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1 Electron dynamics at surfaces

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1.1 Overview

In many surface processes energy is deposited and the surface is brought far off from thermal equilibrium. In particular when photons or electrons hit the surface, the energy is transferred initially to electrons in the surface region. By electron-electron scattering the excess energy is distributed between many electrons on a subpicosecond time scale. These hot electrons transfer their energy to the lattice vibrations (phonons) on a significantly longer time scale, because the electron-phonon coupling is much weaker than the electron-electron interaction. At this time the deposited energy is still in the surface region and only on time scales of microseconds.

*Figure 1.1:* Pathways of energy relaxation from an initial excitation at the surface to thermal equilibrium of the bulk-surface system.
or more surface and bulk reach thermal equilibrium via phonon-phonon scattering, i.e. thermal conduction. These pathways of energy relaxation are sketched schematically in Fig. 1.1 illustrating electron energy or temperature as a function of time. If the scattering processes of electrons with electrons or phonons occur near the surface, the related electron dynamics can be studied with surface sensitive techniques. More conveniently, signatures of it can be found by careful analysis of most obtained signals.

Before we turn to the details, it should be pointed out, that this energy relaxation scheme is quite general and common. It happens when sunlight hits our skin leading to a warm, comfortable feeling. More useful are schemes where not all the energy is converted to heat, e.g. in the conversion of light to chemical energy in photosynthesis or to electrical energy in a solar cell. These processes rely on a sufficiently long lifetime of the electronic excitation, so charge can be transferred and used for the intended purpose. An understanding of electron dynamics is therefore important in many areas of research and applications.

We now consider an excited electron at the surface, e.g. in a surface or adsorbate state. It is going to be scattered and the possible processes can be divided into the following categories:

- **Electron-electron scattering:**
  This most important process for energy relaxation leads to decay into bulk or surface states at lower energy with the simultaneous creation of an electron-hole pair. The coupling to the electronic system can also include other quasiparticles such as excitons, plasmons, and magnons which are not covered in this chapter.

- **Electron-phonon scattering:**
  This scattering process changes mainly the direction of the electron motion and embraces scattering to bulk bands as well as scattering within the surface state band. For molecular vibrations the electron might also lose a significant amount of energy.

- **Electron-defect scattering:**
  Real surfaces contain always a non-negligible amount of defects, such as steps or impurity atoms. The associated electron-defect scattering changes mainly the electron momentum. If we regard a phonon as a distortion of the ideal lattice it is in many aspects similar to electron-phonon scattering.

- **Electron transfer:**
  This mechanism is not related to energy relaxation processes, but it describes the contribution from the energy-conserving resonant electron transfer from an excited electron state to bulk and/or surface states. The electron-transfer mechanism is important for resonance surface and image-potential states on clean or adlayer-covered surfaces. Defects may also lead to a charge transfer between bulk and surface electronic states.

Various scattering processes involving several surface states on the clean Cu(111) and Cu(100) surfaces are sketched in Fig. 1.2. On the way to thermal equilibrium many of these scattering processes occur and in particular electron-electron scattering leads to a cascade of electrons and holes. All scattering processes apply as well to holes in the sense that an electron is scattered into the hole leaving another hole behind. The recombination of a hole with an excited electron is unlikely due to the high density of valence electrons. Only electron-electron scattering is connected with a significant loss of energy of the primary electron.
1.1 Overview

Electron-phonon or -defect scattering involves coupling to atoms and changes mainly momentum. These observations are in agreement with the expectation for the scattering between two particles from classical mechanics. Energy and momentum conservation hold also in quantum mechanics, but one should be aware of momentum provided by reciprocal lattice vectors or collective excitations in condensed matter physics. From an experimental point of view the effect of electron-phonon and -defect scattering can be identified by a systematic variation of the number of phonons through temperature or the concentration of defects through sample preparation, respectively. The remaining many-particle effect of electron-electron scattering may then be estimated by extrapolation to zero temperature and to zero defect concentration.

A successful study and understanding of the decay of electronic excitations in surface states requires appropriate theoretical and experimental methods. The theoretical calculations use different models depending on the interactions relevant for the scattering processes [1]. The decay rate due to inelastic electron-electron scattering, \( \Gamma_{\text{ee}} \), is normally calculated using the GW or GW + T-matrix approximation for the self energy [2, 3, 4, 5, 6, 7, 8, 9]. The contribution to the decay rate from the energy-conserving resonant electron-transfer mechanism, \( \Gamma_{\text{e-e}} \), can be evaluated by using a wave propagation method [1, 10] or Green function method [1]. For the electron-phonon contribution, \( \Gamma_{\text{e-ph}} \), the Eliashberg function is used [11, 12, 13]. The contribution due to scattering by defects, \( \Gamma_{\text{e-def}} \), has been treated for the elastic case by a wave-packet propagation method [14, 15, 16, 17]. Three different experimental techniques can be employed to study the decay of electronic excitations at surfaces. Photoelectron spectroscopy (PES) as described in detail in chapter . . . (see also Refs. [18, 19, 20]) accesses the decay rate through the spectral lineshape and linewidth [21]. It is limited to occupied states below the Fermi energy. The complementary method of inverse

Figure 1.2: Projected bulk-band structure (shaded areas) for the Cu(111) and Cu(100) surfaces with intrinsic Shockley surface-state bands \((n = 0)\) and image-potential bands \((n \geq 1)\). Arrows indicate possible electron-electron \((ee)\), electron-phonon \((ep)\) and defect \((def)\) scattering processes.
photoemission permits the spectroscopy of unoccupied surface states [22, 23]. However, its limited energy resolution does not allow to extract useful information on linewidths except in favorable cases [24]. Scanning tunneling microscopy (STM) and in particular scanning tunneling spectroscopy (STS) as described in detail in chapter . . . (see also Refs. [25, 26, 27]) obtains detailed information on the decay properties of surface states. The topographical images monitor simultaneously the quality and detailed structure of the surface area under investigation. Two-photon photoemission (2PPE) as described in detail in chapter . . . and in Refs. [28, 29] in the time-resolved mode is the only technique which is able to study the decay in the time domain [30, 31]. By combining this information with spectroscopic measurements a very detailed picture of the electron dynamics emerges [1, 32].

Table 1.1 lists the different scattering processes and quasiparticles which can be studied by the various techniques. Each of the techniques has its weaknesses and strengths in addressing specific questions about the electron dynamics at surfaces. Photoelectron spectroscopy can access only occupied states and is therefore restricted to the hole decay. Two-photon photoemission is most successful for measuring image-potential states (see chapter . . .) but the application to other states has a lot of potential. The scanning tunneling methods work particularly well for Shockley-type surface states. As illustrated in Table 1.1 the various methods can tackle almost all the involved problems.

The theoretical description can specifically address the various scattering processes by the development of appropriate models which are presented in Section 1.2. In experiment the combined effect of all scattering processes is usually observed and only by extensive and careful analysis the individual contributions can be disentangled. Therefore, the presentation of the experimental methods is organized according to the physical observables as listed in Table 1.1. The electron dynamics in the time domain is accessible only in time-resolved two-photon photoemission and is discussed in Section 1.3. Photoelectron spectroscopies as well as scanning tunneling spectroscopy access the electron dynamics via the spectral line shape. These aspects are presented in Section 1.4. Real space imaging of electron waves is possible only in scanning tunneling microscopy which is the topic of Section 1.5. The final Section 1.6 compares the information obtained by the various experimental methods with theoretical calculations and presents the current understanding of electron dynamics at surfaces.
1.2 Theoretical description

As discussed in the overview, the decay rate of an excited electron or hole can be presented as a sum of four contributions:

\[ \Gamma_{tot} = \Gamma_{e-e} + \Gamma_{e-ph} + \Gamma_{e-def}. \] (1.1)

The first term, \( \Gamma_{e-e} \), describes the contribution from inelastic electron-electron (\( e-e \)) scattering. The second term, \( \Gamma_{e-ph} \), describes the contribution from the energy-conserving resonant electron-transfer mechanism. The third contribution, \( \Gamma_{e-ph} \), represents the electron-phonon (\( e-ph \)) channel for relaxation of excited electron (hole) via \( e-ph \) scattering. This mechanism is the only one which carries the temperature dependence of the electron (hole) decay in paramagnetic metals. The fourth term, \( \Gamma_{e-def} \), describes elastic scattering of excited electron by defects. Below we give a short description of the calculational methods. For more details we refer the reader to respective original publications. Electron transfer in particular has been reviewed recently in Ref. [1].

In this section atomic units (\( h = e^2 = m = 1 \)) are used, unless stated otherwise.

1.2.1 Electron-electron interaction

The physics of electron dynamics in image-potential and surface states (as well as in bulk states) can be qualitatively understood in terms of a few key ingredients such as initial and final states, density of final states as well as screened electron-electron interaction and electron-phonon coupling. In particular, the linewidth gets wider with (i) a larger overlap between initial and final states, (ii) more states at the energy of the final states (Density of states (DOS) factor), (iii) a larger imaginary part of the screened interaction and the associated weaker screening and (iv) an increased electron-phonon interaction.

Quantitatively, in the framework of many-body theory the damping rate \( \Gamma_{e-e} \), i.e. lifetime broadening contribution for an excited electron with energy \( \epsilon_i > E_F \) can be obtained on the energy-shell approximation in terms of the imaginary part of the complex non-local self-energy operator \( \sigma \) [2, 5] as

\[ \Gamma_{e-e} = -2 \int d\vec{r} \int d\vec{r}' \phi_i^*(\vec{r}) \text{Im} \Sigma(\vec{r}, \vec{r}'; \epsilon_i) \phi_i(\vec{r}'), \] (1.2)

where \( \phi_i \) and \( \epsilon_i \) are the eigenfunctions and eigenvalues of the one-electron Hamiltonian. For a quantum state characterized by one-electron energy \( \epsilon_i \) and spin \( \sigma \) the self-energy can be represented as [6, 7, 8, 9]

\[ \Sigma_{\sigma}(\vec{r}, \vec{r}', \epsilon_i, \sigma) = \Sigma_{\sigma}^{GW}(\vec{r}, \vec{r}', \epsilon_i, \sigma) + \Sigma_{\sigma}^{T}(\vec{r}, \vec{r}', \epsilon_i, \sigma), \] (1.3)

where \( \Sigma_{\sigma}^{GW} \) is the self-energy derived within the GW approximation [2]. In this approximation for the self-energy (\( G \) means a single particle Green function) only the first term in the series expansion in terms of the screened Coulomb interaction \( W \) is retained [2, 4]. The \( \Sigma_{\sigma}^{T} \) is the self-energy contribution obtained from the T-matrix approximation which accounts for multiple electron-hole, electron-electron, and hole-hole scattering [33, 6, 7, 8, 9].
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approximation is normally used to describe electronic structure and excited electron dynamics in paramagnetic systems while the GW+T method represents a generalization of the GW approximation by including the higher-order self-energy terms that allow for the calculation of the quasiparticle decay in ferromagnetic systems on the same footing as in paramagnets.

In the following subsections we discuss mostly the GW approximation. A very brief description of the GW + T method we give in subsection 1.2.1.2.

1.2.1.1 GW Method

In this subsection we consider paramagnetic systems only and thus omit spin index. The imaginary part of the self energy is evaluated in the GW approximation, in terms of the screened interaction and the allowed final states for the decay process:

\[ \text{Im} \Sigma(\vec{r}, \vec{r}', \epsilon_i > E_F) = \sum_f \phi_f^*(\vec{r}) \text{Im} W(\vec{r}, \vec{r}'; \omega) \phi_f(\vec{r}). \]  

(1.4)

Here \( \omega = \epsilon_i - \epsilon_f \) and the prime in the summation indicates that the final-state energies lie between the initial state and the Fermi level. For the holes these energies are below the Fermi level.

The final expression for the inverse lifetime then becomes

\[ \Gamma_{e-e} = 2 \sum_f \int d\vec{r} \int d\vec{r}' \phi_f^*(\vec{r}) \phi_f^*(\vec{r}') \text{Im} [-W(\vec{r}, \vec{r}'; \omega)] \phi_i(\vec{r}) \phi_f(\vec{r}). \]  

(1.5)

The screened interaction \( W \) is given by

\[ W(\vec{r}, \vec{r}'; \omega) = v(\vec{r} - \vec{r}') + \int d\vec{r}_1 \int d\vec{r}_2 [v(\vec{r} - \vec{r}_1) + K_{xc}(\vec{r}, \vec{r}_1)] \chi(\vec{r}_1, \vec{r}_2; \omega)v(\vec{r}_2 - \vec{r}'), \]

or in short notation

\[ W = v + (v + K_{xc})\chi v. \]  

(1.7)

Here \( v \) is the bare Coulomb interaction and \( \chi \) the linear density-density response function, which is given by the following integral equation

\[ \chi = \chi_0 + \chi_0^0(v + K_{xc})\chi. \]  

(1.8)

\( \chi_0 \) is the density-density response function of the non-interacting electron system:

\[ \chi_0^0(\vec{r}, \vec{r}'; \omega) = 2 \sum_{i,j} \frac{\theta(E_F - \epsilon_i) - \theta(E_F - \epsilon_j)}{\epsilon_i - \epsilon_j + (\omega + i\eta)} \phi_i(\vec{r})\phi_j^*(\vec{r})\phi_j(\vec{r}'). \]  

(1.9)

In this equation \( \eta \) is an infinitesimally small positive constant. The kernel \( K_{xc} \) entering Eqs. (1.7) and (1.8) accounts for the reduction of the electron-electron interaction due to the existence of short-range exchange and correlation effects associated with the probe electron
(Eq. (1.7)) and with screening electrons (Eq. (1.8)). Most calculations that have been performed to date of the lifetimes of electrons and holes for surface and image-potential states use the so-called Random Phase Approximation (RPA). In this approximation the exchange and correlation kernel $K^{xc}$ is omitted from both Eqs. (1.7) and (1.8). Inclusion of exchange and correlation effects in the screened interaction (Eq. (1.7)) and in the screening (Eq. (1.8)) act in opposite directions as the evaluation of the lifetimes is concerned [5].

1.2.1.2 GW + T Method

In the GW+T extension of the GW method the central quantity is the T-matrix operator which is defined as a solution of the Bethe-Salpeter (BS) equation [34]

\[
T_{\sigma_1,\sigma_2}(1, 2 | 1', 2') = W(1, 2) \delta(1 - 3) \delta(2 - 4) + W(1, 2) \int d1'd2' K_{\sigma_1,\sigma_2}(1, 2 | 1', 2') T_{\sigma_1,\sigma_2}(1', 2' | 3, 4) \tag{1.10}
\]

Here we use short-hand notation $1 \equiv (\vec{r}_1, t_1)$ etc.. $W$ is a screened potential and the kernel $K_{\sigma_1,\sigma_2}$ is a two-particle propagator. In the case of multiple electron-hole scattering the kernel (electron-hole propagator) is a product of electron and hole time-ordered Green functions

\[
K^{e-h}_{\sigma_1,\sigma_2}(1, 2 | 1', 2') = iG\sigma_1(1, 1')G\sigma_2(2', 2) \tag{1.11}
\]

For electron-electron scattering it is a product of two electron Green functions

\[
K^{e-e}_{\sigma_1,\sigma_2}(1, 2 | 1', 2') = iG\sigma_1(1', 1)G\sigma_2(2', 2), \tag{1.12}
\]

and for hole-hole scattering it is a product of two-hole Green functions

\[
K^{h-h}_{\sigma_1,\sigma_2}(1, 2 | 1', 2') = iG\sigma_1(1, 1')G\sigma_2(2, 2'). \tag{1.13}
\]

Diagrams used for the GW and T-matrix self-energy are shown in Fig. 1.3. With these diagrams and kernel of Eq. (1.11) the self-energy term describing multiple electron-hole scattering can be expressed as

\[
\Sigma^{e-h}_{\sigma_2}(4, 2) = -i \sum_{\sigma_1} \int d1d3G\sigma_1(3, 1)T_{\sigma_2,\sigma_1}(1, 2|3, 4) \tag{1.14}
\]

Similar equations can be obtained for multiple $e - e$ and $h - h$ scattering [8]. In general, the screened potential $W$ is energy dependent. However, to make computations feasible the local and static approximation, $W(1, 2) = W(\vec{r}_1, \vec{r}_2) \delta(\vec{r}_1 - \vec{r}_2) \delta(t_1 - t_2)$, is frequently used. Most calculations for excited electrons lifetimes have been done within this approximation. For details, we refer the reader to Refs. [6, 8].

1.2.1.3 Screened interaction

The Fourier transforms of the screened interaction are very useful entities to understand the physics of electron (hole) dynamics at surfaces. The screened interaction given by Eq. (1.7)
Figure 1.3: Feynman diagrams for GW and T-matrix self-energy of an excited electron. A: GW-term; B: T-matrix direct terms with multiple electron-electron scattering; C: T-matrix direct terms with electron-hole scattering; D: T-matrix exchange terms. The vertical wiggly lines represent static screened potential, and the lines with arrows are Green functions. The time direction is right. By changing time direction, one obtains analogous diagrams for the self-energy of an excited hole. From Ref. [1]

can be written for the homogeneous electron gas using the Fourier transform parallel to the surface:

\[ W(r, r', \omega) = \frac{1}{(2\pi)^2} \int W(z, z', q_{\parallel}, \omega) e^{iq_{\parallel}(r-r')} dq_{\parallel}, \]  

(1.15)

where

\[ W(z, z', q_{\parallel}, \omega) = \frac{1}{(2\pi)} \int W(q, \omega) e^{iq_{z}(z-z')} dq_{z}. \]  

(1.16)

Here \( q^2 = q_{\parallel}^2 + q_{z}^2 \). In reciprocal space the screened interaction, Eq. (1.7), can be presented by using RPA in terms of dielectric function \( \epsilon(q, \omega) = \epsilon_1(q, \omega) + i\epsilon_2(q, \omega) \) as

\[ W(q, \omega) = \epsilon^{-1}(q, \omega)v(q) \]  

(1.17)

In the static limit and for the case of a Thomas-Fermi dielectric function [35], \( \epsilon(q) = 1 + q_{TF}^2/q^2 \), we find

\[ W(z, z', q_{\parallel}) = \frac{2\pi}{\sqrt{q_{\parallel}^2 + q_{TF}^2}} e^{-\sqrt{q_{\parallel}^2 + q_{TF}^2}|z-z'|}, \]  

(1.18)
1.2 Theoretical description

The theoretical description of the imaginary part of the screened interaction for a homogeneous electron gas is as follows. The reduced momentum $q' = q∥/qTF$ is a universal function independent of energy $\omega$ and density parameter $r_s$. The expression for the imaginary part of the screened interaction is given by

$$\text{Im} \left[ -W(z,z',q∥,\omega) \right] = \frac{1}{2\pi} \int \frac{4\pi}{(q^2_z + q^2)} e^{i\mathbf{q}z} e^{i\mathbf{q}z'} dq_z. \quad (1.20)$$

A simpler approximation appropriate for the case of low excitation energies, can be obtained from the low-$\omega$ expansion of the imaginary part of the bulk RPA response function [36].

The case $z = z'$ can be of guidance as the bulk limit of more complicated surface calculations. The diagonal part of the imaginary part of the screened interaction is then given by

$$\text{Im} \left[ -W(z = z',q∥,\omega) \right] = 8\omega \int_0^\infty \frac{dq_z}{\sqrt{q^2 + q^2 (q^2_z + q^2 + q^2_{TF})^2}}. \quad (1.21)$$

As a function of the variable $q' = q∥/qTF$, $\text{Im}W$ given by Eq. (1.21) scales as $r_s^2$. In the bulk the maximum of $\text{Im} \left[ -W(z,z',q∥,\omega) \right]$ occurs at $z = z'$ and is independent of the actual value of $z$. The linear dependence on $\omega$ holds for almost the whole range of energy transfers that are relevant to the dynamics of surface states.
The left part of Fig. 1.4 presents the diagonal part of the scaled imaginary part of the screened interaction as a function of the reduced momentum $q_{||}/q_{TF}$. When scaled by the energy $\omega$ and the square of the density parameter $r_s^2$ the diagonal part of the imaginary part of the screened interaction is a universal function of the reduced variable $q_{||}/q_{TF}$.

Figure 1.4 shows at the right the diagonal part of the screened interaction for Cu(111) calculated using the one-electron model potential described above. The result of neglecting the surface state in the calculation of the response function is also shown, together with what would be obtained describing the system with a jellium model of density equivalent to that of the 4s valence of Cu ($r_s = 2.67$). The surface state makes a strong contribution to $\text{Im} [-W]/\omega$ at the surface. This contribution increases with $\omega$ and decreases with $q_{||}$ [37]. The enhancement of $\text{Im} [-W]/\omega$ at the surface depends on the extent of the wave function into the vacuum and is increased for lower work function [37, 38] or metal overlayers [39].

1.2.1.4 Electron self-energy

The imaginary part of the self-energy involves a sum over final states of the screened interaction weighted by the final-states wave functions (Eq. (1.4)). Figure 1.5 shows the results of calculations of the imaginary part of the self-energy $\text{Im} [-\Sigma(z, z'; k_{||} = 0, E_n)]$ for the $n = 0$ surface-state hole and the $n = 1$ image-potential state at the (111) surface of Cu. The imaginary part of the self-energy is represented in these figures as a function of $z$ and for a fixed value of $z'$. In the bottom panels, $z'$ is fixed at a few atomic layers within the bulk,
showing that \( \text{Im}(-\Sigma) \) has a maximum at \( z = z' \), as in the case of a homogenous electron gas. When \( z' \) is fixed at the crystal edge (\( z' \sim 0 \)), as shown in the middle panels of Fig. 1.5, we find that \( \text{Im}(-\Sigma) \) is still maximum at \( z = z' \), but the magnitude of this maximum is now enhanced with respect to the bulk value. The top panels of Fig. 1.5 correspond to \( z' \) being fixed far from the surface into the vacuum. In this case, the maximum magnitude of \( \text{Im}(-\Sigma) \) occurs at \( z' \sim 0 \) rather than for \( z = z' \), as occurs in the case of the imaginary part of the screened interaction. As the phase space available for real transitions from the \( n = 1 \) image-potential state is larger than that from the excited hole at the edge of the \( n = 0 \) surface state \([E_1 - E_F > E_F - E_0]\), the imaginary part of the self-energy of the \( n = 1 \) image-potential state is larger than in the case of the \( n = 0 \) surface-state hole. Dotted lines in Fig. 1.5 represent the contribution to the imaginary part of the \( n = 0 \) surface-state hole self-energy from transitions to the \( n = 0 \) surface state itself, the so-called intraband transitions. One sees that at the vacuum side of the surface, intraband transitions dominate, while within the bulk they represent a minor contribution.

### 1.2.1.5 Decay rates

**Homogeneous electron gas** For energies very close to the Fermi level and in the high density limit, substitution of the RPA response function of the homogenous electron gas [36] gives the well known Quinn and Ferrell [41] formula for the excited electron lifetime in a 3-dimensional (3D) system:

\[
\Gamma_{3D} = 2.5 r_s^{5/2} (E - E_F)^2
\]

(1.22)

Here \( r_s \) is given in units of the Bohr radii (a. u.). The energy difference from the Fermi energy is given in eV and the inverse lifetime (lifetime broadening) is obtained in meV.

For a 2D electron gas the lifetime broadening is given by [42, 43]

\[
\Gamma_{2D} = -\frac{(E - E_F)^2}{4\pi E_F} \left[ \ln\left( \frac{E - E_F}{E_F} \right) - \ln\left( \frac{2q_{TF}^2}{k_F} \right) - 0.5 \right].
\]

(1.23)

In the last equation the Thomas-Fermi screening vector for 2D space is \( q_{TF}^{2D} = 2 \). The lifetime \( \tau \) can be easily evaluated from \( \Gamma \tau = 658 \) meV fs.

**Surface states** The evaluation of the decay rate involves a double integral of the self energy bracketed with the initial-state wave functions (see Eq. 1.2). For an efficient evaluation a free-electron approximation parallel to the surface simplifies the calculations considerably. Different effective masses may be used for bulk and surface states. The results of such calculations for the occupied Shockley surface state on noble-metal (111) surfaces is shown in Table 1.2.

Separate contributions from intraband (within the surface state itself) and interband (between bulk states and the surface state) transitions to the decay of Shockley surface-state holes at the \( \Gamma \) point of the projected bulk band gap of the (111) surfaces of Cu, Ag and Au are displayed in Table 1.2. We also show the decay rate evaluated within a 3D electron gas model (EGM) for a hole with energy at the bottom of the surface state band. The comparison of the calculated decay rates shows that the EGM gives decay rates values which are significantly
Table 1.2: Decay rates in meV of the Shockley surface-state hole at the $\Gamma$ point of the noble-metal (111) surfaces. The decay rate $\Gamma_{e-e}$ is decomposed into interband ($\Gamma_{\text{inter}}$) and intraband ($\Gamma_{\text{intra}}$) contributions. Decay rates in a 3D electron gas model ($\Gamma_{\text{EGM}}$, see Eq. (1.22)) of holes with the energy of the Shockley surface-state at $\Gamma$ are also displayed. From Ref. [37].

<table>
<thead>
<tr>
<th>Surface</th>
<th>Energy(eV)</th>
<th>$\Gamma_{\text{EGM}}$</th>
<th>$\Gamma_{\text{inter}}$</th>
<th>$\Gamma_{\text{intra}}$</th>
<th>$\Gamma_{e-e}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(111)</td>
<td>-0.445</td>
<td>5.9</td>
<td>6</td>
<td>19</td>
<td>25</td>
</tr>
<tr>
<td>Ag(111)</td>
<td>-0.067</td>
<td>0.18</td>
<td>0.3</td>
<td>2.7</td>
<td>3</td>
</tr>
<tr>
<td>Au(111)</td>
<td>-0.505</td>
<td>10</td>
<td>8</td>
<td>21</td>
<td>29</td>
</tr>
</tbody>
</table>

smaller than those obtained using the model potential. The EGM takes into account only 3D transitions and neglects both band structure and surface effects. The results of the calculations displayed in Table 1.2 show that these effects are crucial for the hole lifetimes in surface states. In particular, intraband transitions within the surface state band itself (2D → 2D transitions) contribute $\sim 80\%$ of the total electron-electron decay rate. These transitions are more efficient in filling the hole than those arising from bulk states 3D → 2D (interband) transitions because of the greater overlap of the initial- and final-state wave functions which exists in the region where the imaginary part of the screened interaction is larger than in the bulk (see Fig. 1.4 right).

Differences between the full interband calculations using the model potential and those obtained from the electron gas model arise from (i) the enhancement of $\text{Im}[-W]$ at the surface, which increases the decay rate, (ii) localization of the surface-state wave function in the direction perpendicular to the surface and (iii) the restriction that only bulk states with energy lying outside the projected band gap are allowed. Both localization of the surface-state wave function and the presence of the band gap reduce the decay rate, and therefore they tend to compensate the enhancement of $\text{Im}[-W]$ at the surface. In the case of Cu(111) this compensation is almost complete, thereby yielding an interband decay rate that nearly coincides with the 3D decay of free holes. However, as can be seen from Table 1.2, this is not necessarily the case for other materials such as Ag or Au and depends in particular on the surface band structure. In the case of the hole at the $\Gamma$ point at Be(0001) the model potential interband value is 40 meV while the 3D electron gas result is 90 meV [44].

Bulk states Calculations of $\Gamma_{e-e}$ for bulk metals have been done by using various ab initio methods for simple [46, 47, 48, 49, 50], noble [46, 47, 48, 51], and transition [6, 45, 49, 52, 53, 54] metals. These calculations showed that, in general, the excited electron decay rate $\Gamma_{e-e}$ (lifetime $\tau_{e-e}$) is strongly anisotropic, i. e. strongly momentum dependent [52, 53]. Only in few simple and noble metals it is practically momentum independent in an energy interval 0–5 eV [46, 48, 51]. At the same time, momentum average lifetime $\tau_{e-e}$ shows a smooth behavior as a function of energy. As an example we show in Fig. 1.6 experimental data and theoretical results for $\tau_{e-e}$ in bulk Mo [45]. The measurements have been done by using thin polycrystalline films. One can see that for energies 1–3 eV a good agreement is observed between the experiment and calculations if the T-matrix contribution to the self-energy is included. This contribution also leads to better agreement for other metals [45, 54]. However,
the T-matrix effects are qualitatively important for the description of a spin-dependent lifetime in ferromagnetic metals [6]. The inclusion of the T-matrix in the calculation results in a strong spin-dependent $\Gamma_{e-e}$ and good agreement with the measured data for spin-minority bulk states in Fe and Ni [6].

### 1.2.2 Electron-phonon interaction

The phonon-induced linewidth broadening $\Gamma_{e-\text{ph}}$ of surface states of energy $E$ and momentum parallel $\vec{k}_{\parallel i}$ that takes into account both the phonon absorption and emission processes can be written as [55]

$$\Gamma_{e-\text{ph}}(E, \vec{k}_{\parallel i}) = 2\pi \int_0^{\omega_m} \alpha^2 F_{\vec{k}_{\parallel i}}(\omega) [1 + 2n(\omega) + f(E + \omega) - f(E - \omega)] d\omega; \quad (1.24)$$

where $f$ and $n$ are the electron and phonon distribution functions, respectively, and $\omega_m$ is the maximum phonon frequency. The Eliashberg function $\alpha^2 F(\omega)$ which is the phonon density of states weighted by the electron-phonon-coupling function $g$, can be written in a quasielastic approximation as

$$\alpha^2 F_{\vec{k}_{\parallel i}}(\omega) = \sum_{\nu, \vec{q}_{\parallel f}} \left| g_{\nu,\vec{q}_{\parallel f}}^{i,\vec{k}_{\parallel i}} \right|^2 \delta(\omega - \omega_{\nu}(\vec{q}_{\parallel})) \delta(\epsilon_f - \epsilon_{\vec{k}_{\parallel i}}), \quad (1.25)$$

where $\omega_{\nu}(\vec{q}_{\parallel})$ is the phonon frequency, $\nu$ is the phonon index and the last $\delta$ function indicates that we consider the quasielastic approximation [13], neglecting the change of the energy of the scattered electron due to absorption or emission of a phonon. The electron-phonon coupling function includes the matrix element between the initial ($i$) and final ($f$) electron band states. For a translationally invariant system the matrix element involves a $z$-integration...

**Figure 1.6:** Calculated (solid and dashed lines) and experimental momentum-averaged excited electron lifetimes $\tau$ in Mo [45]. Open circles are lifetimes obtained from a polycrystalline Mo film, filled circles are lifetimes measured on a polycrystalline Mo sheet. Inset, scaled momentum-averaged electron lifetimes, $\tau(E - E_F)^2$. 

only
\[ g_{i,j}^{\nu}(\mathbf{q}_\parallel) = \frac{1}{\sqrt{2MN \omega_{\nu}(\mathbf{q}_\parallel)}} \langle f| \sum_{\mu} \tilde{\epsilon}_{\mathbf{q}_\parallel \nu}(\mathbf{R}_\mu) \cdot \nabla_{\mathbf{R}_\mu} \tilde{\mathbf{V}}_{\mathbf{q}_\parallel}^{\mu} | i \rangle. \]  

(1.26)

In this expression \( i \) and \( f \) refer to the \( z \)-dependent wave functions \( \phi(z) \). The static screening of the electron-ion potential is used and thus one neglects the frequency dependence of the coupling function \( g_{i,j}^{\nu}(\mathbf{q}_\parallel) \). The coupling function in Eq. (1.26) is the result of the standard first-order expansion of the screened electron-ion potential \( \tilde{\mathbf{V}}_{\mathbf{q}_\parallel}^{\mu} \) with respect to the vibrational coordinate \( \mathbf{R}_\mu \). \( N \) is the number of ions in each atomic layer, \( M \) is the ion mass, \( \mu \) is the layer index and \( \tilde{\epsilon}_{\mathbf{q}_\parallel \nu}(\mathbf{R}_\mu) \) are the phonon polarization vectors. From Eq. (1.24) we easily obtain the \( T = 0 \) result \((n(\epsilon) = 0)\) for \( \Gamma_{e-ph} \)

\[ \Gamma_{e-ph}(E, \mathbf{k}_\parallel i) = 2\pi \int_0^{|E|} \alpha^2 F_{\mathbf{k}_\parallel i}(\omega) d\omega. \]  

(1.27)

For binding energies \(|E| > \omega_m\) the upper limit for the integration should be the maximum phonon frequency \( \omega_m \).

From the knowledge of the Eliashberg function [11, 12], the electron-phonon coupling parameter \( \lambda \) can be calculated as the first reciprocal moment of \( \alpha^2 F \)

\[ \lambda(\mathbf{k}_\parallel i) = 2 \int_{0}^{\omega_m} \frac{\alpha^2 F_{\mathbf{k}_\parallel i}(\omega)}{\omega} d\omega. \]  

(1.28)

If the high temperature limit (\( k_BT \gg \omega_m \), here \( k_B \) is the Boltzmann constant) of Eq. (1.24) is considered, Grimvall [13] has pointed out a very useful result which enables an experimental determination of the mass enhancement parameter

\[ \Gamma_{e-ph}(E, \mathbf{k}_\parallel i) = 2\pi \lambda(\mathbf{k}_\parallel i) k_B T. \]  

(1.29)

The above equations show that the Eliashberg function \( \alpha^2 F \) is a basic function to calculate. Given this function most of the interesting quantities can be calculated, such as the temperature and also binding energy dependence of the linewidth broadening and the electron-phonon coupling parameter. However, this is not a simple task, as all the physics connected to the electron-phonon interaction is buried in \( \alpha^2 F \), the phonon dispersion relation, phonon polarization vectors, one-electron wave functions and the gradient of the screened electron-ion potential – the deformation potential. All these quantities, and finally \( \alpha^2 F \) for bulk metal electron states, can be obtained from first-principles calculations [56, 57], whereas for electron states on metal surfaces these evaluations are very time consuming [58]. Some approximations are needed to make these computations feasible for surfaces.

In particular, the phonon dispersion relations and polarization vectors can be calculated with reasonable accuracy using force constant models [59] or the embedded atom method [60, 61, 62]. In recent calculations of \( \Gamma_{e-ph} \) and \( \lambda \) for surface states, wave functions obtained from the one-electron model potential [63, 64] have been used. For the description of the deformation potential the screened electron-ion potential as determined by the static dielectric function and the bare pseudopotential is used, \( \tilde{\mathbf{V}}_{\mathbf{q}_\parallel}^{\mu}(z) = \int dz' \tilde{\mathbf{e}}^{-1}(z, z'; \mathbf{q}_\parallel) \tilde{\mathbf{V}}_{\mathbf{q}_\parallel}^{\mu}(z', \mathbf{q}_\parallel), \)
Table 1.3: Eliashberg function and phonon contribution to decay for Einstein and Debye models.

<table>
<thead>
<tr>
<th></th>
<th>$\alpha^2 F(\omega)$</th>
<th>$\Gamma_{e-ph}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Einstein (Ref. [13])</td>
<td>$\frac{1}{2} \lambda \omega_E \delta(\omega - \omega_E)$</td>
<td>$\pi \lambda \omega_E$ for $E &gt; \omega_E$; $0$ for $E &lt; \omega_E$</td>
</tr>
<tr>
<td>Debye 3D (Ref. [13])</td>
<td>$\lambda \omega^2 / \omega_D^2$ for $\omega &lt; \omega_D$; $2\pi \lambda \omega_D / 3$ for $E &gt; \omega_D$</td>
<td>$2\pi \lambda \omega_D / 3 / 3$ for $E &lt; \omega_D$</td>
</tr>
<tr>
<td>Debye 2D (Ref. [66])</td>
<td>$(\lambda / \pi) \omega / (\omega_D^2 - \omega^2)^{1/2}$ for $\omega &lt; \omega_D$; $2\lambda \omega_D$ for $E &gt; \omega_D$</td>
<td>$2\lambda \omega_D (1 - \sqrt{1 - (\frac{E}{\omega_D})^2})$ for $E &lt; \omega_D$</td>
</tr>
</tbody>
</table>

Figure 1.7: (a) The phonon-dispersion from a 31 layer slab calculation in the $\Gamma M$ direction of the Surface Brillouin Zone. (b) The Eliashberg function of the hole state in the $\Gamma$ point for Cu (111) (solid line) and the contribution from the Rayleigh mode to the Eliashberg function (dashed line). From Ref. [67].

where $q_\parallel$ is the modulus of the phonon momentum wave vector parallel to the surface and $\tilde{V}^\mu_{bare}$ the 2D-Fourier transform parallel to the surface of the bare electron-ion pseudopotential [65].

A drastic simplification is obtained by taking $g_{i,f}(q_\parallel)$ to be constant. In this case the Eliashberg function is proportional to the product of the phonon and electron densities of states. Assuming a free-electron-gas model for the one-electron states one can obtain simple analytical expressions for the Eliashberg function and for the phonon contribution to the linewidth broadening $\Gamma_{e-ph}$ within the Debye and Einstein models (see chapter ...) for vibrational spectra in terms of the energy-dependent electron-phonon coupling parameter and the characteristic Debye (Einstein) energy $\omega_D$ ($\omega_E$). They are listed in Table 1.3.
Figure 1.8: Adsorbate-induced scattering of the Cu(100) image-potential state electrons. The figure shows the energy of the image-potential states (dashed lines) as a function of the electron momentum parallel to the surface, $k_\parallel$. The shaded area represents the 3D bulk states. The intraband and interband scattering processes, that lead to dephasing and population decay of the image-potential states and that are allowed by energy conservation, are indicated schematically by horizontal arrows. Gray arrows indicate the intraband scattering and black arrows indicate the interband scattering. From Ref. [1]

A proper theoretical analysis of the electron-phonon contribution to the linewidth broadening of surface electron states requires to take into account all electron and phonon states involved in the electron-phonon scattering process. The theoretical analysis of Figuero et al. [67, 68], based on a calculation of the full Eliashberg spectral function, is a step forward in this direction. In this approach the contributions from different phonon modes, in particular the Rayleigh surface mode as well as bulk phonons and the general temperature dependence are taken into account. They also obtain the high temperature behavior represented by $\lambda$. Their approach is based on (i) Thomas-Fermi screened Ashcroft electron-ion potentials, (ii) one-electron states obtained from the model potential (iii) a simple force constant phonon model calculation that gives results for the phonon spectrum in good agreement with recently published experimental data [69, 70, 71, 72].

In Fig. 1.7 the calculated phonon dispersion and the Eliashberg function at the $\Gamma$ point calculated by Figuero et al. [67, 68] is presented for the Cu(111) surface. The Rayleigh surface mode is split off from the bulk phonon band, which gives a lower energy peak in the Eliashberg function of the hole state at the $\Gamma$ point of about $\sim 13$ meV in Cu(111). The oscillations in the Eliashberg function reflect the finite number of layers of the model potential calculation (31 layers) of electron wave functions and thus have no physical significance [67].

The use of the 3D and 2D Debye models in the evaluations of $\Gamma_{e-ph}$ for holes in surface states on the (111) surface of noble metals [69] and Al(100) normally leads to a fairly good agreement with the results of more sophisticated calculations [55, 67, 68].
1.2.3 Electron-defect interaction

The presence of defects (adatoms, vacancies, steps, . . . ) on surfaces results in the loss of 2D-translational symmetry and, in turn, to additional broadening of the image-potential and surface states. Adatoms, in particular, can be very efficient in perturbing the dynamics of excited electrons at surfaces. A single adatom on a surface acts as a scatterer for the excited electrons traveling on the surface in e. g. image-potential or surface states thus perturbing their dynamics. The adatom can also support transient excited states localized at this adatom. When an excited electron moves in an image-potential state two different scattering processes are possible, as shown in Fig. 1.8. In one process, the electron is scattered from an image-potential state into a substrate bulk state or into another state of the image-potential state continuum. This interband scattering process results in a decrease of the excited state population, i. e. to population decay. In another energy-conserving process, the electron remains in the same electronic band: it changes only its momentum. This intraband scattering process leads to the decay of the coherence of the electron, without population decay (process also called ‘pure dephasing’). In the optical Bloch equations formalism which is very often used to analyze the coherence dynamics of a system, these two processes correspond to the population lifetime $T_1$ and to the pure dephasing time $T_2^*$.

For a low density of adsorbates randomly distributed on the surface one can assume that the different scattering centers are independent and incoherent. In this case the corresponding population decay rate $\Gamma_{\text{Decay}}$ and ‘pure dephasing’ rate $\Gamma_{\text{Deph}}$ can be presented as [15, 16, 17]

$$\begin{align*}
\Gamma_{\text{Decay}} &= k_n \sigma_{\text{inter}}, \\
\Gamma_{\text{Deph}} &= k_n \sigma_{\text{intra}},
\end{align*}$$

(1.30)

where $\sigma_{\text{inter}}$ and $\sigma_{\text{intra}}$ are the scattering cross sections for interband and intraband scattering, respectively. $n_0$ is the adsorbate surface density and $k_n$ is the electron traveling momentum in the initial state. Both population decay and ‘pure dephasing’ contribute to the broadening of the level, and the total broadening rate of the excited state is given by:

$$\Gamma_{\text{total}} = k_n n_0 (\sigma_{\text{inter}} + \sigma_{\text{intra}}) = k_n n_0 \sigma_{\text{total}}$$

(1.31)

where $\sigma_{\text{total}}$ is the total scattering cross section, sum of the interband and intraband scattering cross sections.

As an example of scattering by adsorbates of an electron in image-potential states, Fig. 1.9 shows the adsorbate-induced decay rate of the $n = 1$ and $n = 2$ image-potential states on a Cu(100) surface with Cs adsorbates [15]. The decay rate is given for a Cs coverage of the surface equal to one Cs adsorbate per 1000 Cu surface atoms.

One can see that the adsorbate-induced decay rate exhibits a few ((1)-(5)) sharp structures. The structure (1) is associated to the opening of the $n = 2$ image-potential state continuum as a decay channel for scattering of an $n = 1$ electron. Structures labeled (2) and (5) are associated to the thresholds of the $n = 3$ and $n = 4$ states. Other structures, like structures (3) and (4), located slightly below the image-potential state continua thresholds are due to adsorbate-induced resonances, associated to the localization of the image-potential state continua [15]. The decay induced by Cs adsorbates on Cu(100) is quite efficient: for energies close to $\Gamma$, the $n = 2$ decay rate induced by Cs adsorbates amounts to 1.5 meV for a 0.001 ML coverage. This is comparable to the decay rate of the $n = 2$ image-potential state on Cu(100) which
Figure 1.9: (a) Total and partial decay rates (in meV) of the $n=1$ image-potential state on a Cu(100) surface induced by electron scattering from Cs adsorbates. The theoretical results [15] are presented as functions of the electron total energy measured with respect to the vacuum level. The abscissa-axis starts at the bottom of the $n=1$ image-potential state continuum (-0.573 eV). The Cs adsorbate coverage corresponds to 1 Cs adsorbate per 1000 Cu surface atoms. Assignment of the structures is explained in the text. Solid line: total decay rate; dashed line: partial decay rate corresponding to the interband transition into the $n=2$ image-potential state continuum. (b) The same as above for the $n=2$ image-potential state. The abscissa-axis starts at the bottom of the $n=2$ image-potential state continuum (-0.177 eV). Solid line: total decay rate; dashed line: partial decay rate corresponding to the interband transition into the $n=1$ image-potential state continuum. From Ref. [15].

is in the 4–5 meV range [73, 74]. Thus, for Cs coverages in the few $10^{-3}$ ML range, the lifetime of the $n=2$ image-potential state is dominated by adsorbate scattering. So, even trace concentrations of alkali adsorbates are able to significantly affect the dynamics of the image-potential states at surfaces.

1.3 Time-resolved measurements

The most detailed and direct information on the electron dynamics at surfaces stems from time-resolved two-photon photoemission experiments. The method is explained in Section . . . and this section presents important examples for the electron dynamics at surfaces.

1.3.1 Shockley surface states

The Shockley surface states commonly found on many fcc(111) surfaces are occupied for $k_{||}=0$ (see also chapter . . . ). The study of electron dynamics by time-resolved two-photon photoemission, however, is restricted to unoccupied states, because the laser intensities required to induce a detectable change in the population of occupied states are close to the damage threshold of the sample. The Pd(111) surface is one notable exception where the Shockley surface state is found 1.35 eV above the Fermi energy $E_F$ [75]. With time-resolved two-photon photoemission the lifetime of this state was measured to 13 fs as shown in Fig. 4 of Section . . . .
1.3 Time-resolved measurements

The attractive image potential experienced by an electron in front of a metal surface leads to a special class of surface states (see chapter ...). These image-potential states [76] exist on many metal surfaces. The binding energies relative to the vacuum level are $E_B(n) \leq 0.85/n^2 \text{ eV}$. The low values indicate a weak coupling to the surface. Correspondingly image-potential states can have relatively long lifetimes (> 10 fs) and can serve as almost ideal spectator states to monitor subtle changes of the surface [28, 77].

Time-resolved two-photon photoemission measurements for the lowest image-potential states on the Cu(001) surface are shown in Fig. 1.10. Due the logarithmic ordinate axis the exponential decay of the population appears as a linear decrease at large pump-probe delays. The lifetimes for the $n = 1$ and $n = 2$ states are $\tau_1 = 40$ and $\tau_2 = 150$ fs, respectively. Note that the curves cross at large delay times indicating that the $n = 2$ population exceeds eventually the $n = 1$ population. The trace for the $n = 3$ state shows regular oscillations on top of a linear slope corresponding to a lifetime $\tau_3 = 400$ fs. These quantum beats arise from a coherent excitation of the $n = 3$ and $n = 4$ image-potential states by the short laser pulse with a spectral band width comparable to the energy separation of the states [78]. From the oscillation period of $T = 117$ fs the energy difference can be determined very accurately to $|E_B(3) - E_B(4)| = h/T = 35 \text{ meV}$ (see Eq. 3 of Section ...).

The lifetimes $\tau_n$ shown in Fig. 1.10 depend strongly on the quantum number $n$ and consequently binding energy $E_B$. Data for the decay rates $\Gamma_n = h/\tau_n$ are plotted in Fig. 1.11 as a function of binding energy $E_B$ for several copper surfaces. For $n \geq 2$ an $E_B^{-3/2}$ dependence indicated by the dashed lines is observed. It corresponds to the classical expectation of the round trip oscillation of the electron in the potential well formed by the image potential and the solid represented by a hard wall [79]. This picture assumes that decay processes occur predominantly when the electron hits the surface. Since the binding energy $E_B$ is proportional to $n^{-2}$, it follows for the lifetimes $\tau_n \propto n^3$. The same result is obtained when the probability
to find the electron in the bulk is evaluated from the wave function of the image-potential state. The overlap with bulk bands explains also the increase of the decay rate from Cu(001) to Cu(117) in Fig. 1.11. The energies of the image-potential states get closer to the effective band gap and therefore the penetration of the wave function into the bulk becomes larger. The limiting case is reached for Cu(111) where the states $n \geq 2$ are degenerate with bulk bands. The energy of the $n = 1$ state is still in the band gap and has a decay rate smaller than the one of the $n = 2$ state. This state shows a dependence on temperature [80] which is negligible on most surfaces where the image-potential states have only a small overlap with bulk states [81].

The overlap of image-potential states with bulk bands can be reduced by insulating overlayers. In particular for noble gas overlayers the lifetime can be significantly prolonged into the picosecond range [82].

### 1.3.2.1 Momentum dependence of lifetimes

The overlap with bulk states is an important factor determining the lifetimes of surface or image-potential states. For dispersing bands the decay depends also on the parallel momentum. An example is shown in Fig. 1.12 for the $n = 1$ image-potential band on Cu(001) [83] which follows the expected dispersion for a free electron parallel to the surface. The left panel shows that the lifetime decreases with increasing parallel momentum. Two effects contribute to the increase of the decay rate: (i) The energy increases with parallel momentum and the available phase space for inelastic decay increases. (ii) Inelastic scattering processes within the image-potential band become possible for electrons with energies above the band bottom located at $k_\parallel = 0$. These inelastic intraband scattering processes gain importance with energy. Both processes show a linear dependence on energy as shown in the right panel of Fig. 1.12.
1.3 Time-resolved measurements

Figure 1.12: Left: Time-resolved 2PPE signal of the $n=1$ state of Cu(001) for three different values of the parallel momentum $k_{||}$. Interband decay to the bulk and intraband decay within the $n=1$ band are the two basic $k_{||}$-dependent decay processes mediated by bulk electrons as sketched in the inset. Right: Experimental (dots) and theoretical (solid lines) decay rates of the first two image-potential states $n=1, 2$ as a function of excitation energy $E(k_{||})$ above the respective band bottom. Dashed lines show the calculated contribution of interband relaxation. Inset: Measured dispersion of $n=1, 2$ parallel to the surface. Adapted from Ref. [83].

For the $n=1$ band these inelastic scattering processes are calculated to contribute about the same amount to the increase of the decay rate. For the $n=2$ band interband scattering to the $n=1$ band is an important scattering channel and will be discussed in more detail in the following section.

1.3.2.2 Elastic interband scattering

As indicated at the top right of the inset of Fig. 1.12 by a dashed arrow elastic scattering between image-potential states is another important scattering channel. Because the lifetime increases rapidly with quantum number $n$, electrons can still be scattered from the $n=2$ state to the $n=1$ state when the initial population of the $n=1$ band has already decayed (see Fig. 1.10). This leads to a biexponential decay as seen in the time-resolved measurements of Fig. 1.12. The elastic interband scattering involves a negligible change of energy, but a large change of momentum. At the same time the electron moves closer to the surface. The elastic character of the scattering can be proven by the fact that the decay rate of the second (slower) decay measured on the $n=1$ band is identical to the one of the $n=2$ state at the same energy [85] (see also top of right panel in Fig. 1.13). Detailed studies have shown that strong elastic interband scattering is caused mainly by adatoms or steps [84, 85]. The scattering of electrons by these heavy obstacles changes the momentum leaving the energy unchanged. Electron-electron scattering on the other hand involves two particles of equal mass and leads
1.3.2 Elastic intraband scattering

The preceding section showed that elastic interband scattering can be an important process induced by defects or steps. In elastic interband scattering the electron jumps between two
1.3 Time-resolved measurements

bands of different quantum number which have a small overlap. Even more efficient is the elastic intraband scattering, because it involves the spatial overlap between two states with different parallel momenta in the same band. Elastic intraband scattering can not be detected in the usual way by time-resolved two-photon photoemission, because it does not change the population in the band. The scattering however leads to a change of the phase of the wave function which contributes to the spectral linewidth. The details have been discussed in Section .... The importance of the elastic intraband scattering for the $n = 1$ image-potential band has been studied for Cu adatoms on Cu(001) [88, 89]. For higher image-potential states the loss of phase coherence can be directly seen in the disappearance of the quantum beats. An example is shown in Fig. 1.14 where small amounts of CO or Cu destroy the quantum-beat oscillations quite effectively. For Cu this is associated with the observed decrease of the lifetime. For CO the lifetime remains almost unchanged indicating that CO molecules are strong elastic scatterers and induce only little scattering to bulk bands or other inelastic channels [87].

1.3.3 Adsorbate states

So far we have discussed the electron dynamics mainly for image-potential states. Due to their relatively long lifetimes they serve as a model system to study electron scattering processes at surfaces by time-resolved two-photon photoemission. Studies on other systems are relatively scarce, because the overlap of adsorbate or surface states with bulk bands is usually relatively large and the lifetime is below the attainable time resolution. Figure 1.15 shows time-resolved data for the lowest unoccupied molecular orbital (LUMO) of $C_6F_6$ on Cu(111) [90]. The population dynamics is rather complex and involves a slow filling of the state as evident from the delayed onset of the intensity.
Other adsorbate systems with measurable lifetimes are C$_{60}$ on Cu(111) [91] or alkali metals on copper surfaces [92, 93]. For recent reviews see [94, 95]. Resonant Auger spectroscopy is an alternate approach to measure charge-transfer times for adsorbate systems [96].

### 1.3.4 Semiconductor surface states

At metals electron-electron scattering can proceed at arbitrarily small energies, because of the continuum of states at the Fermi level. For semiconductors the band gap energy is the minimum amount of energy needed to excite an electron from the valence to the conduction band. Accordingly the decay of electrons close to the conduction band minimum can proceed only via recombination which is a rather slow process. The same argument applies to electrons at semiconducting surfaces with the associated surface band gap. Several examples have been studied by Haight [98] and the field is expanding [99, 100, 101]. One particularly well-studied surface is the Si(100) c(4 × 2) surface [97, 102, 103, 104]. The dimerization of the dangling bonds leads to occupied and unoccupied surface bands. The unoccupied $D_{down}$ state shows a complex dynamics as shown in the left panel of Fig. 1.16. The state is populated on the time scale of 1.5 ps and shows a biexponential decay with time constants of 5 and 220 ps. The excitation and decay scheme is indicated in the band structure diagram together with calculated bands in the right panel of Fig. 1.16. The infrared laser pulse excites an electron from the occupied $D'_{up}$ band to the unoccupied $D_{down}$ band. Within 1.5 ps the electron relaxes to the band minimum by phonon scattering. The formation of a bound exciton state occurs within 5 ps and this state has a lifetime of almost 100 ns as can be estimated from the top curve in the left panel of Fig. 1.16. The long time constant of 220 ps is attributed to the filling state.
1.4 Energy-resolved measurements

![Figure 1.16](image)

**Figure 1.16:** Left: Time-resolved 2PPE measurements from Si(100) c(4×2) in normal emission recorded with the analyzer tuned to the peak maxima of X (top) and the $D_{down}$-state (bottom). The inset depicts the dynamics of $D_{down}$ population on an enlarged time scale; Right: Measured (symbols) and calculated (solid lines, shaded areas) surface band structure of Si(100) c(4×2) at 90 K. Adapted from Ref. [97].

of the surface band from the bulk conduction band minimum [103].

1.3.5 Lifetimes of hot electrons

At the end of the section on time-resolved measurements we want to mention the work on lifetimes of hot electrons. These data are collected at energies where no specific surface state exists and are, therefore, attributed to the lifetimes of hot electrons in the continuum of bulk states. Because two-photon photoelectron spectroscopy is intrinsically surface sensitive some contribution from the surface is inherent to such data. An example is shown in Fig. 1.17 for Ag(100) films of various thicknesses on a MgO(100) substrate [105]. The left panel of Fig. 1.17 shows two-photon photoemission spectra and the right panel presents the measured lifetimes. The lifetimes decrease approximately with $(E - E_F)^{-2}$ as expected for a free electron gas [41]. Further information about this topic can be found in Refs. [5, 105, 106, 107].
1.4 Energy-resolved measurements

1.4.1 Photoemission lineshape analysis

The complementary method to time-resolved measurements is the spectroscopy in the energy domain. Energy-resolved experiments determine the Fourier transform of the exponential decay in the time domain which yields a Lorentzian for the intrinsic spectral lineshape. As mentioned in Section …, photoemission does not permit to separate inelastic and elastic decay processes, which both contribute to the linewidth. Because the energy resolution of inverse photoemission is usually not sufficient for a lineshape analysis, this section is devoted to photoemission of occupied states providing an additional complementary aspect to the time-resolved measurements of transiently populated unoccupied states by two-photon photoemission. Occupied (initial) states can also be observed by two-photon photoemission spectroscopy. Their linewidth is similar to the values obtained in regular photoemission [108].

In measured data the intrinsic Lorentzian lineshape is broadened by finite resolution of the experiment. In photoemission this comprises the limited energy and angular resolution as well as the spectral linewidth of the photon source. These factors can be accounted for by a convolution of the Lorentzian lineshape with a Gaussian of an appropriate width. The demands on the energy and angular resolution can be fairly high for the strongly dispersing Shockley surface states as illustrated in Fig. 1.18 for the case of Cu(111) [21]. At the bottom left a series of spectra is shown for different emission angles at a constant angular resolution of $\Delta \vartheta = \pm 0.4^\circ$. The bottom right panel illustrates the influence of the angular resolution on the spectra at the band bottom. The influence on the observed linewidth is illustrated in the top panel of Fig. 1.18 in context with the measured dispersion relation. Neglecting the influence of a finite energy resolution it is obvious that for an angular resolution of $\Delta \vartheta = \pm 3^\circ$ the spectra
1.4 Energy-resolved measurements

Figure 1.18: (a) Parabolic dispersion $E_i(k_{\parallel})$ of the Cu(111) surface state around $\Gamma$, the center of the surface Brillouin zone. Vertical solid lines indicate the contribution of different angular resolution $\Delta \theta$ on the observed linewidth of spectra taken at $\theta = 0$ ($k_{\parallel} = 0$). Dotted lines show the increase of broadening with increasing $k_{\parallel}$ due to the dispersion, at constant $\Delta \theta$. (b) Spectra taken at different $\theta$ with fixed $\Delta \theta$. Solid lines are results of a $k$-space integration, with the experimental dispersion from (a) and a fixed $\Delta \theta = \pm 0.4^\circ$. (c) Spectra taken at normal emission with different $\Delta \theta$ as indicated. All data collected at $h\omega = 21.2$ eV. Adapted from Ref. [21].

become asymmetric and the linewidth exceeds 100 meV. A comparable value is obtained for the best value of $\Delta \theta = \pm 0.4^\circ$ at an emission angle $\theta = 3^\circ$.

Using a state-of-the art two-dimensional analyzer with a resolution of 3.5 meV on the energy axis and 0.15° in the angular direction the Shockley surface states for the (111) surfaces on Cu, Ag, and Au have been measured with high accuracy [72]. The agreement between various techniques for the intrinsic linewidth is excellent and is discussed in Section 1.6.1.
Such high-quality results require a careful sample preparation and are very sensitive to sample contamination.

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 $\overline{M}$ Tamm state on Cu(100) is shown in the left panel of Fig. 1.19 [109]. 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.

1.4.1.1 Influence of defects

While striving to reach the best surface quality systematic, quantitative studies of the influence of defects on photoemission spectra have been somewhat neglected. As an example we show the sensitivity of the $\overline{M}$ Tamm state of Cu(100) to the surface quality in the right panel of Fig. 1.19 [71]. The surface quality was varied by argon-ion sputtering and subsequent insufficient annealing and monitored by the width of low-energy electron diffraction spots. The observed linear dependence permits an extrapolation to zero defect density which yields a total linewidth around 30 meV including the experimental resolution. The main difference between the two experiments shown in Fig. 1.19 is the sample temperature. Extrapolating the data of Ref. [71] to low temperature [32] yields an upper limit of $\Gamma \leq 13 \pm 4$ meV in reasonable agreement with the value from Ref. [109].
1.4 Energy-resolved measurements

1.4.1.2 Electron-phonon coupling

The most obvious influence of electron-phonon coupling on photoelectron spectra is the increase of the linewidth with temperature [58]. An example is shown in the inset of the left panel of Fig. 1.20 for the case of a surface state on Be(0001) [110]. When plotted against temperature the linewidth increases linearly for sufficiently high temperatures. From this slope the mass enhancement parameter $\lambda$ can be determined using Eq. (1.29). The electron-phonon coupling in Be is strongly enhanced at the surface [32, 110].

Strong electron-phonon coupling has also consequences on the photoelectron spectra. The lineshape changes and split-off peaks appear [111, 112, 113]. The right panel of Fig. 1.20 shows the spectra of the surface state on Be(0001) near the Fermi energy measured at a sample temperature of 12 K [111]. A sharp peak emerges at $E_F$ and the data show in addition to linearly dispersing peak an additional feature saturating near the maximum phonon energy. The dispersion $E(k_{||})$ is plotted in the inset and agrees well with the calculated quasiparticle dispersion [112].

Figure 1.20: Left: Experimental surface-state linewidth $W$ at $\Gamma$ on Be(0001). The solid line is a fit using the Debye model. The inset shows experimental spectra at $\Gamma$ for various sample temperatures (dots) and the corresponding fits using Lorentzians (solid line) plus a linear background. From Ref. [110]. Right: Photoelectron spectra from Be(0001) close to $E_F$ at 12 K. The inset shows the measured and calculated quasiparticle dispersion. Adapted from Ref. [111].
1.4.2 Scanning tunneling spectroscopy

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 (see chapter ...). 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.

1.4.2.1 Spectroscopy of flat surfaces

The first method simply records the onset of the tunneling into the Shockley surface states. The corresponding spectra are shown in Fig. 1.21 for the (111) surfaces of Ag, Au, and Cu [69]. All spectra were taken at least 200 Å away from impurities and are averages of different single spectra from varying sample locations and tips. In particular the Au(111) spectrum constitutes an average over 17 single spectra taken across various positions across the surface reconstruction (see chapter ...). 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 [114]: $\Delta = \frac{\pi}{2} \Gamma$.

1.4.2.2 Spectroscopy of confined electrons

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. Figure 1.22 presents in the left panel a topographic image of such a confining structure consisting of a ring of 35 Mn atoms on a Ag(111) surface. The right panel shows the spectroscopy results for the Shockley surface state on Ag(111) obtained at the center of the ring [115]. Pronounced peaks are observed which become broader with increasing energy away from the Fermi energy. These peaks correspond to the energy levels...
1.5 Spatially-resolved measurements

The spectroscopy of confined electrons presented in the previous section is closely related to the topic to be discussed now. In the topographic image at the left panel of Fig. 1.22 a circular fine structure is observed inside the ring of Mn atoms. This structure depends strongly on tunneling voltage and correspondingly the spectroscopic results vary with the location inside the ring where the measurements are performed. This leads to the topic of spatially-resolved measurements which are somewhat easier to perform, because data are collected at fixed voltage. In addition no confining structure is needed (see also chapter ...).

1.5.1 Scattering patterns at steps

The most simple structures are steps which are ubiquitous on real surfaces. The left panel of Figure 1.23 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 [116]. The data

![Figure 1.22: (a) Circular array of 35 Mn atoms on Ag(111). Diameter \( \sim 22 \) nm. (b) \( dI/dV \) spectra from the center of the array as measured (top) and calculated (bottom). Adapted from Ref. [115].](image)
can be fitted very well by the following function [118]:

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

(1.32)

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. 1.23 (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 (see also Fig. 1.22). 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 \( m^* \).


1.5.2 Scattering patterns in adatom arrays

The scattering at steps permits an accurate determination of dephasing lengths, but is limited by the necessity to find large enough defect-free terraces in order to exclude interference by scattered waves from other structures. The damping of the oscillations by the finite dephasing length is effective on any length scale and the disturbances by unwanted and unidentified defects can be eliminated by confining the scattering to a well-defined artificial geometry. Figure 1.23 shows in the right panel at the top a topographic image of a triangle constructed by 51 Ag atoms on a Ag(111) surface [117]. The center image shows the \( dI/dV \) data taken in the square marked in the topographic image at a higher tunneling voltage. The calculated image using an optimized parameter set for the dephasing length and scattering properties of the adatom array is presented at the bottom of the right panel of Fig. 1.23.

1.6 Synopsis

The previous sections presented the available methods to obtain information about the electron dynamics at surfaces. This section compares the results obtained by different techniques according to the various scattering processes. More extensive tabulations of results and detailed discussions may be found in recent reviews [1, 32].

1.6.1 Electron-electron interaction

1.6.1.1 Shockley surface states

The Shockley surface states on Cu(111) and Ag(111) are the best studied examples for the electron dynamics at surfaces. They have been measured at low temperatures with photoelectron spectroscopy and scanning tunneling spectroscopy. The experimental results for the bottom of the band at \( k_\parallel = 0 \) are listed in Table 1.4 and compared to calculations. The agreement is perfect and it is worth noting that even at temperatures \(< 30 \text{ K}\) (see also Fig. 1.25) the electron-phonon contribution is significant.

With increasing energy away from the Fermi energy the lifetimes decrease rapidly. Data obtained for the Shockley surface state on Ag(111) by scanning tunneling spectroscopy at steps [118, 119, 120] and in circles formed by Mn atoms [115] are shown in Fig. 1.24. For comparison the results of a full calculation (circles [119]) and the free-electron gas behavior (dashed line) matched to high energy asymptotic are shown. The decrease of the lifetimes for

| Table 1.4: Calculated and measured decay rates \( \Gamma \) at the band minimum, in meV, for the Shockley surface states of Cu(111) and Ag(111). \( \Gamma_{e-e} \) is the calculated lifetime width due to electron-electron scattering [69], \( \Gamma_{e-ph} \) from electron-phonon scattering [68], \( \Gamma_{STM} \) from STM measurements at \( T = 4.6 \text{ K} \) [69], \( \Gamma_{ARUPS} \) from ARUPS measurements [72]. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Cu(111)         | 7.3             | 14.0            | 21              | 24              | 23 ± 1.0        |
| Ag(111)         | 3.7             | 2.0             | 5.7             | 6               | 6 ± 0.5         |
energies above 0.7 eV is attributed to the crossing of the surface band with the bulk band edge and enhanced coupling to bulk states.

### 1.6.1.2 Image-potential states

The image-potential states on (001) surface of copper have been studied by several groups in considerable detail. The inelastic decay rates for the image-potential states on Cu(001) are given in the first two rows of Table 1.5. The agreement between experiment [85, 121] and calculations [73, 83, 122] is almost perfect. This holds for the various scattering rates $\Gamma$ at $k_\parallel = 0$ as well as for the increase with energy denoted by the slope $d\Gamma/dE$.

### 1.6.2 Electron-phonon interaction

The effect of the electron-phonon interaction can be observed most conveniently by an increase of the linewidth with temperature. An example has been presented in Fig. 1.20. For energies close to $E_F$ the contribution to the decay from electron-electron scattering becomes
negligible which opens the opportunity to observe the effects of electron-phonon scattering in more detail. As an example the linewidth broadening for the Shockley surface state on Cu(111) is shown as a function of binding energy in the left panel of Fig. 1.25. The experimental data from high-resolution photoemission experiments are compared to calculations [67]. The decrease towards low binding energies is explained by the decrease of phase space for energy loss to phonons. The calculation reveals the coupling to the Rayleigh phonon modes as a significant decay channel and the negligible contribution by electron-electron scattering.

1.6.3 Electron-defect interaction

The effect of electron-defect scattering has been studied in photoemission by Kevan [71, 123]. For the Shockley surface state an increase of the linewidth with increasing adsorbate coverage was observed. More detailed studies have been done for image-potential states. For Cu and Co adatoms on Cu(001) it was found that adatoms cause mainly elastic scattering within
or between image-potential bands as well as scattering to bulk bands [85, 88, 121, 89]. Figure 1.26 shows that the decay rate of the image-potential states increases linearly with Cu adatom coverage for coverages up to a few percent of a monolayer [122]. The corresponding elastic scattering rates are compared quantitatively in the bottom rows of Table 1.5 with calculations using a wave-packet propagation method [122].

Defects might also be created by thermal excitations through anharmonic effects. In such cases special care has to be taken to separate the contributions from electron-phonon and electron-defect scattering [124].

1.7 Conclusions

This chapter attempted to give an overview on the dynamics of excited electrons at surfaces and the various methods to study it. Most of the techniques are still under active development and the frontiers of their applicability are still under exploration. Considering the tremendous progress in experimental techniques and theoretical methods during the last decade it is to be expected that the field is moving rapidly from exploratory model systems to real life questions in surface physics.
Bibliography

Bibliography

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