Dynamics at Solid State Surfaces and Interfaces

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3 Intrinsic Surface States

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3.1 Introduction

3.1.1 Basic concepts of surface states

The creation of a surface breaks the three-dimensional periodicity of a crystalline solid. The surface possesses two-dimensional periodicity which is often further reduced from the truncated bulk structure by reconstruction due to a rearrangement of surface atoms. The changed periodicity and the missing binding partners affects the electronic structure of the atoms at the surface as well. In fact, the electronic states provide by energy minimization the forces leading to the ground-state configuration of the surface.

The wave functions of surface states are localized mainly in the surface region. These states are accessible by many surface-sensitive techniques and, therefore, their energetics and dynamics have been studied in great detail. In this chapter we concentrate on intrinsic surface states which are a genuine property of single-crystal surfaces. Extrinsic surface states on the other hand are states localized on adsorbed atoms or molecules. These states maintain specific features of the adsorbate and are only modified by the interaction with the substrate surface.

![Figure 3.1: Matching wave functions at the surface can lead to surface states, when the energy is in a band gap of the projected bulk band structure and below the vacuum energy $E_V$.](image-url)
Adsorbate layers will be discussed at the end of this chapter.

The occurrence of intrinsic surface states can be described in a simple one-dimensional picture considering the wave functions perpendicular to the surface. Various possibilities are sketched in Fig. 3.1. For energies above the vacuum energy \( E_V \), propagating wave functions exist in the vacuum region. The wave functions decay rapidly away from the surface for energies below \( E_V \). In the bulk region exponentially decaying standing waves are obtained for energies in a band gap of the projected bulk band structure. Matching the wave function and their derivatives at the surface may lead then to surface states with wave functions localized in the surface region as illustrated in the third row of Fig. 3.1.

Band gaps in the projected bulk band structure are quite common on many metal as well as semiconductor surfaces and depend on the parallel component \( k_\parallel \) of the wave vector relative to the surface normal. It should be noted that the electron outside the surface has the kinetic energy \( \frac{\hbar^2 k_\parallel^2}{2m} \) parallel to the surface. This energy has to be expended for the emission of the electron and the vacuum energy relative to the Fermi energy \( E_F \) is \( E_V = \Phi + \frac{\hbar^2 k_\parallel^2}{2m} \).

The work function \( \Phi \) is the minimum energy required for the emission of an electron.

The propagating wave functions sketched in Fig. 3.1 correspond to free-electron-like plane waves. The modified potential at the surface compared to the bulk may lead to solutions which have a large amplitude near the surface compared to the propagating waves. This situation is termed surface resonance. For the further discussion it is appropriate to distinguish between surface states with larger probability density on the crystal side versus the vacuum side. The former case is sketched in Fig. 3.1 and represents a crystal-induced surface state discussed in more detail in Section 3.2. The latter situation of barrier-induced surface states occurs for image-potential states which are the topic of Section 3.3.1. Relative to the substrate-overlayer interface quantum-well states (see Section 3.3.2) fall also into the class of barrier-induced surface states.

### 3.1.2 Scattering model of surface states

Surface states can be described and calculated in many ways from simple models to density-functional theory. In this chapter we choose a scattering approach which provides an intuitive insight into the nature of crystal- and barrier-induced surface states. Other methods such as the nearly-free electron approximation or numerical integration of the Schrödinger equation in one dimension yield similar results.

In Fig. 3.2 the surface is assumed to be half a layer distance \( a/2 \) away from the topmost layers of surface atoms. At this boundary the wave function traveling to the right towards the barrier returns after scattering at the barrier with complex amplitude \( r_B \exp i\Phi_B \). Similarly the wave function is reflected by the crystal with \( r_C \exp i\Phi_C \). For a stationary condition the reflection amplitudes \( r_B \) and \( r_C \) must be 1. The second requirement is that the phase shifts must add up coherently

\[
\Phi_C + \Phi_B = 2\pi n. \tag{3.1}
\]

The phase shifts are a function of energy and Eq. 3.1 may have several solutions characterized by the quantum number \( n \). The distinction between crystal- and barrier-induced surface states depends on which phase shift \( \Phi_C \) or \( \Phi_B \) varies more rapidly with energy [1]. This criterion is
equivalent to the intuitive argument about the probability density being more in the crystal or outside \([1]\).

The calculation of the barrier phase \(\Phi_B\) depends on the nature of the surface potential and will be deferred to Section 3.3. The crystal constitutes a semiinfinite solid and the existence of surface states depends largely on properties of its band structure. In the one-dimensional scattering approach \([2]\) the potential is assumed to be a periodic arrangement of wells with separation \(a\) as depicted in Fig. 3.2. At the minima exist arbitrarily small regions of constant potential \(V_C\) where the wave function can be expanded into plane waves

\[
\psi(z) = Le^{-iKz} + Lre^{iKz} + Rte^{iKz}.
\]  

(3.2)

The first term describes a wave of amplitude \(L\) travelling to the left. It is reflected by the potential of the layer to the left with a reflection coefficient \(r\). The last term is a wave of amplitude \(R\) which has been transmitted through the layer at the left with a transmission coefficient \(t\). Without absorption the transmission and reflection coefficients fulfill the condition 

\[
|t|^2 + |r|^2 = 1.
\]

The wave vector \(K\) is given by the energy \(E\) relative to the potential \(V_C\) by

\[
E - V_C = \hbar^2 K^2 / 2m,
\]

where \(m\) denotes the (effective) mass of the electron. The solutions in the periodic potential with period \(a\) must obey Bloch’s theorem

\[
\psi(z + a) = e^{ika} \psi(z)
\]

(3.3)

for all \(z \leq a/2\) and in particular between the layers. The solutions for the Bloch wave vector \(k\) can be found from inserting Eq. 3.2 and the plane-wave expansion at \(z = -a/2\) from Fig. 3.2 into Eq. 3.3 and applying the same procedure to the derivatives of the wave functions. The following equations are obtained

\[
L/R = (e^{-i(K-k)a} - t)/r \quad \text{and} \quad R/L = (e^{-i(K+k)a} - t)/r.
\]

(3.4)

Multiplication of these equations yields a second-order equation for \(e^{ika}\) and thus the Bloch wave vector \(k\). The symmetry of the Eqs. 3.4 shows that a solution \(k\) implies the solution \(-k\) with reversed amplitude ratio \(L/R\). For complex wave vectors \(k\) this ensures that there exists always a solution decaying into the bulk \((z \to -\infty)\) with \(\Im(k) > 0\).
The complex band structure obtained from Eqs. 3.4 is shown in Fig. 3.3. The parameters $V_C$, $m$, and $t$ have been adjusted to reproduce the nearly-free electron band gap of the Cu(111) surface. Note that even a high transmission coefficient $t = 0.93$ leads to sizeable band gap. The crystal phase shift can be obtained directly from Eq. 3.2 to

$$e^{-i\Phi_C} = \frac{(1 - e^{i(K-k)a})}{r}$$

and varies in a cosine-like curve from 0 to $\pi$ across the band gap as illustrated by the dashed curve in Fig. 3.3.

Within a nearly-free electron approximation the complex band structure and phase shift $\Phi_C$ can also be calculated analytically [3]. The results are almost indistinguishable from the scattering approach using a constant transmission coefficient $t$ [2]. The scattering model has the advantage, that it may easily be extended to overlayers and alloys [2].

### 3.2 Crystal-induced surface states

#### 3.2.1 Tamm and Shockley surface states

Surface states have been discussed first by Tamm [4], Maue [5], and Shockley [6]. Surface states derived from $d$-bands are often called Tamm states and surface states with a free-electron-like dispersion derived from $sp$-bands are called Shockley states. The common ingredient of these models is a rather abrupt transition of the potential from the crystal to the vacuum at the surface. This leads to an exponentially decaying wave function in vacuum for energies below the vacuum energy $E_V$ as shown in the lower part of Fig. 3.1. To match the
3.2 Crystal-induced surface states

Figure 3.4: Surface band structure of Cu(100) (dotted lines) along high symmetry lines [10].

bulk wave function $\psi(z)$ and its derivative $\psi'(z)$ at the surface $\psi'/\psi$ has to be negative [7]. This condition is often met, when the potential has a minimum at the surface as shown in Fig. 3.2.

For a step-like barrier the phase shift $\Phi_B$ varies with energy from $-\pi$ at the bottom of the valence band to 0 at the vacuum level $E_V$ [3]. The crystal phase shift $\Phi_C$ varies across a band gap in the projected bulk band structure by $\pi$ [8] (see also Fig. 3.3). Note that only for energies inside a band gap the reflection coefficient $r_C$ is 1. A variation from 0 at the bottom of the band gap to $+\pi$ at the top of the band gap is obtained, if the potential at the surface has a minimum (see Fig. 3.2). This situation is called Shockley-inverted gap, because the symmetry of the wave functions with respect to the surface atoms is $p_z$ at the bottom and $s$ at the top of the band gap in contrast to the normal sequence of atomic orbitals. Note that the ranges of the phase shifts permit only the solution $n = 0$ in Eq. 3.1 and that this condition may not be fulfilled at any energy. The energies of the Shockley (or $n = 0$) surface states on the fcc(111) surfaces of noble metals can be calculated quite accurately assuming a step-like surface barrier [3, 9]. For the fcc(100) surfaces only surface resonances exist at $k_{\parallel} = 0$. Examples for the wave function and experimental observation of Shockley surface states are presented later in this chapter.

For the step-like surface barrier the phase is limited to the range $[-\pi, 0]$ and solutions of Eq. 3.1 are obtained only under certain conditions. This result can be generalized that the number of surface states on single-crystal surfaces containing a mirror plane is 0, 1, or 2 [8]. This statement is true anywhere in the projected bulk band gap. Two surface states can be found only at general points of the surface Brillouin zone (i.e. not at the center or zone boundary) [8].

Figure 3.4 shows the surface band structure of Cu(100) along the high symmetry lines of the surface Brillouin zone (see inset) [10]. Surface states are marked by filled dots. The bulk bands appear as discrete lines because of the use of a 11 layer slab used in the calculation. The envelope indicate the projected bulk band structure, i.e. the $E(k_{\parallel})$ regions where bulk bands exits. At the center of the surface Brillouin zone $\Gamma (k_{\parallel} = 0)$ the surface resonance is visible.
Figure 3.5: Dispersion of the dangling-bond states for the Si(001)c(4×2) surface illustrated at the right. The shaded areas indicate the projected bulk bands [11].

around 1 eV. Among the many surface bands in the $d$-band region the surface state at $\overline{M}$ at $-1.5$ eV is a Tamm state with a weak dispersion and narrow linewidth (see also Fig. 3.10).

3.2.2 Dangling-bond states

Surface states on semiconductor surfaces are often described as dangling-bond states reflecting the cutting of the localized bonds between the atoms at the surface. They belong to the class of crystal-induced surfaces states, because the probability density decays rapidly when going away from the surface. On the other hand the electronic structure of the surface atoms is different from the bulk due to the cut bonds. In addition strong reconstructions are commonly found at many semiconductor surfaces which reduce the number of dangling bonds compared to the truncated bulk.

The localized orbitals of the covalent bonds at semiconductors favor the use of tight-binding models. Applied to surfaces one obtains dangling-bond states localized at certain surface atoms. However, the associated bands show considerable dispersion indicating the extended nature of the wave functions. An example is shown in Fig. 3.5 for the Si(001)c(4×2) surface [11]. The shaded areas indicate the projected bulk band structure and the energy scale is referenced to the valence band maximum. The occupied (unoccupied) dangling bonds are localized on atoms shifted up (down) in the asymmetric dimer reconstruction as indicated in the right part of Fig. 3.5. The c(4×2) unit cell contains two dimers tilted in opposite orientation leading to two pairs of dangling-bond bands. Figure 3.5 shows strong dispersion of the bands in the [110] direction of neighboring dimers. In the [110] direction the dispersion is considerably smaller due to the larger separation of the dimer rows compared to the distance...
3.3 Barrier-induced surface states

3.3.1 Image-potential states

When an electron is brought in front of a metal surface the charge is screened in such a way, that the field lines are perpendicular to the metal surface (see Fig. 3.6). The polarization charge induced at the surface acts as if the metal would be replaced by an image charge of opposite sign at the opposite position from the metal surface. The force acting on the charge \(-e\) at a distance \(z\) in front of the surface can be written as

\[
F(z) = -\frac{e^2}{(2z)^2}. \tag{3.6}
\]

Note that there is no force needed to move the charge in the direction parallel to the surface. The factor 2 in the denominator of Eq. (3.6) arises, because charge and image charge are separated by the distance \(2z\).

The image force can be derived from the image potential

\[
V(z) = E_V - \frac{e^2}{4(z - z_{im})}. \tag{3.7}
\]

where \(z_{im}\) is the image-plane position. The potential converges towards the vacuum level \(E_V\) for large distances from the surface. The image plane is typically located about half an interlayer distance outside the outermost atomic layer.

Chulkov et al. [12] suggested a simple one-dimensional model which reproduces energies of the observed surface states at many metal surfaces very well. Figure 3.7 shows the model potential for the Cu(111) surface. In the bulk region it is described by a cosine function which opens the gap in the projected bulk band structure on the surface of interest [13]. In the surface...
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Figure 3.7: One-dimensional model potential and probability density for the Shockley surface state and the first image-potential state ($n = 1$) at the Cu(111) surface. The shaded areas indicate the projected bulk bands bounded by the image plane. The dots give the positions of the atomic planes.

region the model potential is represented by a smooth cosine-like function that reproduces the energy of the Shockley surface state. In the vacuum region this function merges into the long-range image potential in such a way that it describes the experimental energy of the first image-potential state. The position of the image plane $z_{im}$ is obtained consistently from the defining potential equations [12].

The one-dimensional potential is strictly valid only for electrons moving perpendicular to the surface, i.e. with parallel momentum $k_{\parallel} = 0$ at the center of the surface Brillouin zone. It can be extended assuming a free-electron like behavior for the motion parallel to the surface. The effect of the crystal potential might lead to an effective mass different from the free-electron mass.

For a one-dimensional potential such as shown in Fig. 3.7 for the Cu(111) surface it is straightforward to obtain the solutions of the Schrödinger equation, e.g. by numerical integration. The dashed lines in Fig. 3.7 show the energies of two solutions together with the squares of the wave functions. The solution at the lower energy is the well-known Shockley surface state [6] which is only slightly influenced by the image potential. The other solution is the $n = 1$ image-potential state which has most of its probability density outside the surface [14].

The long-range nature of the image potential leads to an infinite series of image-potential states. The energies show a similar dependence as in the hydrogen atom

$$E_n = E_V - \frac{0.85 \text{ eV}}{(n + \alpha)^2}, \quad n = 1, 2, 3, \ldots$$

(3.8)

The energy is scaled down by a factor of 16 relative to the hydrogen atom due to the factor of 4 in the denominator of the potential in Eq. 3.7. Image-potential states always have energies
above the Fermi energy close to the vacuum level, because the image potential and the states require an external charge which is absent in the ground state.

For the one-dimensional Coulomb potential of Eq. 3.7 the barrier phase shift may be written as [3, 15]

$$\Phi_B(E) = \pi \left( \sqrt{\frac{3.4 \text{ eV}}{E_V - E}} - 1 \right).$$

(3.9)

The divergence of $\Phi_B$ for $E \to E_V$ leads to an infinite series of barrier-induced surface states. Inserting the energy $E_n$ into Eq. 3.9 yields in combination with the phase condition of Eq. 3.1 the following expression for the quantum defect $\alpha$ in Eq. 3.8 [3]:

$$\alpha = \frac{1}{2} \left( 1 - \frac{\Phi_C}{\pi} \right).$$

(3.10)

The quantum defect varies from $\frac{1}{2}$ to 0 across the band gap with increasing energy. At the upper edge of the band gap the wave function has a node at the surface and is $s$-like with respect to the atom, whereas at the lower edge it has a maximum and $p_z$ character. The different phase of the bulk wave function can be seen in Fig. 3.7 for the image-potential and Shockley surface state, respectively.

Image-potential states at metal surfaces were predicted by Echenique and Pendry [14, 16] and first detected by inverse photoemission [17, 18]. The inverse photoemission results have been reviewed by Straub and Himpsel [19]. The limited resolution and sensitivity of inverse photoemission allowed only the $n = 1$ image-potential state to be resolved clearly. With two-photon photoemission (see Section 3.4.2) the energy resolution could be improved and the lowest three image-potential states could be identified [20]. The weak coupling of image-potential states to surfaces makes them ideal observer states to monitor the geometric, electronic and magnetic properties of metal surfaces [9, 21, 22]. The electron dynamics in image-potential states at metal surfaces has been discussed in the previous volume [23].

### 3.3.2 Quantum-well states

If a metal overlayer is deposited on top of a metal or semiconductor substrate, electronic states may exist for energies in the projected bulk band structure of the substrate. These states are confined to the overlayer by an effective potential well and are called quantum-well states. It is straightforward to extend the phase accumulation model of Section 3.1.2 and add the phase shift of the Bloch wave of wavevector $k$ after propagating back and forth through $N$ layers of thickness $a'$ [24]:

$$\Phi_C(E) + 2k(E)Na' + \Phi_B(E) = 2\pi n.$$

(3.11)

For clarity the energy dependence of the relevant terms is included, where $k(E)$ is taken from the band structure of the overlayer. The scattering model of Section 3.1.2 is a convenient way to calculate the dispersion $E(k)$. Equation 3.11 shows that the number of layers $N$ can change the phase by large amounts. The crystal phase $\Phi_C$ may change only by $\pi$ across the band gap. The barrier phase $\Phi_B$ varies significantly only close to the vacuum level $E_V$ (see Eq. 3.9) and might otherwise be approximated by the phase for the step potential [3]. The quantum number $n$ describing the total phase shift is therefore determined mainly by the number of layers $N$. It is is convenient to sort the quantum-well states by energy which is achieved by
introducing the quantum number $\nu = N - n$ [24]. This numbering scheme permits the easy comparison of states for different layer thicknesses and fits the obvious sequence of states observed in experimental data. Note that the numbering scheme is not unique and might differ for energies at the bottom or top of a band in the overlayer band structure [24].

A special situation may occur for a quantum well straddling the vacuum energy. Here the second and third term of Eq. 3.11 may vary considerably with energy. The phase shift in the quantum well can be controlled by the layer thickness. One example are image-potential states for Au on Pd(111) [25]. Figure 3.8 shows calculated wave functions for 6 layers of Au on Pd(111). The lowest $\nu = 1$ state is located mainly in the overlayer and has an energy 1.1 eV below $E_V$ which is outside the range given in Eq. 3.10 for positive quantum defects. The $\nu = 2$ state corresponds more to an image-potential state and has properties very similar to the first image-potential state on the clean Pd(111) surface.

### 3.4 Experimental methods

This section discusses briefly the main experimental techniques for the study of intrinsic surface states. Emphasis is put on the analysis of data regarding the dynamics at surfaces. For a comprehensive review of the results obtained by the various techniques and calculations see Ref. [26].

#### 3.4.1 Photoemission

Figure 3.9 shows in the left the energy diagram for the photoemission process. The incoming photon of energy $h\nu$ excites an electron from the initial state $|i\rangle$ with energy $E_i$ to a final state
$|f\rangle$. The final state energy $E_f$ of the emitted electron is measured as the kinetic energy $E_{kin}$ relative to the vacuum level $E_V$. Energy conservation yields

$$E_f = E_i + h\nu = E_{kin} + \Phi. \quad (3.12)$$

The two-dimensional periodicity conserves the momentum parallel to the surface in a reduced Brillouin zone scheme

$$\vec{k}_f^\parallel = \vec{k}_i^\parallel \quad \text{with} \quad |\vec{k}_f^\parallel| = \sqrt{2mE_{kin}/\hbar^2} \sin \vartheta. \quad (3.13)$$

The momentum of the photon can be neglected in most cases. The second equation relates the momentum to the measured kinetic energy $E_{kin}$ and emission angle $\vartheta$. The power of angle-resolved photoelectron spectroscopy lies in a complete determination of the surface band structure $E_i(\vec{k}_\parallel)$.

A typical photoemission spectrum is sketched at the right hand side of Fig. 3.9. At the final state energy $E_f$ a peak in the spectrum appears. The low-energy cutoff arises from electrons at the vacuum level $E_V$ of the sample which have zero kinetic energy at the sample. In practice a small bias voltage is often used to accelerate the emitted electrons towards the analyzer and to ensure that the low-energy cutoff is not set by the analyzer. The maximum energy $E_{max}$ is gained by electrons at the Fermi level $E_F$ which obtain after the absorption of a photon with energy $h\nu$ the kinetic energy $E_{max} - E_V = h\nu - \Phi$. The width of the spectrum given by the low- and high-energy limits can be used to determine the work function $\Phi$ of the sample.

Figure 3.10 presents two examples for photoelectron spectra from surface states. Using a state-of-the-art two-dimensional analyzer with an energy resolution of 3.5 meV and 0.15° angular resolution the Shockley surface state for the Cu (111) surfaces has been measured [27]. It should be mentioned that such high-quality results require a careful sample preparation and
are very sensitive to sample contamination. The lineshape can be fitted by a Lorentzian with a full width at half maximum of 23 meV. The experimental resolution is taken into account by convolution with a Gaussian.

The more localized Tamm surface states show less dispersion and the angular resolution is less important. As an example a spectrum and the corresponding fit for the Tamm state on Cu(100) is shown in the left panel of Fig. 3.10 [28]. The state shows a narrow intrinsic linewidth of $\Gamma = 7$ meV even at an energy of 1.8 eV below the Fermi energy. This is attributed to the localized character of the $d$-states and the small overlap with the $sp$-bands which provide the main decay channel for inelastic decay.

The photoemission lineshape is proportional to the hole spectral function of the sample times the Fermi distribution. The spectral function $A$, in turn, is used to describe the electronic structure of a solid in the presence of many-body effects. $A$ can be viewed as the probability of finding an electron with energy $E_i$ and momentum $\vec{k}$. The spectral function is determined by the unrenormalized dispersion $\epsilon(\vec{k})$ and the complex self-energy $\Sigma = \Sigma' + i\Sigma''$. In general $\Sigma$ depends on the initial state $\epsilon(\vec{k})$ including the momentum $\vec{k}$ and additional parameters of the many-body interactions. For electron-phonon coupling this would be the temperature. Then $A$ has the form

$$A(E_i, \vec{k}) = \frac{\pi^{-1} |\Sigma''|}{[E_i - \epsilon(\vec{k}) - \Sigma']^2 + \Sigma''^2}.$$  \hspace{1cm} (3.14)

With a modern photoelectron spectrometer, the photoemission intensity can be measured for so many values $(E_f, \vec{k})$ that any cut through the spectral function can be extracted. However, we briefly relate the spectral function to the traditional measuring modes of angle-resolved photoelectron spectroscopy, energy distribution curves (EDCs) and momentum distribution curves (MDCs).

An EDC is the photoemission intensity as a function of kinetic energy for a fixed photon energy and a fixed emission angle. The fact that the emission angle, not $\vec{k}$, is constant means that an EDC corresponds to a fairly complicated cut through the spectral function. Under
3.4 Experimental methods

certain conditions, for example for normal emission or for a very small energy range, an EDC is taken at approximately constant \( \vec{k} \). Even then an EDC calculated from (3.14) may have a fairly complicated form. This is due to the energy dependence of \( \Sigma \) which might be relevant in particular close to the Fermi level. A simple scenario arises when we assume that \( \Sigma' = 0 \) and that \( \Sigma'' \) is constant. Then we get

\[
A(E_i, \vec{k}) = \frac{\pi^{-1}|\Sigma''|}{|E_i - \epsilon(\vec{k})|^2 + \Sigma''^2}
\]

which is a Lorentzian with the maximum at \( \epsilon(\vec{k}) \) and a full-width at half-maximum (FWHM) of \( 2|\Sigma''| \) in agreement with the experimentally observed lineshape (see Fig. 3.10). However, care is necessary when an EDC linewidth is identified with \( 2|\Sigma''| \), because of the above-mentioned problem that an EDC is strictly measured at a constant emission angle, not at a constant \( \vec{k} \) [29, 30, 31].

The situation is simpler in case of MDCs because they are readily represented by (3.14). The maximum of an MDC is reached when \( E_i - \epsilon(\vec{k}) - \Sigma' = 0 \). Based on this, the renormalized dispersion is defined as the self-consistent solution of

\[
E_i(\vec{k}) = \epsilon(\vec{k}) + \Sigma'(E_i(\vec{k})).
\]

Equation 3.14 takes on a particularly simple form in the case of a linear dispersion. We consider only one direction in \( \vec{k} \) space and write \( \epsilon(k) = vk \) such that the origin of the coordinates is at the Fermi level crossing. Then it is easy to show that (3.14) is a Lorentzian line in \( k \) for a given \( E_i \) with the maximum at

\[
k_{\text{max}} = (1/v)(E_i - \Sigma') \quad \text{and} \quad \text{FWHM} = 2|\Sigma''/v|.
\]

3.4.2 Two-photon photoemission

Two-photon photoemission can be viewed as regular (one-photon) photoemission from a state after excitation of the surface by another photon. This allows the spectroscopy of excited intermediate states with energies above the Fermi level, which are normally unoccupied. This energy range, in particular the part below the vacuum level, is otherwise accessible only by inverse photoemission.

The excitation of the surface is done by photons and the dipole selection rules apply for both steps in two-photon photoemission. Using two photons expands the parameter space compared regular photoemission by the choice of energy and polarization of an additional photon. In order to reach the high intensities needed for the second-order process femtosecond lasers are used. This adds the possibility to introduce a time delay between the two laser pulses which allows to follow the population in the excited state on short time scales. This last feature in particular is unique to two-photon photoemission and permits the detailed investigation of the electron dynamics at surfaces which is the main topic of the previous volume.

The energy diagram of two-photon photoemission is shown in Fig. 3.9. The first photon with energy \( h\nu_a \) excites an electron from an occupied initial state \( |i\rangle \) below the Fermi energy \( E_F \) to an intermediate state \( |n\rangle \). The second photon of energy \( h\nu_b \) excites the electron into the final state \( |f\rangle \) from where it can leave the surface, if the energy \( E_f \) is above the vacuum energy \( E_{\text{vac}} \). The kinetic energy \( E_{\text{kin}} \) of the emitted electron is measured with an electron
energy analyzer as in regular photoelectron spectroscopy. The photon energies $\hbar \nu_a$ and $\hbar \nu_b$ should be below the work function $\Phi = E_V - E_F$ to avoid one-photon photoemission which is several orders of magnitude more intense than two-photon photoemission.

In two-photon photoemission spectra the assignment of a peak to an initial or intermediate state is not obvious. In addition, the sequence of the photons $\hbar \nu_a$ and $\hbar \nu_b$ may be interchanged or two photons $\hbar \nu_a$ or $\hbar \nu_b$ may emit the electron. The latter possibility can be checked by an intensity variation (simply blocking the respective laser beams). The former possibilities can be checked by measuring spectra at photon energies varied by $\Delta \hbar \nu_a$ and $\Delta \hbar \nu_b$ and determining the change of the kinetic energy $\Delta E_{\text{kin}}$. In most cases only the fundamental photon energy $\hbar \nu_0$ before frequency doubling or tripling is tuned. For surface states $\Delta E_{\text{kin}}$ varies as an integer multiple of the variation of the fundamental photon energy $\Delta \hbar \nu_0$. Bulk bands disperse with momentum perpendicular to the surface and the kinetic energy might vary in a different fashion with photon energies given by the dispersion of the bulk bands [32]. For parabolic bands $\Delta E_{\text{kin}}$ is proportional $\Delta \hbar \nu_0$ with a factor given by the ratio of the effective masses [33]. A different approach to distinguish initial and intermediate states compares one and two-photon photoemission spectra taken at the same total photon energy $\hbar \nu = \hbar \nu_a + \hbar \nu_b$ [34]. Intermediate states are absent in one-photon photoemission spectra.

Two-photon photoemission spectra as a function of photon energy are shown in Fig. 3.11 for the Cu(111) surface [35, 36]. On this surface an occupied Shockley surface state and an unoccupied image-potential state exist as shown in Fig. 3.7. The spectra present two peaks

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure3.11}
\caption{Series of two-photon-photoemission spectra from Cu(111) for various photon energies with $\hbar \nu_a = 3 \hbar \nu_b$. The spectra are normalized to same height and plotted with an offset proportional to $\hbar \nu_b$.}
\end{figure}
3.4 Experimental methods

Figure 3.12: Time-resolved spectra for the surface (open circles, \( n = 0 \)) and image-potential state (open squares, \( n = 1 \)) on Pd(111). The solid dots show the cross correlation determined for the occupied surface state on Cu(111).

which show a different variation of the kinetic energy with photon energy. The peak with the stronger variation with photon energy is assigned to an initial state, i.e. the occupied surface state, because it requires the absorption of two photons of energies \( h\nu_a = 3h\nu_b \) and \( h\nu_b \). The image-potential-state peak shows as intermediate state a weaker variation, because the electron is emitted after absorption of a photon with energy \( h\nu_b \). The peak positions of the spectra in Fig. 3.11 are projected to the base line and marked with dots. Since the offset of the spectra is proportional to the photon energy, we obtain in this way a plot of photon energy versus kinetic energy. The straight lines show the expected linear behavior with different slopes for different states. At the photon energy \( h\nu_b = 1.512 \) eV the two lines cross and a resonant excitation with photon energy \( h\nu_a = 4.536 \) eV from the surface to the image-potential state occurs [37, 38]. The spectra in Fig. 3.11 are normalized to same height, so the intensity enhancement [39] at resonance is not visible.

Two-photon photoemission adds the additional parameter of a time delay between the two laser pulses. This allows to monitor the decay of the population of the intermediate state \( |n\rangle \) as a function of time after the initial excitation. Note, that also scattering into other states \( |n'\rangle \) may be detected as indicated in Fig. 3.9 [40].

An example for time-resolved two-photon photoemission is shown in Fig. 3.12 for the Pd(111) surface which has an unoccupied Shockley surface state and an image-potential state [41, 42]. The latter is excited as for Cu(111), but for the surface state \( h\nu_b \) is absorbed before \( h\nu_a \). The exponential decays (indicated by straight lines in the semilogarithmic plot of Fig. 3.12) appear on different sides relative to the time zero. From this the assignment of the excitation sequence is straightforward, because the probe pulse must come after the pump pulse. The bottom traces of Fig. 3.12 show measurements of the occupied surface Shockley state on Cu(111) which is excited by the simultaneous absorption of two photons. The symmetric shape of the cross-correlation curves indicates a symmetric (Gaussian) pulse shape of
the laser pulses.

Two-photon photoemission involves the absorption of two photons and the two optical transitions can usually be treated as independent consecutive processes. In the following we will discuss a few aspects of time-resolved two-photon-photoemission which are fundamentally different from regular photoemission.

In a time-resolved two-photon-photoemission experiment the pulse duration can be comparable to the timescale of the temporal evolution of the involved states. Alternatively speaking, the separation of the energy levels is comparable to the bandwidth of the laser pulses. The laser fields excite the electronic states $|l\rangle$ into a superposition

$$|\Psi\rangle = \sum_l c_l(t) |l\rangle.$$  \hspace{1cm} (3.18)

After the laser fields are turned off the time dependence of the state $l$ is given by

$$c_l(t) = c_l(0) e^{-t/2\tau_l} e^{i\phi_l(t)} e^{iE_l t/\hbar}.$$  \hspace{1cm} (3.19)

The exponential decay is described by a lifetime $\tau_l$ and the energy $E_l$ determines the quantum-mechanical phase. The term containing $\phi_l(t)$ describes changes of the phase by phase-breaking events, e.g. (quasi-)elastic scattering of the electron with negligible change of energy or population $|c_l(t)|^2$ [43]. The population of the final state $|c_f(t)|^2$ is observed experimentally. It depends on the laser fields of both photons including the time delay between pump and probe pulse.

The time evolution of the population $|c_f(t)|^2$ can be calculated using the density matrix formalism [44]. The external laser fields couple the different states. The interaction with other states of the system is described by decay and dephasing rates which are treated as parameters. The resulting optical Bloch equations [45] may be solved numerically and analytically in certain limiting cases [38, 46].

The description of regular photoemission spectra by two-level optical Bloch equations yields a Lorentzian convoluted with the spectrum of the light source and the analyzer resolution function [46]. Note that an exponential decay in time leads to a Lorentzian in the energy domain. The Lorentzian width contains a sum of decay and dephasing rates of the hole, which cannot be separated. Therefore, the linewidth in photoemission cannot be identified directly with an inverse lifetime of the photohole.

Two-photon photoemission starts like regular photoemission from a constant initial-state population, but the two-photon process samples a time-dependent intermediate-state population with the second photon. This time dependence changes upon tuning the photon energy on or off resonance for a transition between discrete initial and intermediate states. In Fig. 3.11 the linewidth at resonance ($h\nu_b = 1.512$ eV) is narrower than the linewidth observed for each state off resonance [36]. Using optical Bloch equations the experimental lineshape can be described quite well by a Lorentzian and values for the decay and dephasing rates of the surface and image-potential state can be obtained [38]. Decay and dephasing rates can also be separated by measuring the linewidth as a function of delay between pump and probe pulses [46]. For long delays the Lorentzian is determined by the dephasing rate and the decay rate enters only when pump and probe pulse overlap. Note that for femtosecond laser pulses the spectral bandwidth may exceed the energy resolution of the analyzer in two-photon photoemission.

If the energy separation of intermediate states is comparable to the bandwidth of the laser pulses, several states can be excited coherently and the temporal phase of the wave function
3.4 Experimental methods

Figure 3.13: Coherent excitation of the $n = 3$ and $n = 4$ image-potential states leads to beating patterns as a function of pump-probe delay.

enters directly. The optical Bloch equations have to be solved including several intermediate states [47, 48]. When the pump pulse is over, the intermediate state population is given by the square of the sum of all excited states $c_l(t)$ (see Eq. 3.19):

$$| \sum_l c_l(t) |^2 = \sum_l |c_l(0)|^2 e^{-t/\tau_l}$$

$$+ 2 \sum_{l \neq m} |c_l(0)||c_m(0)| e^{-t/2\tau_l-t/2\tau_m-\Gamma_{lm} t/\hbar} \cos((E_l - E_m)t/\hbar).$$

The oscillation frequencies in the last term depend on the energy differences of the coherently excited states. These oscillations are damped by the lifetimes of the states and the loss of phase coherence described by the dephasing rates $\Gamma_{lm}$. The first term of Eq. (3.20) describes the average population decay with time constants $\tau_l$. An experimental illustration is given in Fig. 3.13 for image-potential states on Cu(100) [49, 47]. The oscillatory and exponential contributions can be separated and decay with different time constants. This allows a direct identification of different scattering processes by the analysis of decay and dephasing rates.

3.4.3 Scanning tunneling methods

Scanning tunneling microscopy uses the exponential dependence of the tunneling current on distance and voltage to image the surface with resolution on the atomic scale. In the spectroscopic mode the voltage is varied at fixed distance and the current is sensitive to the electronic structure of the surface (and tip). The high spatial resolution implies an integration over a range of parallel momenta $k_\parallel$. Therefore it seems impossible to determine energetic linewidths in scanning tunneling spectroscopy. However, the features in any energy spectrum have some intrinsic width and in suitable experiments the measured information may be related to the linewidth as measured with other techniques.

The first method simply records the onset of the tunneling into the Shockley surface states. The corresponding spectra are shown in Fig. 3.14 for the (111) surfaces of Ag, Au, and Cu.
Intrinsic Surface States

Figure 3.14: $dI/dV$ spectra for the surface states on Ag(111), Au(111) and Cu(111). Adapted from Ref. [50].

All spectra were taken at least 200 Å away from impurities and are averages of different single spectra from varying sample locations and tips. A step-like onset is observed with a material-dependent width $\Delta$. This width is in good approximation proportional to the intrinsic linewidth $\Gamma$ measured in photoelectron spectroscopy [51]: $\Delta = \frac{\pi}{2} \Gamma$.

The previous method is limited to the onset, i.e. to the bottom of the surface state band. In order to select states at higher energies one can resort to select specific $k_\parallel$ values by confining electrons by suitable barriers [52]. This method is closely related to the spatially-resolved measurements discussed in the following paragraph and might be disturbed by the confining barriers in particular for small structures.

The most simple structures are steps which are ubiquitous on real surfaces. Figure 3.15 shows spectra at a descending step located at $x = 0$ on a Cu(111) surface. The current or more pronounced the differential conductivity $dI/dV$ show an oscillatory pattern as a function of the distance $x$ from the step. This can be explained by the interference of the electron wave reflected by the step with the original wave at the tip position [53]. The data can be fitted very well by the following function [54]:

$$\frac{dI}{dV} \propto 1 - |r| \exp\left(-\frac{x}{L_\phi}\right) J_0(2k_\parallel x)$$

(3.21)

The Bessel function $J_0$ arises from the summation of all possible scattering paths and the exponential term includes additional damping described by the dephasing length $L_\phi$. The arbitrary scaling and offset of the experimental data makes a fit of the reflectivity $|r|$ difficult. The dephasing length $L_\phi$ can be fitted reliably and shows a strong energy dependence as illustrated in Fig. 3.15 (left panel). The analysis of the data yields also the dispersion relation $E(k_\parallel)$ for the Shockley surface state in good agreement with results from photoemission or inverse photoemission. Scanning tunneling microscopy or spectroscopy can be performed at positive and negative voltages which makes occupied as well as unoccupied states accessible. The obtained dephasing lengths can be converted to lifetimes $\tau = L_\phi/v_g$ using the group velocity $v_g = \partial E/\partial k_\parallel = \hbar k_\parallel/m^*$ for a parabolic band with effective mass $m^*$. 

```latex
\begin{align*}
\frac{dI}{dV} & \propto 1 - |r| \exp\left(-\frac{x}{L_\phi}\right) J_0(2k_\parallel x) \\
& (3.21)
\end{align*}
```
Figure 3.15: $dI/dV$ data perpendicular to a descending Cu(111) step obtained by averaging over several line scans of a $dI/dV$ image. Solid lines indicate fits. The significance of the deduced $L$ is demonstrated by the dotted line: neglecting inelastic processes by setting $L_\phi \to \infty$ leads to a much slower decay rate than observed. Adapted from Ref. [53].
Bibliography