Chapter 9

Theoretical Concepts of Spin-Orbit Splitting

9.1 Free-electron model

In order to understand the basic origin of spin-orbit coupling at the surface of a crystal, it is a natural starting point to consider a free-electron model. The model describes a 2D electron gas (2D-EG) with spin-orbit interaction, applicable to surface states that are localized in the near surface plane [83]. The model Hamiltonian will be written as

$$H = \frac{p^2}{2m} + H_R \ , \tag{9.1}$$

with the Rashba Hamiltonian

$$H_R = \alpha \left(\vec{e}_z \times \vec{k} \right) \vec{\sigma} \ . \tag{9.2}$$

Solutions of the Schrödinger equation with the Hamiltonian of Eq. 9.1 can be found analytically. We choose a Cartesian coordinate system with the z-axis perpendicular to the 2D plane of electron motion. It can be shown (see Appendix C) that the free-electron parabolic dispersion will now be split in two parabola, shifted in k direction with energies

$$E_{1,2} = \frac{\hbar^2 k^2}{2m} \pm \alpha \hbar k \tag{9.3}$$

The associated wave functions have the form

$$\psi_1(r) = e^{i\vec{k}\vec{r}}(|\uparrow\rangle + ie^{i\theta_k}|\downarrow\rangle) \qquad for \ \ E_1 = \frac{\hbar^2 k^2}{2m} + \alpha\hbar k, \tag{9.4}$$

$$\psi_2(r) = e^{i\vec{k}\vec{r}}(ie^{-i\theta_k}|\uparrow\rangle + |\downarrow\rangle) \qquad for \ \ E_2 = \frac{\hbar^2 k^2}{2m} - \alpha\hbar k. \tag{9.5}$$

The spin functions $|\uparrow\rangle, |\downarrow\rangle$ denote spin-up and spin-down electron states, respectively, with respect to the z direction; θ_k is the angle between $\vec{k}$ and x-axis, according to geometry illustrated in Fig. 9.1. The linear combination of
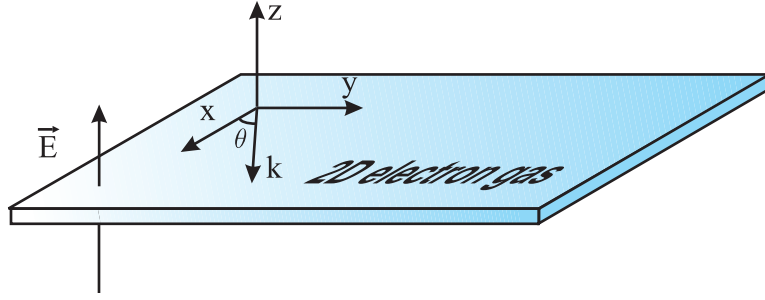
Figure 9.1: Geometry considered in the free-electron model.

spin-up and spin-down states in the eigenfunctions 9.4 and 9.5 describe a spin polarization within the xy-plane (see Appendix C), which is oriented perpendicular to the direction of electron motion. This means that, the electrons with the same k vector and opposite spins will have different energies.

The results derived from this model are illustrated in Fig. 9.2. In the lower part, the Rashba spin-orbit split energy dispersion of a (free-electron like) surface state is presented. The two concentric circles in the upper part represent the corresponding Fermi surfaces, with arrows indicating the in-plane spin orientations that are always perpendicular to the electron momentum.

The most important results of the model are: (1) it correctly describes the nature of the splitting and, (2) it shows that Rashba type spin-orbit interaction will orient the spins of propagating electrons. However, the size of the splitting, estimated by using the surface potential gradient, is much too small compared with experimental values. The surface potential gradient can be roughly approximated by $(\nabla V)_z \approx \Phi/\lambda_F$, with the work function Φ and the Fermi wavelength λ_F [84] . Applied to the case of Au(111) ($\lambda_F = 5\text{Å}$ and $\Phi = 4.3$ eV), this leads to an estimated value of $\Delta E = 10^{-6}$ eV, which is several orders of magnitude smaller than the experimentally observed splitting. This deficit is inherent in the free electron model, which does not account for regions of steep nuclear potential gradients near atomic cores.

Shockley-type surface states penetrate as deep as several atomic layers into the bulk [85]. It has been shown by G. Bihlmayer [70] for the example of the gold surface state, that regions near atomics cores have also to be taken into account when describing the Rashba splitting of a surface state. The potential gradients close to the nucleus of an atom, leading to atomic spin-orbit splitting, are orders of magnitude larger than the gradient of surface barrier, and its consideration leads to an increase of the Rashba splitting.

In order to obtain a better understanding of the atomic contributions to spin-orbit interaction at the surface, a tight-binding model shall be considered next.
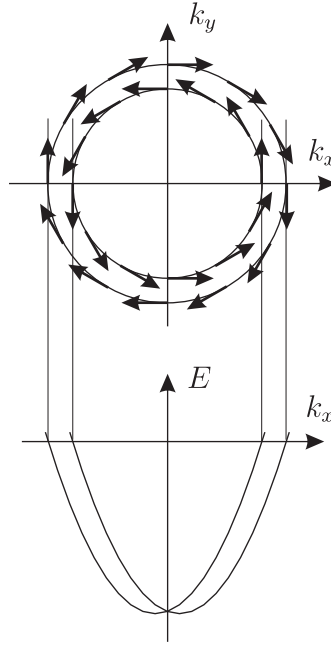
Figure 9.2: Energy dispersion of free-electron state with Rashba splitting bottom part together with the corresponding Fermi surfaces (upper part). Arrows indicate spin orientations of electrons at the Fermi surface.

9.2   Tight-binding model

The free-electron model is built upon the assumption that electrons propagate almost freely and that their wave functions can be approximated by plane waves. As an "opposite" starting point, one can use localized atomic orbitals as a basis set to perform band-structure calculations; this is the tight binding (TB) or linear combination of atomic orbitals (LCAO) approach.

   This approach was developed in molecular physics and has been extended to the description of electronic states in solids. As a starting point, we consider two identical but separate atoms with their (atomic) wave function for a single valence electron. As we bring them together, the interaction between the two valence charges will lead to the formation of new orbitals, the so-called bonding and antibonding orbitals. The energy of the bonding orbital is lowered by an amount that is determined by the interaction Hamiltonian, and the energy of the antibonding orbital is raised by the same amount. The matrix elements of the interaction Hamiltonian between atomic orbitals are usually referred to as overlap parameters. They have a simple physical interpretation as interaction strength between electrons on adjacent atoms. The concept of bonding and antibonding orbitals is easily extendable to crystals, if we assume that atomic orbitals of each atom in the crystal overlap with whose of its nearest neighbors only. This is a reasonable approximation for many solids. As a result of the overlap (during crystal formation) bonding and antibonding orbitals broaden forming valence and conductions bands, respectively. Of course, the crystal

structure strongly affects the overlap between the atomic orbitals.

Surface states at a crystal surface form a two-dimensional manifold of energy eigenstates. For the present approach, we take Wannier functions to form a basis set. Surface states are localized states that decay exponentially into the bulk. To represent the essential physics of spin-orbit interaction, we use p-orbitals as an example, keeping the model simple and transparent, and to reveal the important ingredients of the Rashba effect. For sp-derived surface states, like those at the Au(111) surface, this is sufficient, since s-states do not contribute to spin-orbit interaction (zero angular momentum). For Gd and Tb, however, it is not fully correct to consider p-states, since the surface state in this case has d_{z^2} character (derived from the bulk d-band). Construction of the model with d-orbitals included can be done in full analogy to the case with p-orbitals as a basic set. However, including d-states will increase the number of basis functions and will probably conceal the main idea of this consideration, i.e. to obtain a transparent and clear physical picture of the problem. Instead, we will rather compare with results of density-functional-theory (DFT) calculations, see below.

The Gd(0001) and Tb(0001) surfaces considered in this work have a six-fold symmetry at the surface. Accordingly, surface states are described in the model with sheet of hexagonally arranged atoms using the three atomic orbital functions p_x, p_y, p_z, where the in-plane orbitals p_x and p_y are coupled in the usual way by the help of the directional cosine.

Atomic orbitals can be expressed as the product of a radial wave function and spherical harmonics $Y_l^m(\theta, \phi)$, with the atomic nucleus chosen as the origin. In case of two atoms, it is convenient to choose coordinate axes such that the z-axis is parallel to the vector $\vec{d}$ connecting the atoms, and the azimuthal angles are the same. The interaction Hamiltonian will have cylindrical symmetry with respect to $\vec{d}$ and therefore cannot depend on ϕ. Symmetry consideration permits to gradually reduce the number of overlap parameters, which have to be found by sorting out zero and equals integrals. For a crystal lattice, it is convenient to choose crystallographic axes as coordinate axes, and the spherical harmonics $Y_l^m(\theta, \phi)$ of the atomic orbitals are defined with respect to a fixed coordinate system. In calculating the overlap parameter for any pair of neighboring atoms, one expands the spherical harmonics defined with respect to $\vec{d}$ in terms of $Y_l^m(\theta, \phi)$. Figure 9.3 illustrates this expansion for p-orbitals.

If one considers the surface layer as an isolated system, p_x and p_y would not couple to the p_z orbital. Inversion symmetry $z \rightarrow -z$ would lead to an equally large overlap of a p_x, p_y lobe with the positive and negative p_z lobe, resulting in a zero total overlap. At the surface, this symmetry is obviously broken due to the surface potential, $V(z)$, which breaks the symmetry of the electron density distribution of surface states with respect to the surface plane. Only the p_x, p_y orbitals will retain the symmetry of their atomic counterparts. This effect can be included by actually coupling p_x, p_y, and p_z states.

As was found by Petersen and Hedegard [83], the simplest tight-binding Hamiltonian that allows us to discuss the influence of SOC (on the 2D electronic structure) has the form
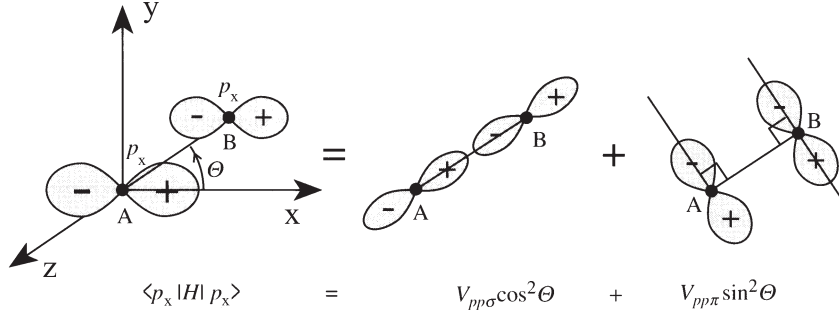
Figure 9.3: Projection of the overlap parameter between p_y orbitals onto directions along the vector $\vec{d}$ joining the two atoms and perpendicular to $\vec{d}$. From Ref. [86].

$$H_0 = \sum t_{\alpha\beta}(\mathbf{R}_i - \mathbf{R}_j) \, |p_\alpha(\mathbf{R}_i), \sigma\rangle \, \langle p_\beta(\mathbf{R}_j), \sigma| \ , \qquad (9.6)$$

where $t_{\alpha\beta}(\mathbf{R}_i - \mathbf{R}_j)$ is the overlap matrix element given by

$$t_{\alpha\beta}(\mathbf{R}_i - \mathbf{R}_j) = \begin{cases} w\cos^2(\theta_{ij}) + \delta\sin^2(\theta_{ij}) & (\alpha,\beta) = (x,x) \\ (w+\delta)\cos(\theta_{ij})\sin(\theta_{ij}) & (\alpha,\beta) = (x,y) = (y,x) \\ w\sin^2(\theta_{ij}) - \delta\cos^2(\theta_{ij}) & (\alpha,\beta) = (y,y) \\ \gamma\cos(\theta_{ij}) & (\alpha,\beta) = (x,z) = (z,x) \\ \gamma\sin(\theta_{ij}) & (\alpha,\beta) = (y,z) = (z,y) \\ -\delta & (\alpha,\beta) = (z,z) \end{cases}$$

for $\mathbf{R}_i$ and $\mathbf{R}_j$ pointing towards nearest-neighbor lattice sites only; all other matrix elements are zero. θ_{ij} is the angle between the vector $(\mathbf{R}_i - \mathbf{R}_j)$ and the x-axis. Parameter w denotes the $V_{pp\sigma}$ and δ is a shorthand for $V_{pp\pi}$. $V_{pp\sigma}$ and $V_{pp\pi}$ are visualized in Fig. 9.3; their physical interpretation is given by the matrix elements of the interaction Hamiltonian (9.6) that have been calculated [87, 88] for different lattices and can be found in the literature. The parameter $\gamma = \langle p_z(\mathbf{R}) | V | p_n(\mathbf{R} + \mathbf{x})\rangle$ $(n = x, y)$ is essentially a measure of the surface potential gradient; it has a similar meaning as $\frac{\partial V}{\partial z}$ in the free electron model discussed above. The case $\gamma = 0$ corresponds to a 2D model with inversion symmetry.

By forming Bloch waves with overlap matrix elements written above and by diagonalizing the resulting matrix, we can solve the problem given by the Hamiltonian (9.6). Without taking into account the electron spin, the resulting matrix will be only 3×3. From here, with $\gamma/w = 0.1$ and $\delta/w = 0.3$, we obtain the band structure shown in Fig. 9.4. The band with a minimum at the Γ point is primarily of p_z character. The true surface states correspond to the free-electron-like part of this band around the Γ point. Also, there are strongly dispersive bands with minima at the M-point and along the Γ-K direction; they have primarily p_x, p_y character. The gaps appear due to the broken symmetry with respect to reflection $z \to -z$, which is controlled by the γ parameter; the
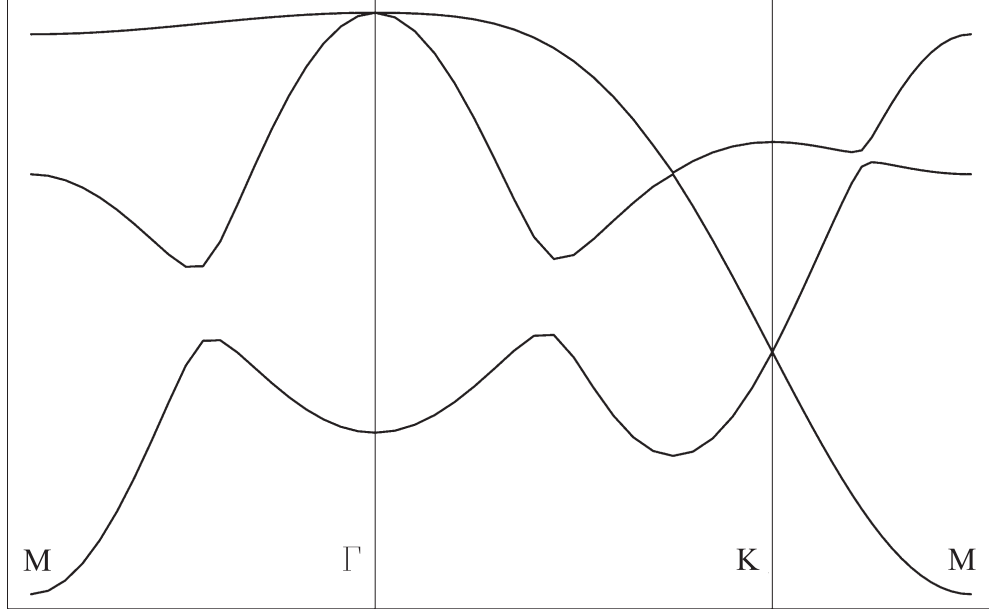
Figure 9.4: Tight-binding-model band structure for surface states in a two-dimensional hexagonal lattice, derived from p-orbitals without spin-orbit interaction. The true surface states belong to the free-electron-like band around the Γ point with primarily p_z character; from Ref. [83].

gaps disappear when $\gamma = 0$, and symmetry is restored. Only the free-electron-like band around the Γ point resides inside a gap of the projected bulk band structure in a real crystal and therefore can be identified as a true surface state.

To introduce spin-orbit interaction into our model, we take the Hamiltonian

$$H_{soc} = \alpha \mathbf{L} \cdot \mathbf{S} = \frac{\alpha}{2}(L^+ \sigma^- + L^- \sigma^+ + L^z \sigma^z), \tag{9.7}$$

where $L^\pm$ are angular momentum step-up/step-down operators and $\sigma^\pm$ are the same for the spin, α is the atomic spin-orbit constant. Now, when taking into account the spin parts of the atomic wave functions used as basis set $\{|p_x, \uparrow\rangle, |p_x, \downarrow\rangle, |p_y, \uparrow\rangle, |p_y, \downarrow\rangle, |p_z, \uparrow\rangle, |p_z, \downarrow\rangle\}$, the resulting matrix becomes

$$H_{soc} = \frac{\alpha}{2} \begin{vmatrix} 0 & -i & 0 & 0 & 0 & 1 \\ i & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & i & 0 \\ 0 & 0 & -1 & 0 & i & 0 \\ 0 & 0 & -i & -i & 0 & 0 \\ 1 & i & 0 & 0 & 0 & 0 \end{vmatrix}. \tag{9.8}$$

Inspection of the H_{soc} matrix directly reveals that, for spin-orbit interaction to become effective, it is necessary to have p_x and p_y states in the model. Otherwise, as can be seen from the 2×2 block of zeros in the lover right corner of the matrix that corresponds to p_z states, no spin-orbit interaction will be present.
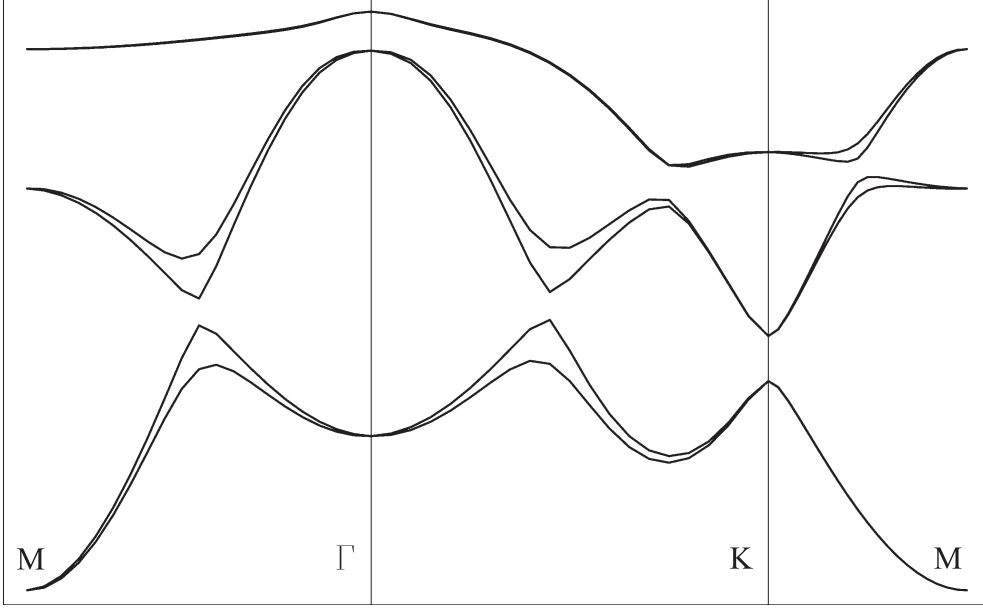
Figure 9.5: Band structure with spin-orbit splitting for surface states within the tight-binding model constructed from p-orbitals in a two-dimensional hexagonal lattice. The true surface states belong to the free-electron-like band around the Γ point. The splitting is determined by the atomic spin-orbit coupling strength, α.

By including H_{soc} in the Hamiltonian (9.6), one can derive the spin-orbit-split band structure. The result of the calculation with $\alpha = 0.2w$ is presented in Fig. 9.5 .

The idea of this section is not only to demonstrate that the free-electron model and the tight-binding model can provide some insight into the role of spin-orbit interaction in the surface electronic structure, but also to demonstrate the important contribution of atomic spin-orbit coupling to the Rashba splitting of surface states. For this purpose, we will limit ourselves to the subspace of the Hilbert space that is spanned by p_z-like states. A simple truncation of the Hamiltonian to this subspace will give no spin-orbit interaction, since this requires breaking parity which is only achieved by an admixture of $p_{x,y}$ states, i.e. by a coupling between p_z and $p_{x,y}$ orbitals. To account for these bands, these virtual transitions to them should be included to second order in the coupling. This is possible as long as the p_z and the p_x, p_y bands are well separated in energy.

From a mathematical point of view, we follow the work by Petersen and Hedegard [83]. One writes the resolvent $(\epsilon - H)^{-1}$, which is the Laplace transformation of the time evolution operator, and consequently includes all necessary information. Since we consider only the subspace spanned by p_z and we are interested in the time evolution of the low-energy bands, our projected resolvent is $P(\epsilon - H)^{-1}P$, where P is the projection operator onto the p_z subspace. From linear algebra one obtains [83]:

$$P\frac{1}{\epsilon - H}P = \frac{1}{\epsilon - PHP - PHQ\frac{1}{\epsilon - QHQ}QHP} \, ,$$

where Q projects onto the complement of P, i.e. $Q = 1 - P$. Therefore the effective Hamiltonian for the p_z subspace takes the form:

$$H_{eff} = PHP + PHQ\frac{1}{\epsilon - QHQ}QHP \, .$$

For ϵ and QHQ in the denominator, we make the following approximation. Since we are interested in k points close to the Γ point, $\epsilon \simeq \epsilon_z^0(k = 0)$ and $QHQ \simeq Q\epsilon_{x,y}^0(k = 0)$ will be a good approximation, where $\epsilon_i^0(k)...$ denotes the unperturbed band structure.

This procedure, performed to second order in α, γ, and k, yields the following expression for the subspace spanned by the p_z orbitals:

$$H_{eff} = \begin{pmatrix} -6\delta + (\frac{3}{2}\delta + 9\gamma^2/w)k^2 & -6i(k_x - ik_y)\alpha\gamma/w \\ 6i(k_x + ik_y)\alpha\gamma/w & -6\delta + (\frac{3}{2}\delta + 9\gamma^2/w)k^2 \end{pmatrix} \, .$$

We can now directly identify the contributions to the Hamiltonian that describe the system with spin-orbit interaction. The diagonal terms are similar to the free-electron-model case, with the effective mass determined by δ. The off-diagonal term corresponds to the Rashba spin-orbit term, and the parameter α_R is equal to $6\alpha\gamma/w$. This explicitly demonstrates that the Rashba spin-orbit interaction at the surface depends on the atomic spin-orbit parameter (α), as well as on the potential gradient at the surface, described by the parameter γ. When setting γ to zero, which corresponds to a switching-on of the inversion symmetry, the Rashba splitting will be removed. Also, the disappearing of the atomic spin-orbit interaction will lead to a vanishing of the Rashba splitting.

With this consideration, we have achieved a connection between the free-electron model and the tight-binding model.

Finally, we like to mention that atomic spin-orbit interaction is responsible for a pronounced Z-dependence of the Rashba surface-state splitting. From the present tight-binding model calculations (Ref. [83]) it can be understood why the Rashba splitting should be of the same order of magnitude as the atomic splitting, and not much smaller as was estimated earlier using the free-electron approach.