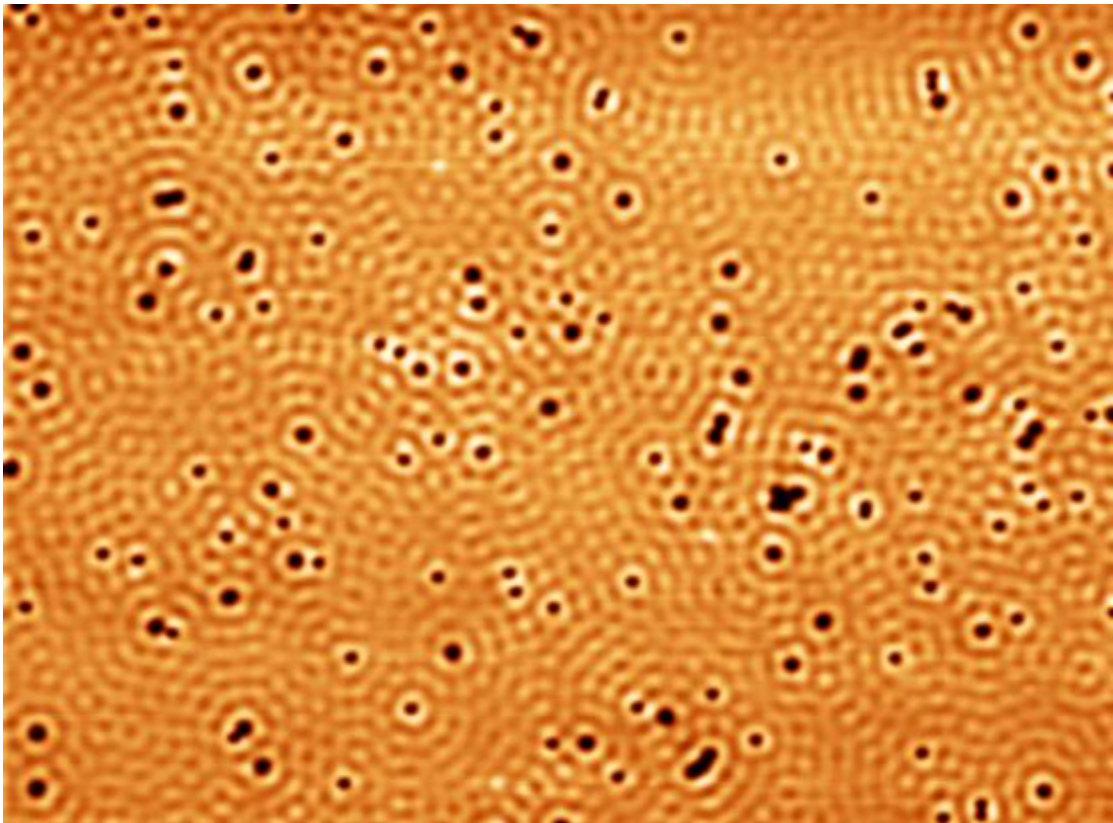


## Measuring surface state dispersion by low-temperature scanning tunneling microscopy (STM)

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## 1 Introduction

This assignment introduces low-temperature scanning tunneling microscopy (STM) and spectroscopy (STS) which provide structural and electrical information of surfaces with atomic spatial resolution. Since its conception in the early 1980s <sup>[1]</sup>, there have been few techniques in the physical sciences that have had as large a conceptual impact as STM. Shortly after its development, the impact of STM was in providing atomically resolved images of well-defined surfaces, such as single crystals of semiconductors and metals. However, the past decade has seen an enormous increase of STM studies focusing specifically on the properties of single molecules and nanostructures <sup>[2,3]</sup>. The strength of STM lies in the combination of high-resolution imaging (information from STM) and spatially resolved electrical spectroscopy (from STS), which is capable of providing the local density of states (LDOS) with atomic spatial resolution.

These techniques will be illustrated by imaging a Cu(111) surface and measuring the dispersion of the two-dimensional free electron gas (surface state) present on the surface. This can be achieved by measuring the oscillations in the local density of states arising from the scattering of surface state electrons from surface impurities.

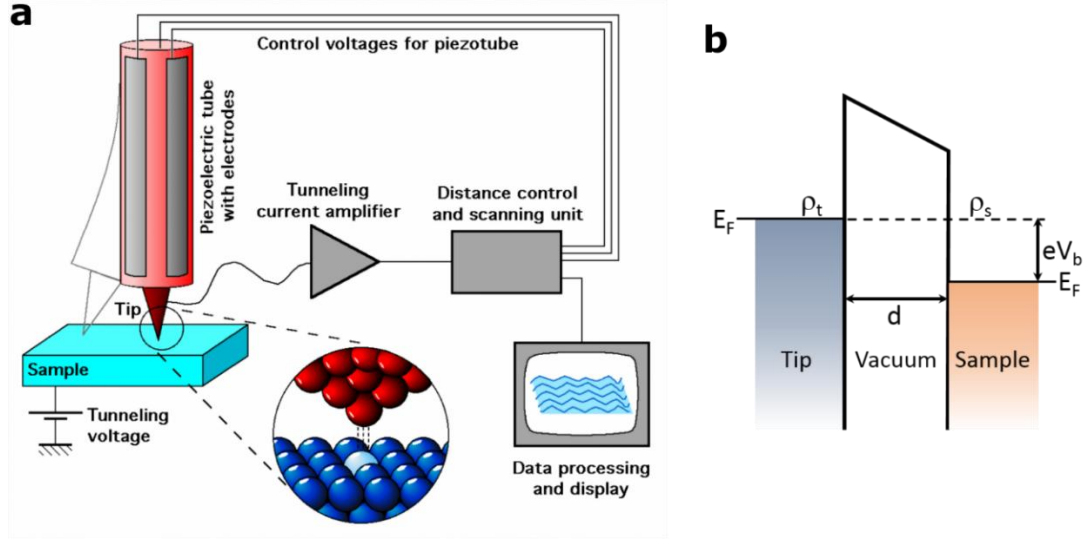
After reading these instructions and watching the introduction video, you should be able to answer the following questions:

1. Explain the working principle of STM.
2. How can the local density of states be measured with STM?
3. What is a surface state and what is its electronic structure?
4. How can dispersion be measured with STM?

After answering these questions, you will get access to the actual measurement data for analysis.

### 2.1 Scanning tunneling microscopy

STM works on the principle of quantum mechanical tunneling of electrons between an atomically sharp probe (“tip”) and a conductive surface through a thin vacuum barrier (typically  $\sim 1$  nm). The STM setup is shown in Figure 1a. Here, the tip raster scans the sample surface while recording the tunneling current at an applied bias voltage  $V_b$ . This voltage refers to the potential of the sample with respect to the tip. The tip is attached to a scanner with piezoelectric elements that can be used to control the x-, y-, and z-position with picometer accuracy. Piezoelectrics are materials that can expand or contract by applying a voltage, and since the deformation is very small, they are often used in applications requiring precisely controlled movements.



**Figure 1.** (a) Schematic of the STM set-up: bias voltage is applied to the sample and the current between the tip and the sample is measured. The tip position is controlled by piezoelectric elements. Figure credit: Michael Schmid, TU Wien. (b) Schematic energy diagram as a positive bias voltage is applied to the sample. In this case, the current is the result of electrons tunneling from the tip to empty states of the sample over the energy window set by the bias voltage (0 to  $eV_b$ ). This corresponds to measuring empty states of the sample.

Scanning is typically carried out in the so-called constant current mode, where the tip height is controlled by a feedback loop such that the tunneling current between tip and substrate stays constant. The obtained image contains information of the tip's position in  $z$ -height in the  $xy$ -plane, which is referred to as a topograph. A typical STM image of a (111)-terminated copper surface is shown in Figure 2a. The black depressions are carbon monoxide (CO) and oxygen ( $O_2$ ) impurities. It is important to realize that the resulting "apparent height" of the surface features contains information on both the topographic properties ("true height") and the electronic properties of the sample. On the one hand, the tunneling current between the STM tip and the surface depends exponentially on their separation  $d$  (see Figure 1b), *i.e.*  $T \propto \exp(-2\kappa d)$ , where  $\kappa$  is the decay constant. For a vacuum barrier, the tunneling current decreases by roughly one order of magnitude per one Ångström ( $10^{-10}$  m) increase in  $d$ . This would relate to the "true height" of the features (such as surface steps) on the surface. On the other hand, the tunneling current depends on the local density of states (LDOS) of the sample  $\rho_s$  and the tip density of states (DOS)  $\rho_t$

$$I(V_b) \propto \int_0^{V_b} \rho_t(E - eV) \rho_s(E) T(E, V, d) dV \quad (1)$$

where  $T(E, V, d)$  is a tunneling matrix element between the tip and the sample. Back to Figure 2a: the impurities have a smaller LDOS than the copper surface, so even though the impurity protrudes from the surface topographically, the tip must approach the surface in order to maintain a constant tunneling current.

Differentiating Eq. (1) w.r.t. the bias voltage and assuming that the transmission and tip DOS are constant, we get

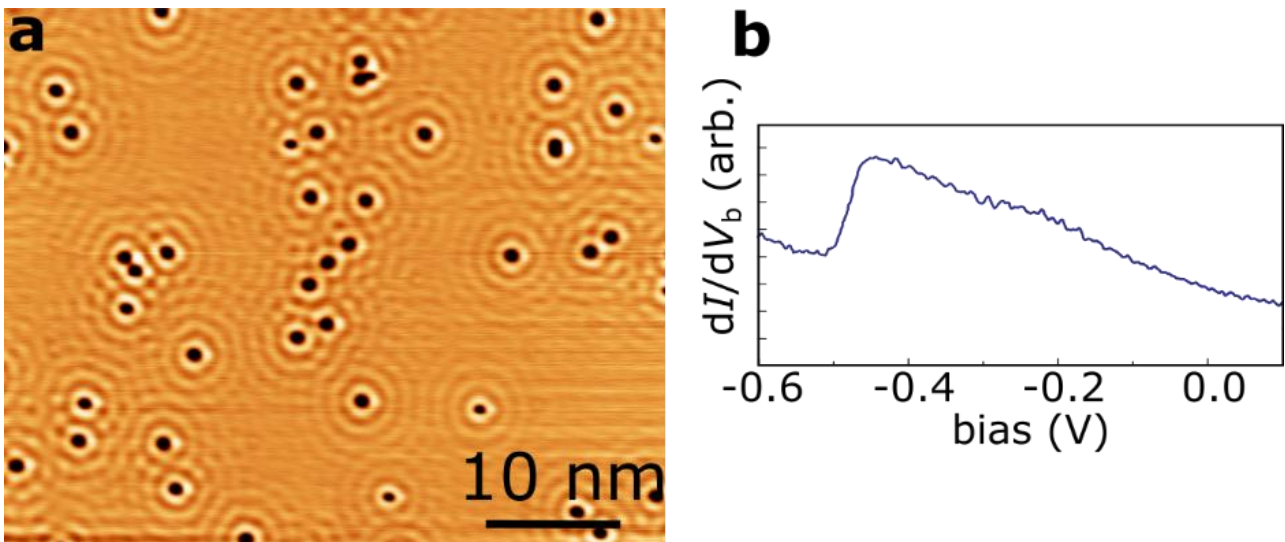
$$dI/dV_b \propto \rho_s(eV_b) \quad (2)$$

at the position of the tip. This essential result forms the basis for all scanning tunnelling spectroscopy (STS) experiments, in which the  $dI/dV_b$  signal is interpreted as being proportional to the LDOS of the sample at the position of the tip. While the procedure for rigorously recovering LDOS from the measured  $dI/dV_b$  spectra has been discussed at length in the literature <sup>[4-6]</sup>, the interpretation that  $dI/dV_b(V_b, x, y) \propto \text{LDOS}(eV_b, x, y)$  is usually sufficiently accurate.

The simplest way to obtain a  $dI/dV_b$  spectrum is to obtain an  $I(V_b)$  curve and subsequently differentiate it with respect to  $V_b$ . However, numerical differentiation would amplify any noise present in the data, obscuring the spectral features. This drawback can be avoided using a lock-in amplifier to obtain  $dI/dV_b$ , which improves the signal-to-noise ratio significantly. The lock-in amplifier is used by adding a periodic modulation  $V_m \sin(\omega t)$  to the sample bias  $V_b$ . By applying a Taylor series expansion at  $V = V_b$ , the tunneling current  $I$  can be rewritten as

$$I(V_b + V_m \sin(\omega t)) = I(V_b) + \left. \frac{dI(V)}{dV} \right|_{V=V_b} \cdot V_m \sin(\omega t) + \left. \frac{d^2I(V)}{dV^2} \right|_{V=V_b} \cdot \frac{1}{2} V_m^2 \sin^2(\omega t) + \dots \quad (3)$$

The lock-in amplifier can extract the first harmonic signal at the modulation frequency  $\omega$ , which is proportional to the differential conductance signal  $dI/dV_b$ .



**Figure 2.** (a) Zoomed-in STM topographic image of a Cu(111) surface. The surface state is scattered of surface impurities (typically carbon monoxide). (b)  $dI/dV_b$  spectrum measured on a Cu(111) surface showing the onset of the surface state at a bias of ca. -0.45 V.

An example of such a spectroscopic STM measurement can be found in Figure 2b, which shows the measured  $dI/dV_b$  signal as a function of the bias voltage on a Cu(111) surface. The onset of the surface state is seen as a step in the  $dI/dV_b$  signal at a bias of  $-0.45$  V. From the definition of the bias (sample w.r.t. to the tip), we can infer that at negative bias, we are probing occupied states in the sample, and at positive bias, the unoccupied part of the DOS (see Figure 1b). This result shows that the Cu(111) surface state onset is located ca.  $0.45$  eV below the Cu Fermi level.

## 2.2 Physics of surface states

The bulk electronic properties of crystalline solids can be described by their band structure, *i.e.* the dependence of the electron energy on its wave vector. An example of a calculated band structure is given in Figure 3a. The letters on the x-axis refer to different symmetry points in the 1<sup>st</sup> Brillouin zone shown in Figure 3b. In the bulk, the wavefunctions are given by the three-dimensional Bloch waves

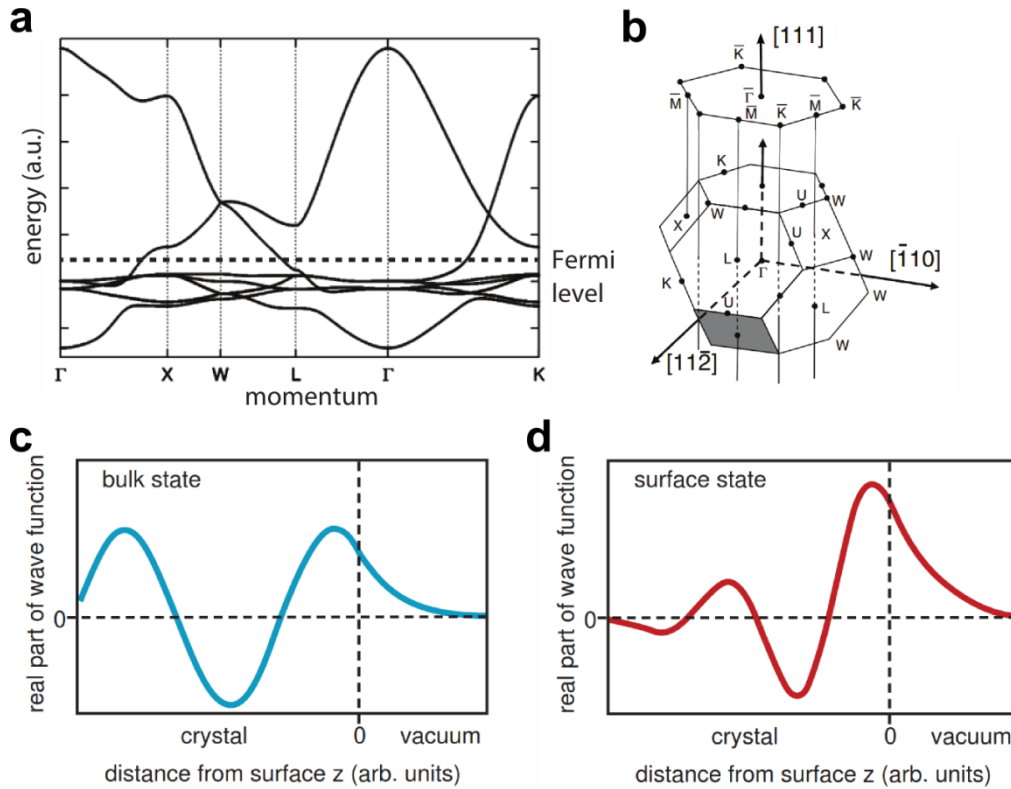
$$\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_{\mathbf{k}}(\mathbf{r}) \quad (4)$$

where  $u_{\mathbf{k}}(\mathbf{r})$  is a function with the same periodicity as the lattice. The presence of a surface results in a behaviour similar to what happens at the edge of a particle in a box problem (with finite barrier height). Considering only the situation perpendicular to the surface, the Bloch wave function outside the surface decays exponentially to the vacuum (with the boundary condition that the wave function and its derivative are continuous at the bulk-vacuum boundary). This is shown in Figure 3c.

The presence of the surface destroys the translational periodicity perpendicular to the surface but the periodicity parallel to the surface is maintained. Therefore, parallel to the surface, the electronic states are still two-dimensional Bloch waves. The wave vector  $\mathbf{k}$  of a bulk Bloch wave is purely real but this is not a restriction stemming from the Schrödinger equation. In the case of a particle in a box, the wave vector outside the box is purely imaginary, which results in an exponential decay of the wavefunction. In a similar manner, if we assume that the perpendicular component of  $\mathbf{k}$  is complex, the wave function can be expressed as

$$\psi_{\mathbf{k}_{\parallel}}(\mathbf{r}) = \exp(i\mathbf{k}_{\parallel} \cdot \mathbf{r}_{\parallel}) u_{\mathbf{k}}(\mathbf{r}) \exp(i\kappa z) \quad (5)$$

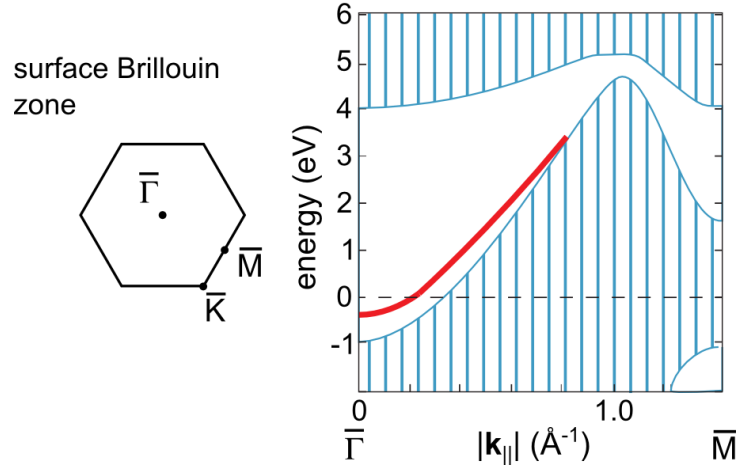
where  $\mathbf{k}_{\parallel} = (k_x, k_y)$  and  $\mathbf{r}_{\parallel} = (r_x, r_y)$ . This type of wavefunction is not physically meaningful in a bulk solid in that it is exponentially increasing in the  $+z$ -direction and finally the lead to an “explosion” of the wave function. However, the existence of the surface makes such solutions with a complex wave vector possible and an example is given in Figure 3d. As the crystal is terminated by the surface, it has to be matched to an exponentially decreasing wave function outside the surface and it can still be normalised. This solution is a surface-localised electronic state, and its energy is a real number. Note that the wave number  $\kappa$  in the  $z$ -direction is complex and not purely imaginary. Therefore, the wave function in the  $z$ -direction is not just exponentially decaying but still has an oscillating Bloch character.



**Figure 3.** (a) Calculated band structure of Cu. (b) 1<sup>st</sup> Brillouin zone of an fcc crystal, with the projection onto the (111) surface. (c) Schematic wavefunction of a bulk Bloch state at the surface. (d) Schematic wavefunction of a surface state.

These states are characterised by a quantum number  $\mathbf{k}_{\parallel}$  and energy  $E(\mathbf{k}_{\parallel})$ . On the contrary, the wave vector perpendicular to the surface  $\mathbf{k}_{\perp}$  is not a good quantum number because the periodicity is broken in that direction. A “true” surface state cannot be degenerate with any bulk state. This means that for a surface state with a certain  $\mathbf{k}_{\parallel}$  and  $E(\mathbf{k}_{\parallel})$ , there cannot be any other bulk states with the same  $\mathbf{k}_{\parallel}$  and energy for any value of  $\mathbf{k}_{\perp}$ . In other words, along entire  $\mathbf{k}_{\perp}$  rod passing through a certain  $\mathbf{k}_{\parallel}$  of a correspondent surface state, it should not overlap with other bulk states. If there was such an overlapping bulk state, the surface state could couple to it and penetrate indefinitely into the bulk, and could not be a so-called “true” surface state (such a degenerate surface state is called a “surface resonance”). This requirement gives a necessary condition for the existence of a surface state: it must lie in a projected band gap of the bulk electronic structure. The projected band structure for a specific  $\mathbf{k}_{\parallel}$  is defined as all the energies for which bulk states exist that have the same  $\mathbf{k}_{\parallel}$  and an arbitrary value of  $\mathbf{k}_{\perp}$ .





**Figure 4.** Surface Brillouin zone of Cu(111) and the projected bulk band structure (shaded in blue). The surface state (red line) exists inside the projected gap of the bulk band structure.

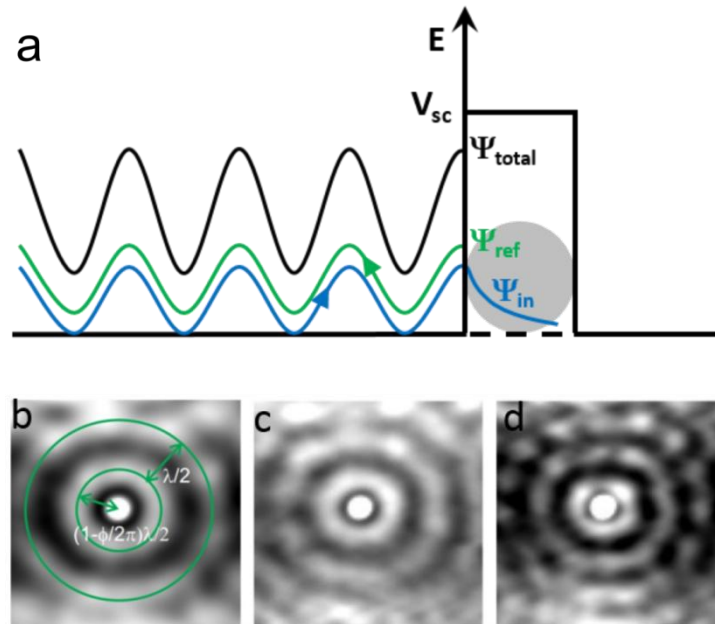
This is illustrated for the case of Cu(111) surface in Figure 4, which shows the surface Brillouin zone (left) and the projected band structure along the  $\bar{\Gamma} - \bar{M}$  axis. The bulk bands' energies and momenta are indicated with blue shading. There is a gap around the Fermi energy at the  $\bar{\Gamma}$ -point. A surface state inside this gap is indicated with the red line and it exhibits a free electron -like parabolic dispersion

$$E = \frac{\hbar^2}{2m_{\text{eff}}} |\mathbf{k}_{\parallel}|^2 \quad (6)$$

with an effective mass of ca.  $m_{\text{eff}} = 0.4$ .

### 2.3 Scattering of surface electrons

The surface state electrons scatter from surface impurities (e.g. CO and O<sub>2</sub> on Cu(111)) and step-edges present on the surface. The scattering of the surface states refers to an electron wavefunction encountering a scatterer on the surface. We can understand this by a one-dimensional schematic shown in Figure 5a, where the scatterer (shown as a grey circle) constitutes a rectangular potential barrier of height  $V_{\text{sc}}$ . As the incident electron wavefunction ( $\Psi_{\text{in}}$  with energy  $E_b$ ) hits the barrier from the left side, a part of it is reflected back ( $\Psi_{\text{ref}}$  with energy  $E_b$ ). When the phase of the reflected wave matches constructively to the incident wave, a standing wave ( $\Psi_{\text{total}}$ ) forms due to interference. The resulting standing wave pattern can be probed by STM by measuring the local density of states ( $\rho_s \propto |\Psi_{\text{total}}|^2$ ) at energy  $E_b$  ( $E_b = eV_b$ ) at each point of the standing wave. Alternatively, a two-dimensional  $dI/dV_b$  map can be recorded at bias  $V_b$  in order to map the standing wave pattern. The standing wave pattern will appear as oscillations in LDOS map [7]. Examples of such maps are shown in Figure 5b–d at energies -300, -200, and -100 meV. The wavelength (or wave vector  $\mathbf{k}_{\parallel}$  at energy  $eV_b$ ) of the standing wave can be extracted from line profiles of a recorded  $dI/dV_b$  map. The extracted wavelength will depend on the energy of the electrons contributing to the  $dI/dV$  signal.



**Figure 5.** (a) One-dimensional schematic of scattering of an electron wavefunction due to a scatterer shown by a grey circle representing potential barrier of height  $V_{sc}$ . The wavefunctions have been shifted vertically up for clarity. (b–d)  $dI/dV_b$  maps recorded in the vicinity of a Cu adatom on Cu(111) surface at (b)  $-300$  mV, (c)  $-200$  mV, and (d)  $-100$  mV. Antinodes of the standing waves are shown by green circles in (b).

If the impurity coverage is large, the wavelengths become hard to extract from line profiles in real space. In that case, the wavevector of the standing wave can be extracted from the fast Fourier transform (FFT) the image. Plotting the energies as a function of the extracted  $k_{||}$  can then be used to reconstruct the dispersion curve of a two-dimensional surface state.

### 3 The experiment

Due to the ongoing Covid-19 pandemic, a live measurement session cannot be arranged in the laboratory: you will be supplied with data from earlier experiments, which you will analyze. We will briefly outline the experimental setup in this section: please also refer to the video material in MyCourses. We recommend freely available software, such as Gwyddion and SpectraFox, for analysing the data: import functions for Matlab are also supplied for both the point spectra (.VERT) and scan (.dat) files.

#### 3.1 Sample preparation

A (111)-terminated Cu single crystal is first cleaned by sputtering / annealing cycles in an ultra-high vacuum (UHV) environment. This cycle consists of Ne ion bombardment of the crystal at 1 keV and  $\sim 10^{-5}$  mbar pressure for 10 minutes (sputtering), followed by heating the crystal to 600 °C for a few minutes (annealing). After three cycles, the sample is inserted into the low-temperature STM where it is cooled down to 4 K. Afterwards, imaging and spectroscopy measurements of the clean Cu(111) sample is carried out.



To deposit CO impurities on the Cu surface, we open a leak valve and dose some CO gas into the UHV chamber. A shutter door to the STM head is opened to allow CO molecules to adsorb on the Cu surface (CO molecules are not desorbed back into the vacuum from cold surfaces). Excess CO molecules are pumped out of the vacuum chamber, and the sample is cooled back to 4 K (due to infrared radiation the sample heats up to ~20 K when the STM shutter door is opened).

### 3.2 STM imaging and spectroscopy

The experiment starts by approaching the tip to the sample (using the control software). A couple of large and small scale STM images are taken to confirm that the tip-sample tunneling junction is stable. Then the LDOS is checked by recording  $dI/dV$  point spectra, which should exhibit a step-like feature with an onset at  $-0.45$  V. If the tip is not stable or the spectrum does not have the expected shape, the structure of the tip apex is conditioned by gentle voltage pulses and controlled tip crashes to the sample.

### 3.3 Measurement of the surface state dispersion

We look for a suitable terrace (flat area) of the Cu(111) surface to measure the LDOS of the sample as a function of the bias voltage. The experiment data involves the  $dI/dV_b$  signal over an area containing some impurities (why?) in the constant height mode (why?) at different bias voltages through the onset of the surface state band. The  $dI/dV_b$  maps contain information on the scattering of surface state electrons by the impurities. The wavelength of the standing waves can be extracted from the map for different bias voltages. The plot of bias voltage (energy) as a function of the wave vector will give the dispersion of the surface states from where effective mass of electrons can be extracted.

## 4 Report

The report will consist of:

- (a) A large scale (typically 100 nm x 100 nm) and a small scale image (typically 10 nm x 10 nm) of Cu(111) image. Find the step height of the Cu(111) surface from the line profile. Comment on the features present on the image. Why can we not use topographic images to extract the wavelength ( $\mathbf{k}_{||}$  vector) of the standing wave?
- (b)  $dI/dV_b$  point spectrum recorded on the surface to show the surface state onset. The range of  $V_b$  is typically  $-1$  V to  $+1$  V. Discuss the shape of the spectra.
- (c) Constant height LDOS maps at different bias values ( $V_b$ ) to cover the energy range tentatively. Using either the line profile or the fast fourier transform (FFT) to obtain the wavelength (or  $\mathbf{k}_{||}$  vector) of the surface standing waves. Extract the wavelength (or  $\mathbf{k}_{||}$  vector) from the raw data provided to you in a similar way.

- (d) Make the  $E-k_{||}$  plot to generate the dispersion curve. Extract the electron effective mass by fitting with dispersion relation given in equation (6). Comment on the calculated effective mass.
- (e) Extract the surface state onset energy from the  $E-k_{||}$  plot and compare it to value extracted from  $dI/dV_b$  point spectrum.

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