Chapter 10
Surface States

When the electronic structure of (crystalline) materials is described, usually the bulk is considered. Since the STM probes the electronic states at the surface we will now consider also the electronic states at the surface, the surface states. We use the single electron approximation and start with a very brief review of the bulk electronic structure. Then the surface states are discussed in one dimension within the quasi-free electron model. We will see that solutions of the Schrödinger equation with complex wave vectors lead to surface states. While these solutions are not allowed in (infinite) bulk crystals, they are allowed if a surface is present. Finally, we transfer the one-dimensional model qualitatively to three dimensions and discuss the two-dimensional surface states of a three-dimensional solid.

## 10.1 Surface States in a One-Dimensional Crystal

The well-known parabolic bands are found in the one-dimensional model of a periodic solid [14]. At the Brillouin zone boundary, different bands cross each other. If a weak lattice periodic potential $\hat{V}$ is present this leads to a splitting of the bands at the zone boundary. Due to the presence of the potential $\hat{V}$ a band gap free of electron states occurs. According to the Bloch theorem, the wave function in a one-dimensional lattice periodic potential $\Psi_k(z)$ can be written as a plane wave modulated with a lattice periodic modulation factor $u_k(z)$:

$$\Psi_k(z) = u_k(z)e^{ik\cdot z}, \tag{10.1}$$

with the lattice periodic function $u_k(z) = u_k(z + z_n)$ and the translational lattice vector z_n. Of course, also a corresponding solution exists for $-k$.

This applies to the bulk electronic structure, but what happens at the surface? To answer this question we consider a one-dimensional model of a quasi-free electron in a periodic potential ending at the surface as shown in Fig. 10.1. Inside the solid ($z < 0$) the general one-dimensional bulk solution applies, which can be written as

Fig. 10.1 Lattice periodic
potential inside the
one-dimensional crystal
which ends at the surface
($z = 0$). In the vacuum
region outside the crystal the
potential has the constant
value of E_{vac}
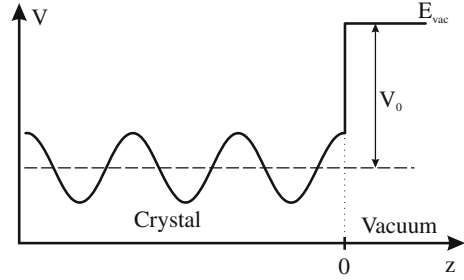
a linear combination of the solutions for k and $-k$ as

$$\Psi_{bulk}(z) = Au_k(z)e^{ik \cdot z} + Bu_{-k}(z)e^{-ik \cdot z}, \tag{10.2}$$

with real wave numbers k and $-k$ as well as energies in the allowed bands, i.e. outside
the band gaps. However, any solution inside the crystal has to match the solution Ψ_{vac}
for the region outside the crystal ($z > 0$). For the constant potential on the vacuum
side, the solution is an exponentially decaying wave function (a wave function with
a positive exponential cannot be normalized) as

$$\Psi_{vac} = D \, \exp\left[-\sqrt{\frac{2m}{\hbar^2}(V_0 - E)}\, z\right], \quad E < V_0. \tag{10.3}$$

The two solutions inside (10.2) and outside (10.3) the crystal and their derivatives
have to be matched at the surface $z = 0$ as

$$\Psi_{bulk}(z = 0) = \Psi_{vac}(0) \ \ \text{and} \ \ \Psi'_{bulk}(z = 0) = \Psi'_{vac}(0). \tag{10.4}$$

These two equations plus one equation from the normalization of the wave functions
fix the three unknowns A, B, and D, and the matching condition can be fulfilled for
any value of the coefficient k [15]. Thus, all energies which are allowed in the bulk
crystal are also allowed for the surface problem. The resulting wave function is a
bulk Bloch wave with an exponentially decaying tail into the vacuum (Fig. 10.2a).
This solution is not really a surface state but it is a bulk electronic state up to the very
surface where it is matched to an exponentially decaying tail.

    Additionally to these bulk states decaying at the surface, there are solutions to the
Schrödinger equation which are confined close to the surface and which are called
surface states. We consider here the general concept of how surface states can arise
from the presence of the surface. Usually the wave vector (wave number in the 1D
case) k is considered to be real. However, Bloch's theorem does not require that the
wave number k is real, it also allows Bloch functions with complex wave numbers.
The (now) complex wave number k consists of a real part k' and an imaginary part
κ as $k = k' + i\kappa$. Considering solutions with a complex wave number additional

Fig. 10.2 Real part of the one dimensional wave function, for **a** a Bloch wave matched to an exponentially decaying tail in the vacuum and **b** a surface state wave function Ψ_{surf}. This surface state wave function consists of a part $\Psi_{\text{surf}}^{\text{bulk}}$ which is oscillatory inside of the crystal ($z < 0$) and exponentially increasing towards the surface. At the surface this wave function is matched to an exponentially decaying tail in the vacuum outside the crystal $\Psi_{\text{surf}}^{\text{vac}}$ for $z > 0$
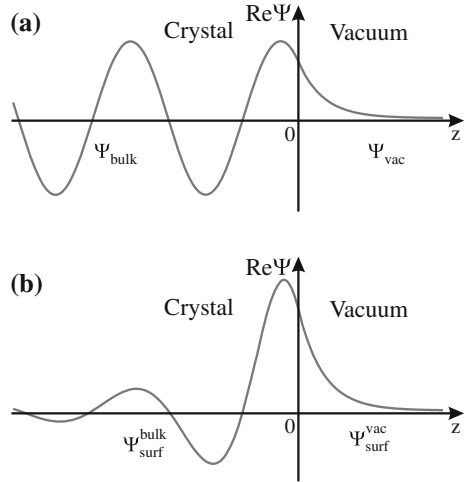
(1D) solutions to the Schrödinger equation can be found inside the bulk which can be written as

$$\Psi(z) = u_k(z)e^{i(k'+i\kappa)\cdot z} = \left[u_k(z)e^{ik'\cdot z}\right]e^{-\kappa\cdot z}. \tag{10.5}$$

These wave functions grow without bound in one direction and decay exponentially in the opposite direction (depending on the sign of κ). Since the wave function has to be finite everywhere, such solutions have no relevance in the infinite crystal. However, this is no longer true at surfaces. Here the presence of the surface stops the exponential rise of the wave functions, at $z = 0$ the wave functions have to be matched to the exponentially decaying tail in the vacuum, $z > 0$. Wave functions may be obtained which are strongly localized at surfaces, have real energy eigenvalues, and can be normalized, as shown in Fig. 10.2b.

Thus we have grasped that the surface states arise due to wave functions with an imaginary part of the wave number. These wave functions can be normalized inside the crystal, since they grow to infinity only outside the finite crystal. Before we discuss the surface state wave functions further, we consider the range of wave numbers and energies for which surface states exist (a detailed treatment of this issue can be found in [15, 16]). If a complex wave number k is inserted into the expression for the energy as a function of k (dispersion relation) in the nearly-free electron approximation [15], the requirement that the energy has to be real leads to restrictions for the (complex) wave vector. For real wave numbers ($\kappa = 0$), of course, the usual solutions exist with k-values from $k = 0$ to $k = \pm\pi/a$, and subsequent higher bands (solid lines in Fig. 10.3) [16]. Furthermore, for complex wave numbers real energies are obtained if, and only if $k' = \pm\pi/a$ (as shown in [15]). This means that complex wave numbers occur only at the zone boundaries of the real part of the wave number ($k = \pm\pi/a + i\kappa$). In Fig. 10.3 also these solutions with an imaginary part of the wave number κ are shown as dashed lines at the zone boundary of k'.
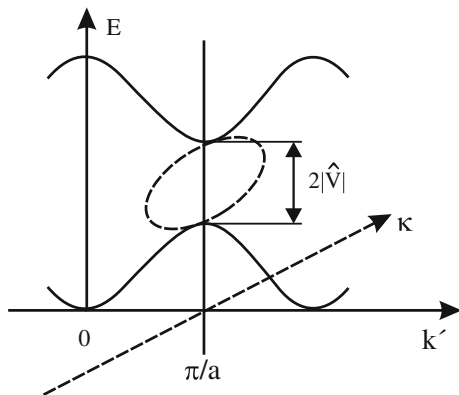
Fig. 10.3 Sketch of the electronic band structure for a 1D semi-infinite chain of atoms in the nearly-free electron model with an interaction potential $\widehat{V}$. Bulk states which decay exponentially at the surface into the vacuum give rise to energy bands shown as *solid lines*. Genuine surface states such as the ones shown in Fig. 10.2b are found in the band gap of the bulk states. They have complex wave vectors with a real part at the zone boundary $k' = \pm\pi/a$ and an imaginary part of the wave vector κ. These surface states with real energies are shown as *dashed lines*. The wave function matching condition restricts this continuous range of surface state wave functions to one particular surface state per bulk band

These solutions are the surface states and have real energies in the forbidden bulk band gap.

Due to the restriction of the real part of the wave number k to the zone boundary ($k' = \pm\pi/a$), the surface state wave functions can be written as

$$\Psi_{\text{surf}}^{\text{bulk}}(z) = A u_k(z) e^{i(\frac{\pi}{a}+i\kappa)\cdot z} + B u_{-k}(z) e^{-i(\frac{\pi}{a}+i\kappa)\cdot z}. \qquad (10.6)$$

For $\kappa > 0$ the first term will grow without bond inside the crystal $z < 0$, because it is proportional to $e^{-\kappa z}$. Since this would violate the finiteness of the wave function, A has to be zero. Correspondingly for $\kappa < 0$ B has to be zero.

Up to now we have only considered the part of the wave function inside the crystal. In the next step, the solution inside the crystal, (10.6) i.e. for $z < 0$ will be matched to an exponential tail in the vacuum. The two equations from the wave function matching conditions (wave functions and derivative at $z = 0$) plus the condition for the normalization of the wave function fix the three parameters B, D, and k. The wave function matching condition picks one k value out of the continuous range of values within the forbidden bulk energy gap (Fig. 10.3). Only one particular energy within the bulk band gap is compatible with the wave function matching conditions. The present consideration for a semi-infinite chain therefore yields one single electronic surface state per bulk band, which is located somewhere in the gap of the bulk states. Electrons in these states are, localized within a few Å of the surface plane (Fig. 10.2b).

10.2 Surface States in 3D Crystals

Now we consider the generalization of the results for the one-dimensional semi-infinite chain to a 2D surface of a 3D crystal. We now call the real part of the wave vector (perpendicular to the surface) named k' in the 1D model, $k_\perp$. As we have already discussed, the value of $k_\perp$ for surface states is at the Brillouin zone boundary. In the 3D case we have an additional wave vector parallel to the surface $k_\parallel$. Because of the 2D translational symmetry parallel to the surface, the general form of a surface state wave function is of the Bloch type with coordinates parallel to the surface. The energy eigenvalues of the surface states become functions of the wave vector $k_\parallel$ parallel to the surface as shown by the dashed lines at $k_\perp = \pi/a$ in Fig. 10.4. We thus arrive at a 2D band structure for the energies E_{surf} of the electronic surface states. A surface state is described by its energy level E_{surf} and its wave vector $k_\parallel$ parallel to the surface, $k_\perp$ is in any case at the Brillouin zone boundary. The plane in the reciprocal space given by the two components of the wave vector $k_\parallel$ parallel to the surface forms the surface Brillouin zone. In the dispersion relation in Fig. 10.4, only one of the two directions parallel to the surface is shown.

For the bulk states both $k_\parallel$ and $k_\perp$ components are allowed ranging from zero to the zone boundary, i.e. $k_\perp$ is not restricted to the value at the zone boundary ($k_\perp = \pi/a$). Therefore, a 3D band structure results as shown in Fig. 10.4. If all the bulk states are projected along $k_\perp$ onto the plane $k_\perp = \pi/a$ the shaded area in Fig. 10.4 results. If the surface state bands lie in this band gap of the projected bulk band structure, they are true surface states. Surface resonances lie inside the region of the projected bulk
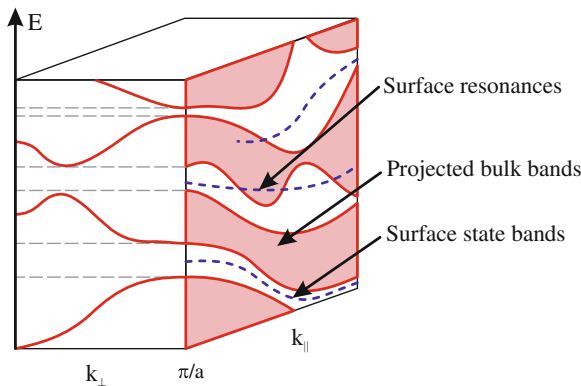

Fig. 10.4 Schematic of an electronic band structure of a three-dimensional crystal. The *shaded areas* arise by projecting the bulk band structure along $k_\perp$ onto the plane at $k_\perp = \pi/a$. The *dashed lines* in this plane indicate surface state bands. They can either lie in a gap of the projected bulk band structure (true surface states) or in areas inside the projected bulk band structure. In the latter case, these states are called surface resonances

band structure. Surface resonances have wave functions present throughout the bulk and, additionally, a large amplitude at the surface. Fig. 14.4 is an example in which no bulk band gap exists (energy range without states in the bulk), however, gaps in the projected bulk band structure exist.

10.3 Surface States Within the Tight Binding Model

So far we have discussed surface states within the picture of the quasi-free electron, which are sometimes, for historic reasons, called Shockley surface states. However, the surface states can also be described within the tight binding approximation; in this case they are called Tamm states. We will discuss this only qualitatively here. For the topmost surface atoms the bonding partners on one side are missing completely, which means that the wave functions have less overlap with the wave functions of the neighboring atoms. The shift of the atomic energy levels (into the electronic bands of the crystal) is thus smaller at the surface than in the bulk. The surface states split off from the bulk bands as shown in Fig. 10.5. Every atomic orbital leading to one of the bulk electronic bands should also give rise to one surface state level. The stronger the perturbation induced by the surface, the greater is the deviation of the surface level from the bulk electronic bands. When a particular orbital is responsible for chemical bonding, e.g. the sp^3 hybrid in Si or Ge, it is strongly affected by the presence of the surface. Bonds are broken and the remaining lobes of the orbital sick out from the surface. They are called dangling bonds. The energy levels of such states are expected to be significantly shifted from the bulk values.

Fig. 10.5 Qualitative origin of surface states in the tight-binding picture. The surface atoms have less bonds to neighboring atoms. Therefore the energy shift from the atom levels is less than for the bulk atoms
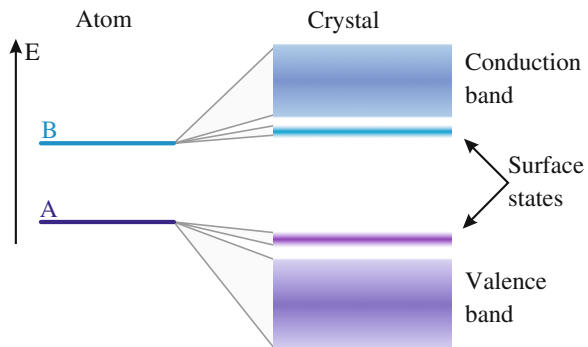
10.4 Summary

- When a surface is present, the bulk states of the infinite crystal are still solutions of the semi-infinite solid if the bulk wave functions are matched to an exponentially decaying tail in the vacuum.
- In the semi-infinite solid (terminated by a surface), additional solutions exist which have a complex wave vector. This leads to an exponential increase of the wave function in the direction of the surface. Unlike the case of the infinite crystal, this is no problem since the crystal is finite and the exponential increase of the wave function stops at the surface.
- The energies of the (1D) surface states lie in the band gap of the bulk band structure and the real part of the surface state wave vector is at the zone boundary, i.e. π/a.
- True surface state bands are characterized by energy levels E_{surf}, which are not degenerate with bulk bands. They lie in the gaps of the projected bulk band structure.
- Surface resonances lie in parts of the surface Brillouin zone, where projected bulk states exist.