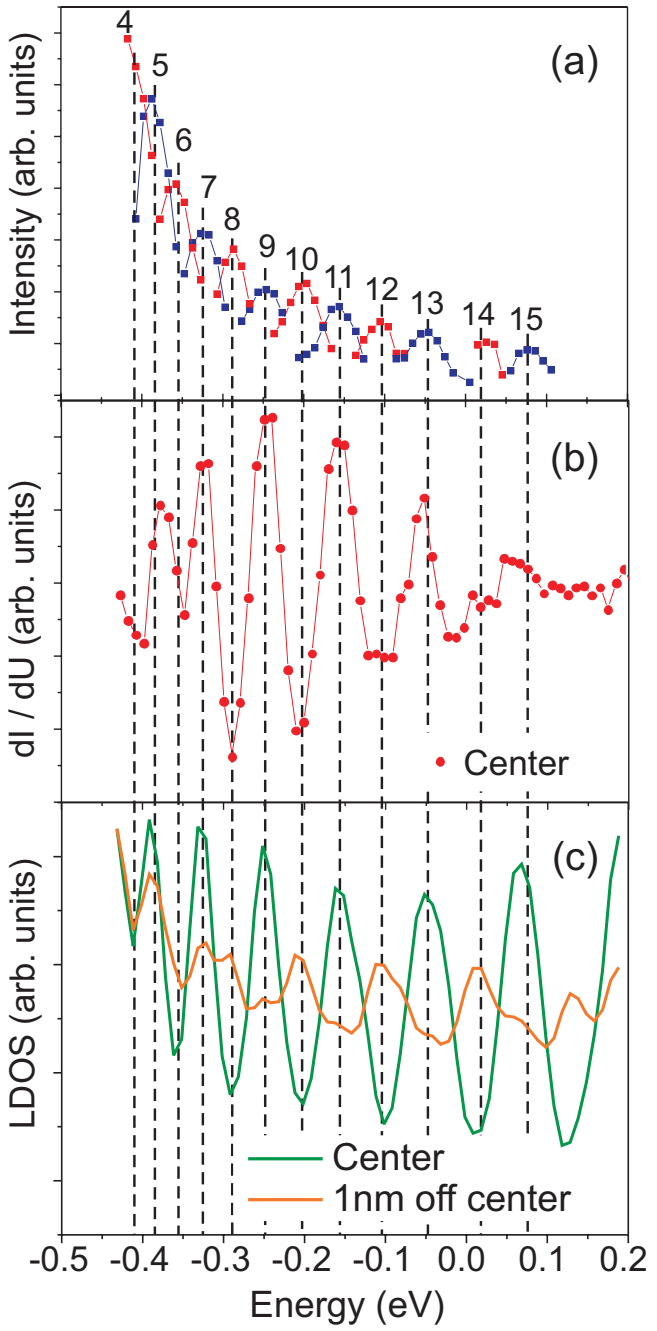

FIG. 3. (Color) (a) Intensity of each eigenstate as extracted from the FT analysis according to Fig. 1. Adjacent states with index n are plotted in red and blue for clarity. (b) dI/dU spectrum taken at the center of the 20.5 nm hole. To enhance the appearance of minima and maxima, we have subtracted the dI/dU spectrum taken at a flat Cu terrace. (c) Calculated LDOS at the center position and 1 nm off center within the confined system. The dashed lines show clearly the correspondence of peak positions of (a) and minima and maxima of (b) and (c).

we find no indication that the crystalline order of the nanostructure breaks the inversion symmetry of the confining potential. We ascribe this to the much shorter length scale of the order of a tenth of a nanometer, which describes structural details, as opposed to the coarser electron wavelength of the order of nanometers, which determines the formation of the LDOS modulation pattern.

In addition to the sequence of quantized k values, important additional information on the electron eigenstates and their energy width can be extracted from the FT analysis of the LDOS pattern, as presented in Fig. 1.

We have extracted the amplitude of every peak of the linescan (bottom row of Fig. 1) through the FT map of the LDOS pattern and plotted it as a function of energy in Fig. 3(a). We thus obtain a sequence of individual peaks composed of distinct data points, as shown in Fig. 3(a). Figure 3(a) indicates that all data points composing one individual peak are given by the data of one corresponding k-state, as indicated by the red arrows in Fig. 2(a) of the 20.5 nm crater. We conclude that maxima of the peak positions of Fig. 3(a)

correspond to the energy of electron eigenstates of the confined system.

In order to compare our study with previously published approaches which rely on an energy analysis of local dI/dU spectra,[9,10] we have plotted in Fig. 3(b) a dI/dU spectrum measured at the center of the 20.5 nm crater. Comparing Figs. 3(a) and 3(b), it is striking that all maxima *and* minima of the dI/dU spectrum coincide with peaks of the FT-based analysis, as shown by the dashed lines.

Previous works have ascribed maxima of dI/dU spectra recorded at the center of the nanostructure to eigenstates. For hexagonal systems, the labeling scheme of observed states relies on an involved analysis.[9] These local dI/dU measurements detect only a subset of eigenstates. Other eigenstates are accessible by measuring off center.[10] In contrast to the previous local STS analysis, the FT-based analysis exploits the complete two-dimensional LDOS modulation pattern within the nanostructure, and this reveals all eigenstates. Our results show that each step of the discontinuous dispersion curve of the confined system of Fig. 2 gives rise to an extremum (maximum or minimum) of the density of states. This means that we identify even and odd states, whereas maxima of local dI/dU measurement at the center of the structure identifies only even states.

Figure 3(c) presents our calculations of the LDOS spectra within the nanostructure. We find close agreement between the peak positions of the measured dI/dU curve of Fig. 3(b) and the calculated LDOS for the center position. However, calculating the LDOS off center gives minima at positions where maxima were located for the center position. The comparison between experiment and theory shows that where the calculated LDOS spectra have a vanishing slope, peaks of the FT analysis are observed. This finding corroborates our claim that the FT analysis of the LDOS modulation pattern identifies the complete eigenstate spectrum.

In conclusion, we have presented clear experimental and theoretical evidences for electron wave-vector quantization in a confined system. The resulting discontinuous steplike dispersion relation has been exploited to derive the complete set of eigenstates of a confined system in a model-free approach. We find that the two-dimensional nature of our FT-based analysis is the key point which identifies the complete set of even and odd eigenstates. Our approach offers a detailed understanding of the relation between quantized wave vectors, LDOS, and eigenstates of a nanostructure.

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