Chapter 5

Photoelectric Emission

There are few emission mechanisms that promote bound electrons of solids into free space, like the thermionic emission, secondary-electron emission, Auger electron emission, or field emission. An important tool is the photoelectric emission, that provides the basic, direct, and most relevant information about the material and the physics of the emission process. Photoemission is one of the most elaborate and costly techniques, because one needs a synchrotron-radiation source, complicated monochromator, ultra-high vacuum, etc. Still the method is widely employed because of the wealth of information we can extract from the results. The first question is why we would prefer photoemission over other spectroscopic tools. The answer is that in a photoemission experiment we detect a photoelectron, and we exactly know its history from the excitation to detection process. A photon with energy $h\nu$ is absorbed leading to an electronic excitation from an initial state $\psi_i$ with an energy $E_i$ to a final state $\psi_f$ with an energy $E_f$. This process gives us insight into, e.g., the band structure of the solid. Electrons are photoexcited somewhere in the solid and move to the surface. The analysis of emitted electrons contains information about electron scattering processes. We may also learn about the atomic structure at the surface. Electrons which arrive at the surface escape into vacuum if their energy overcomes the potential barrier, the work function. This process gives us the opportunity to study surface chemical processes.

5.1 Photoemission Process

5.1.1 Optical Excitation: Conservation rules

Photoemission process starts with the optical excitation. Photons, as light quanta with energy $h\nu$, are absorbed by an electron such that $E_f - E_i = h\nu$. It is essential that the energy transfer is definite and the photon transmits all its energy. This is not the case in excitation processes using electrons or ions. If the ground state is associated with $N$ electrons, the final state is a system with $(N - 1)$ electrons and a photoelectron. We observe two different cases. Often, $h\nu$ is absorbed by
one electron and other \((N - 1)\) electrons remain in their initial states which they have occupied prior to the excitation. We may call these \textit{spectator electrons}. This case is referred to as the \textit{one-electron approximation}. If the spectator electrons are perturbed during optical excitation process, some of the excitation energy remains in the \((N - 1)\) electrons. The electrons are correlated.

The absorption process is illustrated in Fig. 5.1 in an \(E(\vec{k})\) diagram where the energy conservation is evident. The photon energy is \(E = h\nu\) and is given by

\[
E(eV) = \frac{12400}{\lambda(\text{Å})}
\]

as mentioned in Section 2.3. Thus 10 eV photons have a wavelength of 1240 Å. The momentum of these photons is \(p_\lambda = \hbar k = h/\lambda = h/1240\). For a conduction electron, on the other hand, we may write \(p_e = \hbar k_B = h/a = h/2\), using a lattice constant of \(a = 2\) Å. \(k_B\) is defined by the Brillouin zone.

![Figure 5.1](image_url)

Figure 5.1: Plot of energy \(E\) versus wave vector \(k\) for the excitation of the initial state \(\psi_i\) to \(\psi_f\) by absorbing a photon \(h\nu\). Since the momentum of the photon is negligibly small optical transitions are virtually vertical.

These numbers show that photons have energy, but no momentum, and for a photoexcitation process using \(h\nu = 10\) eV the momentum transfer is negligible: \(\Delta \vec{p} = \hbar \Delta \vec{k} \approx 0\). This \textit{momentum conservation} is expressed by vertical transitions in Fig. 5.1.

Not all energy and momentum conserving transitions take place. There are other restrictions to optical transitions due to \textit{selection rules}. The simplest case is illustrated in an atom with its spherically symmetric wave functions. The matrix element for optical transitions is given by \(M = \langle \psi_f | V | \psi_i \rangle\). For linearly polarized light the electric field vector \(\vec{E}\) is parallel to, e.g., \(x\). Then, \(V \propto x\), which means that it has negative parity and changes sign for inversion (\(x \rightarrow -x\), etc.). Depending on
the state of the wave function, i.e., \( s, p, d, \ldots \) the spherical functions may have either parity: \( \psi(\vec{r}) = \psi(-\vec{r}) \) or \( \psi(\vec{r}) = -\psi(-\vec{r}) \). Then, the matrix element \( M = \int \psi_f(x) \psi_i \) gives zero, if \( \psi_f \) and \( \psi_i \) have the same parity, and it is nonzero, if \( \psi_f \) and \( \psi_i \) have different parities. As a result, \( s - p \) transition is allowed, but \( s - d \) or \( s - f \) transition is forbidden. Practically, optical transitions take place if \( \Delta \ell = \pm 1 \).

In solids, we have mixed states, and their symmetry is not necessarily spheric. Yet, there are strict selection rules for optical transitions that allow us to draw conclusions on the symmetry of the wave functions \( \psi_i \) and \( \psi_f \). This information is relevant for surface chemistry and catalysis.

In summary, optical excitations are selective with respect to energy, momentum, and selection rules. This is a general issue valid for optics. The advantage of photoemission is that emitted photoelectrons are detected and thus the final state is observed and can be localized in the Brillouin zone.

### 5.1.2 Energy Conservation

In the one-electron approximation only one electron changes its state as a result of photon absorption, and the other \( (N-1) \) electrons keep their states. Thus, we can write \( E_B = h\nu - \Phi - E_{\text{kin}} \).

![Figure 5.2: Plot of electron energy for the photoemission process in one-electron approximation. \( E_B \) is the binding energy and \( E_{\text{kin}} \) the kinetic energy of the photoemitted electron, \( \Phi \) the work function of the metal.](image)

The binding energy \( E_B \) of the electron is defined in the absolute energy scale and measurable in the ground state. This is only possible if the photoelectron does not undergo any energy dissipating collisions during the emission process. In summary, the one-electron approximation can be applied for cases where the hole state does
not interact with other electrons of the material. This is true for the conduction
electrons with extended character of several metals. One-electron approximation
cannot be applied if the hole state is only partially screened by the electron gas,
e.g., for core states in atoms and molecules.

5.1.3 Conservation of Momentum

In a photoemission experiment one measures the kinetic energy of electrons along
the direction of emission, the measurement mode is called angle- and energy-resolved
measurement.

![Figure 5.3: We measure $E_{\text{kin}}$ of the photoemitted electron under the
appropriate emission angle. The relationship between the measured
quantity and the vacuum momentum $\vec{p}_{\text{vac}}$ is $E_{\text{kin}} = \frac{\vec{p}_{\text{vac}}^2}{(2m)}$.]

Now we need a relationship between the vacuum and crystal momentum of
the electron in the solid before the excitation process. We assume that optical
absorption causes transitions between Bloch states. The momentum of the excited
electron in the crystal is found by writing $\psi(\vec{r}) = u_\vec{k}(\vec{r}) e^{i\vec{k} \cdot \vec{r}}$ with $u_\vec{k}(\vec{r} + \vec{a}) = u_\vec{k}(\vec{r})$
owing to the translational invariance (periodicity) of the crystal. Fourier expansion
yields

$$\psi(\vec{r}) = \sum_{\vec{G}_i} a_{\vec{G}_i} e^{i(\vec{k} + \vec{G}_i) \cdot \vec{r}}$$

with $\vec{G}_i$ the reciprocal lattice vector. If $\vec{K}_i$ is the total $k$-vector and $\vec{k}$ the $k$-vector
in the reduced scheme, then $\vec{K}_i = \vec{k} + \vec{G}_i$. Since there is only invariance with respect
to translations by $a$ the lattice vector, $\vec{K}_\parallel$ is conserved. Hence it is a good quantum
number.

The conserved quantities can be expressed as

$$\vec{p}_\parallel_{\text{vac}} = \vec{K}_\parallel_{\text{crystal}} = \vec{k}_\parallel_{\text{crystal}} + \vec{G}_\parallel$$

(5.3)
The translational symmetry is broken normal to the surface and hence momentum is not conserved

\[ \vec{p}_\perp \text{vac} \neq \vec{K}_\perp \text{crystal} \] (5.4)

During the photoemission process, electrons have a kinetic energy \( \hbar^2 \vec{K}_\perp \text{crystal}^2/(2m) \) normal to the surface, while the kinetic energy after the escape process reduces to \( \hbar^2 \vec{p}_\perp \text{crystal}^2/(2m) \). During escape, forces act on the excited electron and it slows down; the perpendicular component of the momentum is not conserved. In summary, in an angle-resolved photoemission process we can determine the binding energy \( E_B \) of the electron before the process in its ground state and its \( \vec{K}_\parallel \) in the crystal. So, just using the conservation rules we can have a detailed picture of photoemission without a microscopic description. This is sufficient in order to experimentally map the dispersion relation, the band structure, of solids.

### 5.1.4 Three-Step Model

For complicated quantum-mechanical problems, as it is the case in photoemission, it is customary to divide the process in smaller, more manageable subprocesses. Accordingly, photoemission is imagined as a three-step process.\(^1\)

![Three Step Model](image)

Figure 5.4: Photoelectrons are excited in the solid. Subsequently, they travel to the surface. In the third step, they overcome the surface barrier and are emitted into vacuum. Ref. [1].

Figure 5.4 depicts these processes. We have dealt with optical excitations and energy conserving processes. This is the first step. The second step is the motion of photoexcited electrons to the surface. The absorption coefficient of photons is in the order of $\mu$m. Yet the photoexcited electrons travel much shorter distances without inelastic collisions. This effect makes photoemission spectroscopy a surface sensitive tool. It also introduces into the measured spectrum a sea of electrons that have lost energy, the secondary electrons. These are undesirable, because we can apply the conservation rules only to primary electrons which are emitted without energy losses. The third step is the escape of electrons into vacuum overcoming the potential barrier, the work function $\Phi$. For the primary electrons the momentum parallel to the surface is conserved and we can track back the electrons in order to obtain information on their initial states.

5.2 Applications

5.2.1 Band Structure

Now we show some relevant historical results. Recall that in angle-resolved photoemission experiments we know the initial- and final-state energies exactly. The emission angle helps us find the crystal momentum. Hence, we can locate the transition in the Brillouin zone in the reduced-zone scheme.

![Figure 5.5: Valence-band dispersions $E(\vec{k})$ of GaAs along major symmetry directions. Dashed curves are theoretical dispersion curves for valence bands. Ref. [2].](image)
Figure 5.5 shows one of the first results investigating the band structure. Data have been obtained in a wide range of $\vec{k}$ so we can easily compare them with computations. The parabolic shape of the $sp$ states at the $\Gamma$ point are well reproduced. It is worth noting that the ideas of Bloch states and energy-band dispersions have been used since the advent of solid state physics. Yet the experimental verification of these ideas had to await until about 1977.

5.2.2 Surface States

Surface states exist in SC’s and metals in the bulk band gap. For a Cu crystal there exists a band gap along the $\Gamma - L$ line. The binding energy of these states at the $\Gamma$ point, the center of the 2DIM Brillouin zone, is 0.4 eV relative to $E_F$, and they disperse parabolically upward as the momentum parallel to the surface is increased. Some typical high-resolution spectra are shown in Fig. 5.6.

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Figure 5.7: Energy-dispersion relation for the surface state. The solid curve is a parabolic least-square fit. The shaded region is the projected bulk continuum of states. Ref. [3].

Figure 5.7 shows the dispersion relation $E(\vec{k}_\parallel)$ of the surface state along with the projected bulk continuum. The surface state enters the bulk continuum just above $E_F$. A least-squares analysis of the $E(\vec{k}_\parallel)$ points produces the fit $E(k_\parallel) = 8.25k_\parallel^2 - 0.389$, with $E$ in eV and $k_\parallel$ in Å$^{-1}$. This way we can find the effective mass of surface-state electrons.

### 5.2.3 Spin Spectroscopy

In a ferromagnet the spin moments are aligned in the initial state along a quantization axis which we define in an appropriate way. We measure in photoemission electron spin polarization (ESP) of the photoemitted electron, which is defined as $ESP = (N \uparrow - N \downarrow)(N \uparrow + N \downarrow)^{-1}$ where $N \uparrow (N \downarrow)$ represents the number of electrons with spin parallel (antiparallel) to the quantization axis. The photoemission process is faster than the spin-flip process. Therefore, the spin direction is another conserved quantity in photoemission, and a measurement of ESP gives information about the alignment of spins in the initial state.

Figure 5.8 shows on the left-hand side the spin-resolved density of states in Ni. Below the Curie temperature ($T_C$), the number of electrons with the spin moment parallel to magnetization direction is larger than that with antiparallel spins. This is because of the exchange energy $J$, namely electrons with parallel spins avoid each other. The exchange energy itself is in competition with the kinetic energy, while the potential energy is reduced because of correlation. If $J$ is sufficiently large and similarly $D(E_F)$ the density of states at $E_F$, then the so-called Stoner criterium...
for ferromagnetic order $J \cdot D(E_F) > 1$ is fulfilled. This means that the cost in kinetic energy is small for transporting an electron from $\uparrow$ band into $\downarrow$ band. Thus Ni is a strong ferromagnet. $D(E_F)$ is apparently high and consists of minority-spin electrons.

Figure 5.8: (Left) The exchange-split 3$d$ bands of ferromagnetic Ni. The density of states consists of minority-spin electrons at $E_F$. (Right) Energy-distribution curves of Ni proving the existence of the exchange splitting in 3$d$ bands. Ref. [4].

The photoemission results near the $E_F$ provide a test for the ideas presented above. On the right-hand side of the figure we observe spin-resolved energy distribution curves obtained from Ni(110) at different temperatures below $T_C$. Indeed, the emission of electrons with antiparallel spins dominate at $E_F$, and the two exchange-split bands are well resolved. The splitting is more pronounced as the temperature is lowered thus proving that the splitting is of magnetic origin.\footnote{E. Kisker et al., Phys. Rev. Lett. 43, 966 (1979).}

ESP is determined in a so-called Mott scattering of electrons at energies above 100 keV. It makes use of the relativistic effect that there is a left-right intensity asymmetry for large scattering angles in the scattering plane proportional to ESP. To avoid multiple scattering, the experiments are done either at atomic beams or at extremely thin films of heavy metals, preferably Au. Thus, the efficiency of Mott scattering is around $10^{-4}$, which presents a drawback for the spin-resolved experiments.
5.2.4 Localized States

Nearly-free electron states are well accounted for by the one-electron approximation. Localized electrons, on the other hand, are confined near the atomic core where a positive charge due to a core state is effectively screened by the conduction electrons. As a result, localized electrons feel the hole state in photoemission as an additional positive charge, and the orbitals adjust themselves depending on the interaction with the hole state. Most often there are several holes for a given $h\nu$, and we observe several different final states, called the multiplets.

\[
\text{Neodymium} 
\begin{align*}
4f^3 & \to 4f^2 + e^- \\
l_1 = l_2 = 3 & \quad L = l_1 + l_2, \ldots, |l_1 - l_2| \\
& = 6, 5, 4, 3, 2, 1, 0 \\
J = L+\Sigma, \ldots, L-\Sigma
\end{align*}
\]

\[
\text{Hund rule} 
\begin{align*}
ground \text{ state} & \quad S \text{ max} \\
& \quad L \text{ max} \\
& \quad J = L - S / L + S
\end{align*}
\]

Figure 5.9: Photoemission spectrum from Nd near $E_F$ and a calculation of the multiplet structure of the final state. Ref. [5].

The 4$f$ electrons of rare earth metals are located near $E_F$ and show an atomic behavior. They do not participate in chemical bonding. Neodymium has in the ground state 4$f^3$ configuration. To find the symmetry in the ground state we apply the Hund’s rules. Three electrons result in a total orbital moment of $L = 6$ as the boxes show. Total spin moment is $3/2$. Since the $f$ band is less than half full, the total $J = L - S = 9/2$. The resulting term symbol is then $^4I_{9/2}$.
Photoemission leaves behind the $f$ band with one hole, in the $4f^2$ configuration. As seen from Figure 5.9 there are 13 final-state multiplets. This multiplet structure dominates the photoemission spectrum. We observe a huge emission intensity due to the $4f$ electrons at an energy which corresponds to a binding energy of about 5 eV. This is in fact not the binding energy, but the correlation energy we have to pay additionally to remove an electron from the $4f$ band.

Figure 5.10: The periodic table for the rare earth elements and photoemission spectra of $4f^{n-1}$ state in Gd, Tb, Dy, and Sm. Ref. [5].

Figure 5.10 shows on the left-hand side the multiplet manifolds of the $4f^7$, $4f^8$, and $4f^9$ final states in Gd, Tb, and Dy, respectively.\(^5\)

In localized systems, the occupation is always an integer number, like in atoms, because these states do not mix with others. The binding energy of the localized states is a function of the occupation, as it is known from atoms. In SmB$_6$, Sm exists in two different valencies, as Sm$^{3+}$ and Sm$^{2+}$, because interestingly the energies of $4f^{n+1}$ and $4f^n5d$ state ($n = 5$) are almost the same. As a result the system fluctuates between the two states. Photoemission is faster than the fluctuation frequency and hence records both states in one single spectrum. The multiplets of Sm ion with fluctuating valency are displayed on the right-hand side of the figure.

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5.2.5 Resonant Photoemission

For the $3p - 3d$ excitation in $3d$ transition metals there is a large overlap between the $3p$ hole and the excited $3d$ electrons, and the Coulomb interaction between the initial and final state is large. As a result, the independent electron description breaks down, and the $3p - 3d$ transition spectrum resembles that encountered in isolated atoms. Thus, the observed structure in the emission spectrum is due to the final-state multiplets arising from the $3p^63d^N \rightarrow 3p^53d^{N+1}$ excitation, broadened asymmetrically by resonant interaction between the different discrete configurations and continua.\(^6\) The excited state rapidly decays via $3p^53d^{N+1} \rightarrow 3p^63d^{N-1} + e^-$. The $3p^63d^{N-1}$ state can directly be reached by the excitation of a $3d$ electron. Whenever there are two coherent channels leading from an initial to the same final state, resonances are encountered between the discrete channels and continua. Such resonances are also referred to as Fano resonances.\(^7\) The emitted electron carries information about the detailed processes.

![Figure 5.11: Resonant photoemission in a gadolinium film grown on copper. Ref. [8].](image)

These are atomic-like processes because a) $d$ bands are narrow, b) there is a large overlap between the states involved, c) the time scale for the decay of the self-screened state is extremely short. These processes are also encountered in the $4d$ transition metals and $4f$ rare earth metals.

In Gd the $4d - 4f$ transition energy is about 140 eV leading to the transition $4d^{10}5s^25p^64f^7 \rightarrow 4d^95s^25p^64f^8$. By analyzing the photoemitted electron from different...\(^6\)L.C. Davies and L.A. Feldkamp, Solid State Commun. 19, 413 (1976).

ferent states of Gd at the photon energy of about 140 eV, we investigate different
decay channels of the excited state.\(^8\)

Figure 5.11 displays photoemission spectra recorded at different photon energies
below and above the \(4d - 4f\) transition energy. The spectra are presented in three
regions, where we observe the \(4f\), \(5p\), and \(5s\) resonances. The former is displayed
at the right-hand side at low binding energies up to 20 eV. In this energy region
we observe the direct recombination \(4d^95s^25p^64f^8 \rightarrow 4d^{10}5s^25p^64f^6 + e^-\). The
strength of resonance emission is evident at the relevant \(d - f\) transition energy as \(h\nu\) is scanned.

Figure 5.11 shows in the middle panel spectra in the \(E_B\) region of Gd \(5p\)
electrons. Different spectra are obtained at various \(h\nu\) scanning the \(d - f\) transition
energy. Now we focus on the recombination \(4d^95s^25p^64f^8 \rightarrow 4d^{10}5s^25p^54f^7 + e^-\) as
observed in the enhancement of emission for the \(5p\) states.

We observe finally the recombination of \(5s\) states in the same figure on the left-
hand side panel. \(E_B\) is tuned for the appropriate energy. The decay channel is
\(4d^95s^25p^64f^8 \rightarrow 4d^{10}5s^15p^64f^7 + e^-\), and the emitted electron carries information
about the intriguing processes. Note that the system behaves like an atom far from
the independent-electron approximation.

\(^8\)J.A. Scarfe et al., phys. stat. sol. (b) 171, 377 (1992).