3

Electron Dynamics in Image Potential States at Metal Surfaces

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3.1 Scattering Processes

Electron dynamics describes the temporal evolution of an electronic state due to interactions with particles or quasiparticles. The ground state of the system is characterized by the stationary states whose time dependence is determined by the energy of the state. In the present context, we consider an excited electron at the surface, for example, in a surface or adsorbate state. On its relaxation path to the ground state (or thermal equilibrium) 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 simultaneous creation of an electron–hole pair. The coupling to the electronic system can also include other quasiparticles such as excitons, plasmons, and magnons that are not covered in this chapter.

- **Electron–phonon scattering**: This scattering process mainly changes the direction of the electron motion and embraces both scattering to bulk bands and scattering within the surface state band. The energy loss is usually rather small compared to electron–electron scattering. Temperature is a convenient control of electron–phonon scattering.

- **Electron defect scattering**: Real surfaces contain always a nonnegligible amount of defects, such as steps or impurity atoms. The associated electron defect scattering mainly changes the electron momentum leaving the energy almost unchanged. In many aspects, it is similar to electron–phonon scattering. Electron defect scattering can be identified by controlling the defect density.

Image potential states [1] are a special class of surface states that exist on many metal surfaces (see Chapter 3 of volume 2). The small binding energies relative to the vacuum level point to a weak coupling to the metal. Correspondingly, image potential states can have relatively long lifetimes (>10 fs) and can conveniently be studied with
time-resolved two-photon photoemission in considerable detail. Therefore, image
potential states serve as a model system to investigate the various scattering
processes. Figure 3.1 shows the parabolas of the lowest two image potential bands
close to the vacuum level $E_{\text{vac}}$ in the projected bulk band structure of Cu(001). Arrows
illustrate possible scattering processes between surface states and bulk states.

Any scattering event will change energy and momentum of the electron. However,
it is pragmatic to distinguish between processes with small energy loss (or gain) and
ones with large energy loss. The latter processes are inelastic and imply the energy
transfer to another particle (or quasiparticle) as illustrated in Figure 3.1 by arrows
labeled $\Gamma_{\text{nm}}$. If the energy loss is small compared to the experimental resolution, the
scattering is called quasielastic or just elastic for short. The corresponding horizontal
arrows are labeled $c_{\text{nm}}$. Nevertheless, the momentum may be changed consid-
erably in quasielastic scattering processes. An example is shown in Figure 3.1 by the
arrow $\gamma_{11}$ where the momentum is reversed in the $n = 1$ band by a scattering event.

An additional classification of scattering events is done according to whether the
electron remains in its initial band or ends up in a different band. The former is
termed intraband scattering as opposed to interband scattering. The processes $\Gamma_{11}$ and
$\gamma_{11}$ are intraband scattering processes depicted in Figure 3.1. Intraband scattering
leads to a redistribution of the population within the band. All other arrows indicate
interband scattering. The most prevalent interband scattering is scattering to bulk
bands that decrease the population in the image potential bands. For image potential
states, interband scattering from the $n = 2$ bands to the $n = 1$ band is of particular
interest. The processes are indicated by the arrows $\Gamma_{21}$ and $\gamma_{21}$ and are associated with
a transfer of electrons from the $n = 2$ to the $n = 1$ band.

The distinction between the various scattering processes is summarized in
Table 3.1 together with the notation used. Inelastic scattering rates are denoted by
$\Gamma$ and elastic scattering rates by $c$. The indices indicate the initial and final state bands.
Natural numbers are used for the image potential bands, whereas the index $b$
represents bulk bands in Figure 3.1.

![Figure 3.1](image.png)

*Figure 3.1* Projected bulk band structure (shaded area) for the Cu(001) surface with image
potential bands ($n = 1, 2$). For clarity, the binding energy of the image potential states has been
scaled by a factor of 2. Arrows indicate possible scattering processes.
Table 3.1 Classification and notation of scattering processes.

<table>
<thead>
<tr>
<th>From band ( n ) to</th>
<th>Inelastic</th>
<th>Interband</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band ( n )</td>
<td>( \Gamma_{nn} )</td>
<td>( \Gamma_{mn} )</td>
</tr>
<tr>
<td>Band ( m )</td>
<td>( \gamma_{mn} )</td>
<td>( \gamma_{nm} )</td>
</tr>
<tr>
<td>Bulk ( b )</td>
<td></td>
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3.2 Energies and Dispersion of Image Potential States

As evident from Figure 3.1, there are many scattering processes possible involving image potential bands and other states. In order to determine the associated scattering rates elaborate measurements are needed. As in conventional photoemission, the normal mode of two-photon photoemission (2PPE) is to count the number of emitted electrons as a function of the kinetic energy \( E_{\text{kin}} \). An example is shown in Figure 3.2 for the Cu(001) surface\(^1\) where the energy scale has been transformed to binding energy relative to \( E_{\text{vac}} \). Three peaks can be identified for the lowest image.

![Figure 3.2](image)

**Figure 3.2** Two-photon photoemission spectra for the lowest image potential states on Cu(001) for different emission angles. The electrons are excited by photons with 4.62 eV energy into the image potential states and emitted by photons with an energy of 1.54 eV.

1) The small concentration of Cu adatoms is not relevant for the current discussion.
potential states. For a discussion of the binding energies of image potential states, the reader may refer to the literature [2].

Spectra in Figure 3.2 were taken for different emission angles $\theta$ and the peaks show a parabolic dispersion. Using the expression for the parallel momentum $k_\parallel = \sqrt{2mE_{\text{kin}}/\hbar \sin \theta}$, the dispersion relation $E_n(k_\parallel)$ is obtained as depicted in Figure 3.3. It can be described well by parabolas $E_n(k_\parallel) = E_n(0) + \hbar^2 k_\parallel^2 / 2m^*$ with effective masses $m^*$ close to the free electron mass $m$.

The dispersion is derived from the energy of the peak maxima. Additional information provides the peak width that is determined by the energy resolution of the analyzer, the spectral bandwidth of the laser pulses, and the intrinsic linewidth of the electronic state. The last point will be discussed in more detail in Section 3.4.3. Figure 3.4 shows that the peak width increases with emission angle. The main reason is the limited angular resolution that translates into an energy width for strongly dispersing bands [5]. For the image potential bands with a parabolic dispersion characterized by an effective mass $m^*$, the kinetic energy varies with emission angle as described by the following expression:

$$E_{\text{kin}}(\theta) = \frac{E_{\text{kin}}(0)}{\frac{m^*}{m} \sin^2(\theta)}. \quad (3.1)$$

If the electron energy analyzer has an angular resolution $\Delta \theta$, the following contribution $\Delta E_{\text{kin}}(\theta)$ has to be taken into account for the energetic peak width:

$$\Delta E_{\text{kin}}(\theta) = \frac{dE_{\text{kin}}(\theta)}{d\theta} \cdot \Delta \theta = \frac{E_{\text{kin}}(0) \cdot \frac{m^*}{m} \sin 2\theta}{(1 - \frac{m^*}{m} \sin^2 \theta)^2} \cdot \Delta \theta. \quad (3.2)$$

Figure 3.4 shows the experimental results together with a fit to Eq. (3.2). The angular resolution $\Delta \theta$ is obtained as $1.6^\circ$. Other experimental contributions to the measured linewidth are the energy resolution of the analyzer and the spectral bandwidth of the pump and probe laser pulses. The decay and dephasing rates of the measured states may also contribute to the linewidth as discussed in Section 3.4.3. These last contributions may also depend on the energy and emission angle as shown in Section 3.3.2.
3.3 Inelastic Scattering

In many spectroscopies, inelastic scattering is detected directly by the loss of energy and the particle appears with a reduced energy after the scattering event. In two-photon photoemission, the energy loss of an electron can be observed in two ways: (i) the electron appears after a scattering event at lower energy at a later time. (ii) The number of electrons in a particular state decreases with time. This decay of population can in many cases be attributed to inelastic scattering.

3.3.1 Lifetimes of Image Potential States

Two-photon photoemission has an additional experimental parameter compared to regular photoemission, that is, the time delay between the two laser pulses. Figure 3.5 shows an intensity map as function of pump–probe delay and binding energy. The data [6] were obtained on a Ru(0001) surface using a time-of-flight detector for

![Figure 3.4](image1)  
Figure 3.4  Peak width of the lowest image potential states on Cu(001) as function of emission angle. Adapted from Ref. [4].

![Figure 3.5](image2)  
Figure 3.5  Two-photon photoemission intensity (logarithmic gray scale) for the lowest image potential states on Ru(0001) as a function of energy and pump–probe delay. Adapted from Ref. [6].
electrons that analyzes arbitrary kinetic energies. The intensity maxima for the image potential states are clearly recognized. The energies of the peaks are independent of the time delay. For hemispherical analyzers that detect only a preset kinetic energy (or range of energies), it is convenient to measure the intensity of the peaks as a function of pump–probe delay. Such data are shown in Figure 3.6, for the lowest image potential states on the Cu(001) surface. 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 bandwidth comparable to the energy separation of the states [7]. From the oscillation period of $T = 117$ fs, the energy difference can be determined very accurately to $|E_3 - E_4| = \hbar / T = 35$ meV.

The lifetimes $\tau_n$ shown in Figure 3.6 depend strongly on the quantum number $n$ and consequently binding energy $E_B$. It is convenient to convert lifetimes to total decay rates $\Gamma_n = \hbar / \tau_n$ that are the sum of all scattering rates associated with a decrease in the population in the state $n$ at a particular momentum or energy. Total decay rates $\Gamma_n$ are plotted in Figure 3.7 as a function of binding energy $E_B$ for several copper surfaces. For $n \geq 2$, an $E_B^{-1/2}$ 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 [8]. 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 $\tau_n \propto n^{-1}$. The same result is obtained when the probability

![Figure 3.6](image-url) Two-photon photoemission signal for the lowest image potential states on Cu(001) ($k_z = 0$) as a function of pump–probe delay.
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 in the decay rate from Cu(001) to Cu(117) in Figure 3.7. The energies of the image potential states get closer to the effective bandgap and therefore the penetration of the wave function into the bulk becomes larger [9]. 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 bandgap and has a decay rate smaller than the one of the \( n = 2 \) state [10].

Table 3.2 summarizes the available experimental data on lifetimes of image potential states on clean metal surfaces for normal emission \( (k_z = 0) \). The main factors determining the lifetimes are (i) the bulk penetration of the wave function that

<table>
<thead>
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<th>( \tau_1 ) (fs)</th>
<th>( \tau_2 ) (fs)</th>
<th>( \tau_3 ) (fs)</th>
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<tr>
<td>Cu(001)</td>
<td>40 ± 6</td>
<td>120 ± 15</td>
<td>300 ± 20</td>
<td>[7, 11]</td>
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<tr>
<td>Cu(1 1 15)</td>
<td>22 ± 3</td>
<td>55 ± 3</td>
<td>165 ± 10</td>
<td>[12]</td>
</tr>
<tr>
<td>Cu(1 1 11)</td>
<td>14 ± 2.5</td>
<td>45 ± 3</td>
<td>170 ± 10</td>
<td>[12]</td>
</tr>
<tr>
<td>Cu(119)</td>
<td>9 ± 2.5</td>
<td>39 ± 3</td>
<td>130 ± 10</td>
<td>[12]</td>
</tr>
<tr>
<td>Cu(117)</td>
<td>9 ± 2.5</td>
<td>39 ± 3</td>
<td>130 ± 10</td>
<td>[12]</td>
</tr>
<tr>
<td>Cu(115)</td>
<td>(&lt; 5)</td>
<td>20 ± 3</td>
<td>65 ± 5</td>
<td>[12]</td>
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<tr>
<td>Cu(111)</td>
<td>18 ± 5</td>
<td>14 ± 3</td>
<td>40 ± 6</td>
<td>[10, 13, 14]</td>
</tr>
<tr>
<td>Cu(775)</td>
<td>18 ± 2</td>
<td></td>
<td></td>
<td>[15]</td>
</tr>
<tr>
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<td>160 ± 10</td>
<td>360 ± 15</td>
<td>[11]</td>
</tr>
<tr>
<td>Ag(111)</td>
<td>36</td>
<td>18 ± 2</td>
<td></td>
<td>[16–18]</td>
</tr>
<tr>
<td>Ru(0001)</td>
<td>11 ± 2</td>
<td>57 ± 5</td>
<td>174 ± 10</td>
<td>[6, 19]</td>
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<td>Ni(111)</td>
<td>7 ± 3</td>
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<td>[20]</td>
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<td>Pd(111)</td>
<td>25 ± 4</td>
<td></td>
<td></td>
<td>[21]</td>
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<tr>
<td>Pt(111)</td>
<td>26 ± 7</td>
<td>62 ± 7</td>
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Figure 3.7 Decay rates for the image potential states as a function of binding energy for Cu(111) (squares), Cu(117) (circles), and Cu(001) (diamonds). The dashed lines indicate \( E_b^{1/3} \) dependence.
strongly depends on the relative position in the bandgap of the projected bulk band structure [2]. This effect can be seen nicely for the copper surfaces where the effective bandgap depends on the surface orientation [12]. (ii) The density of available final states in particular close to the Fermi energy [23]. This influence can be pinpointed in Table 3.2 at the short lifetimes of the d-band metals compared to the noble metals. In fact, for many d-band metals the lifetimes are too short to be reliably measured in time-resolved 2PPE.

3.3.2
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 Figure 3.8 for the \( n = 1 \) image potential band on Cu(001) [24]. The data show that the lifetime decreases with increasing parallel momentum. Two effects contribute to the increase in 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 \( k = 0 \).

Two experimental data sets for the decay rates \( \frac{1}{\tau} \) are shown in Figure 3.9 by filled [24] and open circles [25] that agree within the error bars. The linear dependence with energy (i.e., a quadratic dependence on parallel momentum) is characterized by a slope of 0.047 [24] compared to 0.035 [25]. The apparent discrepancy of the values for the slope arises from the larger error bars of the former data set that gives the values for small energies more weight.

![Figure 3.8](image_url)

**Figure 3.8** Time-resolved 2PPE signal of the \( n = 1 \) state of Cu(001) for three different values of the parallel momentum \( k \). The computed instrument function is shown as a dotted line. Adapted from Ref. [24].
The experimental data agree very well with the calculation (solid lines) [24]. Both inelastic intraband scattering processes and inelastic interband scattering processes to bulk bands (dashed lines) demonstrate a linear dependence on energy as shown in Figure 3.9. For the \( n = 1 \) band, both processes are calculated to contribute about the same amount to the increase in the decay rate [24].

3.3.3 Inelastic Intraband Scattering

In the previous section, inelastic intraband scattering was identified as one contribution to the momentum dependence of the decay rates. The other contributing factor is the energy dependence of the decay rate, and a quantitative assessment can be obtained from calculations [24]. A different approach is illustrated in Figure 3.10 that shows time-resolved 2PPE data for the \( n = 1 \) image potential state on Cu (001) [26]. They are taken at the bottom of the \( n = 1 \) band for \( k_z = 0 \). The intensity is plotted on logarithmic scale and shows good statistics over four orders of magnitude. The lower curve of Figure 3.10 is a reference measurement that was taken with a photon energy of 4.43 eV that is below the threshold for excitation of the \( n = 2 \) state. It shows a simple linear decay in the semilogarithmic plot. For photon energies above this threshold, the data exhibit a biexponential decay. The short timescale corresponds to the lifetime of the \( n = 1 \) state, whereas the longer timescale is discussed in more detail in Sections 3.3.4 and 3.4.1.

The observed difference in the lifetimes of 36 fs for excitation with 4.43 eV photon energy and 40 fs with 4.65 eV photon energy is explained by cascade processes of inelastic intraband scattering (\( \Gamma_{11} \) in Figure 3.1) along the \( n = 1 \) band [24]. Electrons excited high into the image potential band decay downward in the band. The required
time for the downward scattering is seen as an apparent longer lifetime. In order to avoid these cascade processes, pump pulses close to the excitation threshold should be used in order to obtain accurate lifetimes.

3.3.4 Inelastic Interband Scattering

Because the long-range image potential leads to a series of bands, scattering between these bands is possible. This provides a convenient model system to study the associated effects in detail, which are usually much harder to identify at other surfaces. Figure 3.6 shows a biexponential decay for the \( n = 1 \) state. The slower decay has within the statistical errors the same slope as the decay of the \( n = 2 \) state. This biexponential decay is also seen in Figure 3.8 for different parallel momenta. Figure 3.10 proves that the effect is due to the scattering from the \( n = 2 \) band to the \( n = 1 \) band because the slowly decaying component is absent for photon energies below the excitation threshold of the \( n = 2 \) band \[24\]. The relative intensity at which the number of electrons scattered from the \( n = 2 \) to the \( n = 1 \) band becomes comparable to the rapidly decaying population excited directly by the pump pulse into the \( n = 1 \) band is a measure for the strength of the interband scattering. More quantitative results are obtained from rate equation models \[26\] or fits using the optical Bloch equations \[3\]. Results for the clean Cu(001) surface are shown in Figure 3.11 by open symbols as a function of energy relative to the band bottom of the \( n = 1 \) band. The interband scattering rate is almost independent of energy (i.e., parallel momentum). For comparison, the total decay rate \( \Gamma_2 \) of the \( n = 2 \) band is plotted in the inset of Figure 3.11 that is on the clean Cu(001) surface more than one magnitude larger than the interband scattering rate \( \Gamma_{21} \).
Quasielastic scattering describes events with energy losses small compared to the experimental energy resolution. In the case of intraband scattering of image potential states, the electron just changes its direction or momentum. For perfect stepped surfaces, the momentum relative to the steps is reversed leading to asymmetries in the step-up or step-down directions. For point scatterers such as adatoms, the net population within the image potential band is not changed in intraband scattering. Consequently, it cannot be detected in time-resolved measurements and we have to resort to linewidth analysis as explained in Section 3.4.3.

Elastic interband scattering is observed from the appearance of the electron in a different image potential band at the same energy. A special case occurs when two image potential bands cross due to band umklapp. The strong coupling leads to a resonant interband scattering process. Elastic interband scattering to bulk bands (rate $\Gamma_{\text{nb}}$) cannot be directly detected because the lifetime in bulk bands is quite short. It can be inferred indirectly from the difference of the total scattering rate $\Gamma_n$ (measured by the lifetime) to the individual interband contributions $\Gamma_{\text{nm}} + \Gamma_{\text{nm}}$.

### 3.4.1 Elastic Interband Scattering

Inelastic interband scattering from the $n = 2$ to the $n = 1$ band has been discussed in Section 3.3.4. There the $n = 2$ decay was observed at the bottom of the $n = 1$ band. For elastic interband scattering, the $n = 2$ decay has to be observed on the $n = 1$ band at the same energy. This implies measurements at finite parallel momentum. For the clean surface, the elastic interband scattering is quite small as can be seen in Figure 3.11 (open symbols). For 1% Cu adatoms, the interband scattering rate...
increases significantly for energies above the bottom of the \( n = 2 \) band \([25]\). The elastic character of the interband signal is proven by the fact that the decay rate measured for the \( n = 2 \) band (filled symbols in the inset of Figure 3.11) agrees within the experimental errors with the decay rate obtained for the slowly decaying component on the \( n = 1 \) band (crosses) at the same energy. Scattering of electrons by Cu adatoms changes the momentum with negligible change of energy. Scattering by other electrons is possible only on the clean surface that is always associated with an energy loss for the creation of an electron–hole pair. The scattering by the Cu lattice is incorporated via the crystal potential in the electronic band structure.

The total decay rate \( \Gamma_2 \) in the \( n = 2 \) band significantly increases by the addition of Cu adatoms as can be seen in the inset of Figure 3.11. This increase corresponds quite well to the elastic interband scattering rate as shown by the solid line in the main figure. From this good agreement, we conclude that elastic scattering from the \( n = 2 \) band to bulk bands by adatoms (\( \gamma_{ab} \)) is small \([25]\).

### 3.4.2 Resonant Interband Scattering

Elastic interband scattering can be significantly enhanced on stepped surfaces. In addition, the interband scattering rate can show pronounced peaks as a function of energy in contrast to the smooth dependence observed for adatoms shown in Figure 3.11. Therefore, we use the term resonant interband scattering for stepped surfaces. The effect was discovered first on a clean Cu(001) surface \([26]\). Later results suggest that the sample used in the pioneering work must have had a nonnegligible number of steps \([27]\).

Time-resolved two-photon photoemission measurements for the Cu(1 1 1) surface are shown in Figure 3.12 on a logarithmic intensity scale \([12]\). As indicated in the inset, the data are obtained on the \( n = 1 \) image potential band from the band bottom \( E_1 \) up to the vacuum energy. For energies below approximately 330 meV, a single exponential decay is observed. When the energy of the \( n = 2 \) band minimum is reached, a biexponential decay appears. For energies above the bottom of the \( n = 2 \) band, the interband scattering contribution becomes even stronger and a \( n = 1 \) decay is hardly visible in the spectra of Figure 3.12. The \( n = 2 \) contribution becomes weaker at even higher energies when a third component appears corresponding to the \( n = 3 \) decay with its typical quantum beat oscillations \([7]\).

The relative contributions of the interband scattering processes can be obtained by fitting the experimental spectra of Figure 3.12 \([28]\). The results presented in Figure 3.13 show that the interband scattering from the \( n = 2 \) band can reach over 90% for Cu(1 1 11). The maximum contribution is observed for energies above the band minimum \( E_2 \) at energies depending on the terrace width \([12]\). These maxima coincide with the intersection of the \( n = 1 \) band with the backfolded \( n = 2 \) band (see inset in Figure 3.12 and Ref. \([12]\)). The periodic step lattice provides an interaction that leads to mixing of the \( n = 1 \) and \( n = 2 \) bands. Therefore, the distinction between \( n = 1 \) and \( n = 2 \) bands disappears \([29]\).
Figure 3.12  Time-resolved two-photon photoemission intensity measured on the $n = 1$ image potential band for the Cu(1 1 1) surface plotted on a logarithmic scale. The energy above the band bottom is indicated by the numbers (in meV) and marked in the band structure plot. Adapted from Ref. [12].

![Figure 3.12](image1)

Figure 3.13  Interband scattering probability from $n = 2$ (filled circles) and $n = 3$ (open circles) to $n = 1$ image potential states as a function of energy above the band bottom $E_1$ for Cu(1 1 1).

![Figure 3.13](image2)
3.4.3 Elastic Intraband Scattering

The pump pulse in two-photon photoemission excites the image potential bands up to a maximum energy given by the photon energy. States with all possible parallel momenta according to the dispersion relation are populated. Because for low-index surfaces the dispersion shows no azimuthal dependence, elastic intraband scattering just redistributes the electron population in the band. This can be modeled quantitatively, for example, in a wave packet propagation approach [30, 31]. As a result, usual time-dependent measurements as a function of pump–probe delay at fixed energy do not yield information on elastic intraband scattering. However, the scattering event leads to a change in the phase of the wave function. This dephasing can be detected in the energetic linewidth.

A set of energy spectra from a Cu(001) surface for various pump–probe delays is plotted in Figure 3.14. The width of the peaks changes noticeably. The full width at half maximum of the peaks is shown in Figure 3.15 as a function of pump–probe delay. At negative time delay, the linewidth decreases linearly and attains a constant value for long positive delays. These surprising observations can be explained by describing the two-photon photoemission process in a density matrix formalism. The resulting optical Bloch equations [32] can be solved for special cases [33, 34]. The scattering processes are introduced by decay and dephasing rates $\Gamma$ and $\Gamma'$, respectively. The resulting line shape is represented in very good approximation by a convolution of a Lorentzian and a Gaussian function. The latter is determined by experimental parameters, that is, energy resolution of the analyzer and spectral bandwidth of the laser pulses. The Lorentzian is often referred to as the intrinsic linewidth. In 2PPE, it corresponds to twice the dephasing rate plus a delay-dependent term containing the decay rate that goes to zero for long delays [33]. In normal

![Figure 3.14](image_url)

**Figure 3.14** Two-photon photoemission spectra for the image potential states on Cu(001) for different pump–probe delays taken with $\hbar v = 1.49$ eV probe and $3\hbar v$ pump pulses. All spectra are normalized to the same height.
photoemission, the intrinsic linewidth contains the sum of decay and dephasing rates, which cannot be disentangled.

The results of calculations are compared with the data in Figure 3.15. The decay and dephasing rates as well as the experimental parameters match the values obtained by independent measurements [33]. The almost identical linewidths for both image potential states at long delays (see Figure 3.15) indicates that the dephasing rates are the same for \( n = 1 \) and \( n = 2 \) image potential states. Taking into account the information about the experimental parameters, dephasing is found to be negligible on the clean Cu(001) surface [10].

Decay and dephasing can be illustrated nicely in the quantum beat pattern of Figure 3.6. The trace for the \( n = 3(4) \) states shows an exponential decay and a superimposed oscillation. The decay rate is determined by the average decrease in the population. The temporal interference pattern depends on the relative phase of the time-dependent wave functions. The observation of the beating pattern with a constant amplitude on the logarithmic scale indicates that the scattering events change only the population and not the phase. Dephasing is therefore also negligible for the higher image potential states on clean Cu(001). Adsorbates can influence the decay or the dephasing in the quantum beat pattern depending on the associated scattering potential [35].

### 3.5 Electron–Phonon Scattering

Scattering by phonons is usually quasielastic because typical phonon energies at metal surfaces are smaller than the experimental resolution. An exception might occur for molecules [37]. The influence of phonons can conveniently be controlled by temperature. The number of phonons for sufficiently high temperatures is proportional to the absolute temperature \( T \). The number of scattering events and the associated dephasing rate entering the linewidth are then expected to increase linearly with temperature. Figure 3.16 presents two-photon photoemission spectra.
from Cu(111) for temperatures between 25 and 460 K [36]. The two peaks correspond to the occupied surface state ($n = 0$) and the $n = 1$ image potential state. The peak shifts with temperature are explained by the variation of the bandgap due to the thermal expansion of the lattice [36]. The linewidths also change with temperature that allows to determine the dephasing rates plotted in Figure 3.17. For both states, a

![Figure 3.16](image)

**Figure 3.16** 2PPE spectra from Cu(111) for various temperatures taken with $h\nu = 2.37$ eV probe and $2h\nu$ pump pulses. All spectra are normalized to the same height. From Ref. [36].

from Cu(111) for temperatures between 25 and 460 K [36]. The two peaks correspond to the occupied surface state ($n = 0$) and the $n = 1$ image potential state. The peak shifts with temperature are explained by the variation of the bandgap due to the thermal expansion of the lattice [36]. The linewidths also change with temperature that allows to determine the dephasing rates plotted in Figure 3.17. For both states, a

![Figure 3.17](image)

**Figure 3.17** Pure dephasing rates versus temperature derived from the linewidths of the $n = 0$ and $n = 1$ states using the optical Bloch equations. The mass enhancement parameters $\lambda$ are obtained from linear fits using the relation $\Gamma_{n,\text{ph}}^\ast = 2\pi\lambda k_B T$. From Ref. [36].
linear increase with temperature is found. For the \( n = 1 \) state, a deviation is found above 400 K because the energy of the state is outside the bandgap in this temperature range \[36\]. The associated larger penetration into the bulk increases the coupling to bulk phonons and accordingly the dephasing rate.

The linear increase in the dephasing rate with temperature has a slope relative to the electron–phonon mass enhancement parameter \( \lambda = \Gamma_{e-ph}^{\text{rel}}/2\pi k_B T \) \[38\]. For the \( n = 0 \) state, the value \( \lambda = 0.14 \pm 0.02 \) is in excellent agreement with the results of photoemission experiments \[39–41\]. For the \( n = 1 \) image potential state, \( \lambda = 0.06 \pm 0.01 \) is obtained. The smaller value for the \( n = 1 \) state is explained by the smaller overlap with bulk wave functions for the \( n = 1 \) state compared to the \( n = 0 \) state \[36\].

An extrapolation to \( T = 0 \) K yields dephasing rates of 40 and 14 meV for the \( n = 0 \) and \( n = 1 \) states, respectively. This indicates a significant amount of defects even on Cu(111) surfaces prepared according to the state of the art. For the occupied surface state, the value agrees with results from photoemission, scanning tunneling spectroscopy, and theoretical calculations \[41\]. Results for the \( n = 1 \) image potential state from other methods are not available. Values for the parameter \( \lambda \leq 0.011 \) have been calculated for \( n = 1 \) states on the (001) surfaces of Cu and Ag \[42\] in agreement with the small penetration of the wave function into the bulk for image potential states close to the center of the bandgap. No temperature dependence has been found experimentally for the Cu(001) surface in agreement with the negligible dephasing found in Section 3.4.3 \[23\]. For Pd(111), a strong temperature dependence of the linewidth is observed \[43\] in spite of the fact that the overlap with bulk bands should be similar to the case of Cu(001). A consistent interpretation of the data using \( \lambda = 0 \) is obtained when thermally created defects are taken into account \[43\].

### 3.6 Electron Defect Scattering

Surfaces with adatoms and steps have been discussed in previous sections to illustrate various scattering processes for electrons in image potential states. In the following section, the dependence on adatom concentration and step density will be discussed.

#### 3.6.1 Scattering by Adatoms

The decay rates and interband scattering rates introduced in Figures 3.9 and 3.11 are plotted in Figure 3.18 as a function of Cu coverage. The top panel shows the average interband scattering rates for elastic \( (E > E_1) \) and inelastic \( (E < E_1) \) interband scattering. The elastic scattering rate \( \gamma_{21} \) increases strongly with Cu coverage confirming that this process is caused by the Cu adatoms. The linear increase is consistent with the occurrence of individual adatoms in the relevant coverage and temperature range \[44, 45\]. The inelastic interband scattering rate \( \Gamma_{21} \) shows no
significant dependence on Cu coverage. The slightly larger rates for 3% ML Cu coverage in Figure 3.18 could indicate the breakdown of the assumption of well-separated adatoms. Therefore, electrons scattered elastically (\(C_{21}\)) to the \(n=1\) band and then inelastically (\(C_{11}\)) down to the bottom of the \(n=1\) band do not contribute significantly to the long-lived component from which \(C_{21}\) is derived. Inelastic interband scattering \(C_{21}\) from the \(n=2\) to the \(n=1\) band must then be due to the interaction of the electrons in the \(n=2\) state with the underlying electron system in the bulk. These arguments are supported by the excellent agreement for \(C_{21}\) with theoretical calculations [46].

At the band bottom of the \(n=1\) band decay can proceed only via scattering to bulk band, and the total decay rate \(\Gamma_n(E_n)\) is the sum of the inelastic decay rate \(\Gamma_{1b}\) and the elastic scattering rate \(\gamma_{1b}\): \(\Gamma_n(E_n) = \Gamma_{1b} + \gamma_{1b}\). \(\Gamma_1(E_n)\) grows linearly with adatom coverage (bottom panel of Figure 3.18, filled circles). For the bottom of the \(n=2\) band, inelastic and elastic interband scattering terms have to be added: \(\Gamma_n(E_n) = \Gamma_{2b} + \gamma_{2b} + \Gamma_{21} + \gamma_{21}\). \(\Gamma_{21}\) and \(\gamma_{21}\) are obtained from independent measurements of the scattered components on the \(n=1\) band (Figure 3.11). Figure 3.18 shows that \(\Gamma_{21}\) is independent of coverage and \(\gamma_{21}\) is proportional to the adatom concentration. If the bulk provides most of the final states for inelastic decay and the contribution of the adatoms is negligible, it is plausible that the inelastic decay rates \(\Gamma_{1b}\) are independent of coverage and the coverage dependence is carried by the elastic decay rates \(\gamma_{1b}\). Note that inelastic and elastic processes are also described by different theoretical models [46, 47]. The results support the simple picture that scattering of
electrons by a heavy adatom is elastic, whereas interaction with another electron of the same mass permits the exchange of energy leading to an inelastic scattering process. Both processes are usually accompanied by a change of momentum.

Data for scattering rates have been obtained for Cu and Co adatoms on the Cu(001) surface [25, 48]. The agreement for the inelastic scattering rates is excellent. The moderate agreement for the elastic scattering rates might be attributed to the fact that both experiment and theory are very sophisticated and challenging.

3.6.2 Scattering by Steps

In Section 3.4.3, it was shown that the linewidth for long delays contains information on the elastic intraband scattering rate. Such data are presented in Figure 3.19 for the \( n = 1 \) state at various stepped copper surfaces. The linewidth increases significantly with step density. The associated elastic intraband scattering rate is only slightly smaller than the decay rate [12]. The increase with step density is plausible because the step edges are the obvious scatterers. However, for a perfect step array the scattering by the steps should be incorporated in the band structure leading to small bandgaps at the intersection of backfolded bands [49]. The elastic intraband scattering should be negligible as demonstrated for the clean Cu(001) surface. The conclusion is that the observed increase in the linewidth with step density is primarily caused by disorder and fluctuation of steps.

Another interesting observation for stepped surfaces is the asymmetry of the resonant interband scattering rate for the upstairs and downstair directions [12, 50]. This asymmetry can also be observed in scanning tunneling spectroscopy, and a good agreement with 2PPE measurements is obtained [49]. The asymmetric scattering rate can be explained only if some of the electrons are scattered into bulk bands.

![Figure 3.19](image_url)

Figure 3.19 Linewidth of two-photon photoemission spectra for the \( n = 1 \) image potential state at \( k || = 0 \) as a function of pump–probe delay for stepped copper surfaces. Adapted from Ref. [12].
3.7 Summary and Outlook

Time- and angle-resolved two-photon photoemission of image potential states permits a detailed study of scattering processes at metal surfaces. Many scattering rates can be determined quantitatively in good agreement with theoretical calculations. This thorough understanding helps to identify and clarify scattering processes at other surfaces [51, 52]. However, a lot of interesting questions are still open for image potential states. The scattering behavior of adatoms has been studied in full detail only for Cu and Co on Cu(001). Other adsorbates such as small molecules might exhibit a different scattering behavior [14]. On stepped surfaces, the influence of the step regularity (terrace width distribution and frizziness) is not well understood. The study of surfaces with better ordered and straighter steps than vicinal copper surfaces would be worthwhile. Finally, both paths of research could join in the investigation of steps with adatom decoration.

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References
