Theory of anisotropic Rashba splitting of surface states

E. Simon\textsuperscript{1,2}, A. Szilva\textsuperscript{3}, B. Ujfalussy\textsuperscript{1}, B. Lazarovits\textsuperscript{1,3}, G. Zarand\textsuperscript{3}, and L. Szunyogh\textsuperscript{1}\textsuperscript{3}

\textsuperscript{1}Hungarian Academy of Sciences, Institute for Solid State Physics and Optics, H-1525 Budapest, PO Box 49 H-1525 Hungary
\textsuperscript{2}\Lránd Eötvös University, Department of Physics, H-1518 Budapest POB 32, Hungary
\textsuperscript{3}Department of Theoretical Physics, Budapest University of Technology and Economics, Budafoki út 8., H-1111 Budapest, Hungary

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We investigate the surface Rashba effect for a surface of reduced in-plane symmetry. Formulating a $k\cdot p$ perturbation theory, we show that the Rashba splitting is anisotropic, in agreement with symmetry-based considerations. We show that the anisotropic Rashba splitting is due to the admixture of bulk states of different symmetry to the surface state, and it cannot be explained within the standard theoretical picture supposing just a normal-to-surface variation of the crystal potential. Performing relativistic \textit{ab initio} calculations we find a remarkably large Rashba anisotropy for an unreconstructed Au(110) surface that is in the experimentally accessible range.

Metallic surfaces often exhibit Shockley-type surface states located in a relative band gap of the bulk band structure, and forming a two-dimensional electron gas. One of the most intriguing manifestation of spin-orbit coupling (SOC) at surfaces is the splitting of these surface states, known as Rashba splitting \cite{1,2}. Such Rashba splitting was observed via photoemission by LaShell \textit{et al.} \cite{3} for the $L$-gap surface state at Au(111) and explained theoretically in terms of a tight-binding model \cite{4} and \textit{ab initio} electronic structure calculations \cite{5,6}, but several studies of the Rashba splitting were published in recent years on Bi(111) and Bi\textsubscript{2}/Ag(111) \cite{7,8}, as well as on Bi\textsubscript{2}Pb\textsubscript{1−x}/Ag(111), where atomic Bi\textsubscript{2}Pb\textsubscript{1−x} orbitals lead to a more pronounced spin-orbit splitting \cite{9,10,11}.

Describing and controlling the Rashba splitting of surface states is crucial for spintronics applications. The famous Datta-Das transistor relies on the electric tuning of the Rashba splitting \cite{12} and the Rashba splitting is responsible for the spin Hall effect in two dimensions \cite{13} and the anomalous Hall effect \cite{14} as well.

The simplest way to understand the origin of the Rashba effect is to take nearly free electrons, confined by a crystal potential, $V(r) = V(z)$, and having a plane-wave-like wave function, $\psi_{s,k}(r) = e^{ikr} \phi(z) \chi_s$, with $\chi_s$ some spinor eigenfunctions, and $k$ the momentum parallel to the surface. The crystal potential $V(z)$ obviously produces an electric field, $E$, perpendicular to the surface, which, in the presence of spin-orbit interaction leads to the following spin-orbit term in the effective Hamiltonian,

$$H_R(k) = \alpha_R (k_x \sigma_y - k_y \sigma_x) ,$$

called Rashba-Hamiltonian. In Eq. 1, $\sigma_i$ denote the Pauli matrices and $\alpha_R = \frac{\hbar^2}{2m_e} \int d^2r |\phi(z)|^2 \partial_z V(r)$ is the so-called Rashba parameter. The eigenvalue problem can then easily be solved, resulting in a splitting of the spin-degeneracy of the surface states, $\varepsilon_{\pm}(k) = \frac{\hbar^2}{2m_e} k^2 \pm \alpha_R |k|$, with $m^*$ the effective mass of the surface electrons \cite{15,16}. Clearly, the above dispersion is isotropic in $k$-space, hence we term it as isotropic Rashba splitting.

Although real systems cannot be described in terms of free electrons, and for quantitative estimates of $\alpha_R$ the atomic structure of the potential needs be taken into account \cite{17}, the structure of the Rashba interaction, Eq. 1, is very robust for surfaces of high point-group symmetry such as $C_{3v}$ or $C_{4v}$ \cite{18}.

The situation is, however, quite different for surfaces (or points in the surface Brillouin zone) of reduced symmetry. Such Shockley-type surface states emerge, e.g., around the $\Gamma$ point of the Surface Brillouin Zone of unreconstructed and $(2\times1)$ reconstructed Au(110) surfaces, as revealed by recent high-resolution photoelectron spectroscopy experiments \cite{19}. In this case, the $C_{2v}$ point-group symmetry of the system not only implies the asymmetry of the effective mass, $m^*_x \neq m^*_y$ (for the crystal axes see Fig.1) but, in leading order in $k$, representation theory also predicts the following simple form of the effective Hamiltonian \cite{19},

$$H(k) = \varepsilon_0 + \frac{k^2}{2m_e} \sigma_x + \frac{k^2}{2m_e} \sigma_y - \alpha_{R,x} k_x \sigma_y - \alpha_{R,y} k_y \sigma_x .$$

The above expression can easily be justified by simple symmetry analysis, just by noticing that $\sigma_y$ and $-\sigma_x$ transform as $p_x$ and $p_y$ under the operations of the double groups of $C_{2v}$ and $C_{4v}$. From this observation it also follows that in case of $C_{4v}$ point-group symmetry $\alpha_{R,x} = \alpha_{R,y}$ must be satisfied, and the Hamiltonian 1 is recovered. \cite{20}

Although the above form of the Rashba interaction has been predicted in Ref. 15, no microscopic theory has been constructed so far to support it. While previous \textit{ab initio} calculations \cite{17,18} did find a Rashba splitting of the Au(110) surface state, they focused only on the dispersion along the $\Gamma\bar{V}$ direction, and therefore the anisotropy of the Rashba term remained unnoticed. In the present paper, we provide such a microscopic analysis.
for an Au(110) surface with $C_{2v}$ point-group symmetry. First, constructing a $\mathbf{k} \cdot \mathbf{p}$ perturbation theory for the surface states we show that the above anisotropic Rashba structure appears naturally, and is due to the finite momentum mixing of the bulk $p$ states to the surface-state. We also perform ab initio calculations of the Rashba-split surface state of an unreconstructed Au(110) surface and confirm with a high numerical accuracy that there is a large anisotropy in $k$-space, $\alpha_{R,x} \sim 5 \alpha_{R,y}$, in agreement with Eq. (2). The predicted anisotropic Rashba splittings turn out to be within the range of experimental accuracy.

Bloch-states of Au(110) can be characterized by a surface momentum, and can thus be written as

$$\psi_{\mathbf{Q}+\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}\phi_{\mathbf{Q},\mathbf{k}}(\mathbf{r}) ,$$

with the momentum $\mathbf{k}$ measured with respect to the momentum $\mathbf{Q}$ associated with the $\bar{Y}$ point of the Surface Brillouin Zone. Here the functions $\phi_{\mathbf{Q},\mathbf{k}}(\mathbf{r})$ are lattice-antiperiodic in the $x$ direction, while they are lattice periodic in the $y$ direction of the (110) plane, see Fig. 1. For any given momentum, $\mathbf{k}$, there exist an infinite number (continuum) of eigenstates, the energy of which ($\varepsilon_k$) is determined by the condition that the states $\psi_{\mathbf{Q}+\mathbf{k}}$ be eigenstates of the Hamiltonian, $H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) + H_{SO}$, with $H_{SO}$ denoting the spin-orbit coupling,

$$H_{SO}(\mathbf{r}) = \frac{\hbar^2}{4m^2c^2} (\nabla V(\mathbf{r}) \times \mathbf{p}) \sigma .$$

As a consequence, the functions $\phi_{\mathbf{Q},\mathbf{k}}$ must satisfy the equation,

$$\left( \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) + \frac{\hbar^2}{2m} \mathbf{k} \cdot \mathbf{p} + H_{SO}(\mathbf{k},\mathbf{r}) \right) \phi_{\mathbf{Q},\mathbf{k}}(\mathbf{r}) = \varepsilon_k \phi_{\mathbf{Q},\mathbf{k}}(\mathbf{r}) ,$$

with $\tilde{H}_{SO}(\mathbf{k},\mathbf{r})$ being the effective SO coupling,

$$\tilde{H}_{SO}(\mathbf{k},\mathbf{r}) = H_{SO}(\mathbf{r}) + \frac{\hbar}{4m^2c^2} (\nabla V(\mathbf{r}) \times \mathbf{p}) \sigma .$$

Similar to Bloch wave functions, for any fixed momentum, $\mathbf{k}$, (and for any value of $\tilde{H}_{SO}$) the functions $\phi_{\mathbf{Q},\mathbf{k}}$ form a complete set for functions having the previously-mentioned periodicity property. In the spirit of $\mathbf{k} \cdot \mathbf{p}$ perturbation theory, we can thus take the complete set of $\mathbf{k} = 0$ and $\tilde{H}_{SO} = 0$ solutions, satisfying

$$\left( \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) \right) \phi_{i,n_i}(\mathbf{r}) = \varepsilon_{i,n_i} \phi_{i,n_i}(\mathbf{r}) ,$$

and expand $\phi_{\mathbf{Q},\mathbf{k}}$ in terms of these. Here we classified the solutions according to the four one-dimensional irreducible representations of the $C_{2v}$ symmetry associated with the point $\bar{Y}$, $\mathbf{i} \in \{x, y, xy\}$, and labeled solutions of a given symmetry by $n_i$. As shown in Fig. 1, the spectrum contains a discrete surface state of $s$-symmetry and the projected bulk continuum forming the gap. Let us denote the $\mathbf{k} = 0$ surface state by $\phi_0$, and its eigenenergy by $\varepsilon_0$. Then states with $\mathbf{k} \neq 0$ but with $\tilde{H}_{SO} \equiv 0$ can be expressed in terms of the states $\phi_{i,n_i}$ by performing second order perturbation theory in $\mathbf{k}$, which amounts in a surface state

$$|\phi_k^0\rangle = |\phi_0\rangle + \frac{1}{m} \sum_{i,n_i \neq 0} |\phi_{i,n_i}\rangle \langle \phi_{i,n_i} | \frac{\mathbf{k} \cdot \mathbf{p}}{m} | \phi_0 \rangle ,$$

with approximate dispersion

$$\varepsilon_k^0 = \varepsilon_0 + \frac{\hbar^2}{2m} \mathbf{k}^2 + \frac{\hbar^2}{2m} \mathbf{k}^2 ,$$

$$\frac{1}{m} = \frac{2}{m} \sum_n |\langle \phi_{i,n_i} | \mathbf{p} | \phi_0 \rangle|^2 \frac{\varepsilon_0 - \varepsilon_{i,n_i}}{i} \quad (i = x, y) .$$

The index 0 in $\varepsilon_k^0$ and $|\phi_k^0\rangle$ is meant to remind us to the absence of SO interaction.

To obtain the surface states, $|\phi_k\rangle$, we then carry out first-order perturbation theory with the SOC operator, $\tilde{H}_{SO}$, using the states $|\phi_k^0\rangle$ as a starting point. Keeping just contributions linear in $\mathbf{k}$ we get two terms to the effective Rashba Hamiltonian. The second term in Eq. (10) gives rise to the usual isotropic Rashba model,

$$\hat{H}_R^{iso}(\mathbf{k}) = \alpha_R (\mathbf{e}_z \times \mathbf{k}) \cdot \sigma ,$$

with $\alpha_R = \frac{\hbar^2}{4m^2c^2} (|\phi_0\rangle \partial_z V/\partial z |\phi_0\rangle)$. The term $H_{SO}$ in Eq. (6), however, gives also a finite contribution due to the admixture of $p_{xy}$ states from the continuum and, in fact, this is precisely the term that leads to an anisotropic Rashba coupling,

$$H_R^{anis}(\mathbf{k}) =$$

$$= \frac{1}{m} \sum_{i=x,y} k_i \sum_{n_i} \langle \phi_{i,n_i} | \mathbf{p} | \phi_0 \rangle (|\phi_0\rangle \mathbf{a} | \phi_{i,n_i} \rangle \sigma ) + h.c. ,$$

where $\mathbf{a} = (\mathbf{e}_x \times \mathbf{k}, \mathbf{e}_y \times \mathbf{k})$.

FIG. 1: (Color online) Left: Sketch of the fcc(110) Surface Brillouin Zone. The dark area denotes the projection of the L-gap of bulk Au. Right: Structure of the surface energy spectrum in the absence of SO interaction, along the line $\mathbf{k} = (k_x, 0)$. Surface states in the relative gap with $\mathbf{k} \neq 0$ can be built up from states indicated by the thick black lines and the black circle at $\mathbf{k} = 0$. Note that $\mathbf{k} = 0$ corresponds to the $\bar{Y}$ point of the Brillouin zone, see Eq. (3).
where we defined the (axial)vector operator related to SOC, \( \mathbf{a} = \frac{1}{\hbar} (\nabla V(\mathbf{r}) \times \mathbf{p}) \). Using the symmetry of the unperturbed wave functions, a particularly simple form of the above anisotropic Rashba Hamiltonian can be obtained,

\[
H_R^{\text{anis}}(\mathbf{k}) = \lambda_x k_x \sigma_y + \lambda_y k_y \sigma_x ,
\]

with the coefficient \( \lambda_x \) expressed as

\[
\lambda_x = \frac{2}{\hbar} \sum_{n_x} \text{Re} \left( \langle \phi_{x,n_x} | p_x | \phi_0 \rangle \langle \phi_0 | a_y | \phi_{x,n_x} \rangle \right) (\varepsilon_0 - \varepsilon_{x,n_x}) ,
\]

and \( \lambda_y \) given by a similar expression. The structure of this term is identical to the one obtained by symmetry analysis. Decreasing the in-plane asymmetry of the potential (e.g., considering \( C_{4v} \), point group symmetry), the relationship, \( \lambda_x = -\lambda_y \), is satisfied, i.e., the Rashba splitting becomes isotropic. Nevertheless, even in this case, the anisotropic Rashba term, Eq. (13), arising from the mixing of the surface state with bulk states, also contributes to the Rashba splitting. Thus we find that, up to second order in \( \mathbf{k} \), surface states of Au(110) are described by Eq. (2), with \( \alpha_{R,x} = \alpha_R + \lambda_x \) and \( \alpha_{R,y} = -\alpha_R + \lambda_y \).

To obtain a quantitative estimate of the parameters \( \alpha_{R,x/y} \) and the induced Rashba splittings, we performed calculations of the surface states of unreconstructed Au(110) surface near the \( \bar{Y} \) point of the Surface Brillouin zone, using the relativistic Screened Korringa-Kohn-Rostoker (KKR) method. Details of this method are described in Refs. [21, 22]. The computed dispersion relations along the \( \bar{Y} (x) \) and the \( \bar{Y}S (y) \) directions are plotted in Fig. 2. The maximum binding energy, \( \varepsilon_0 \approx 370 \) meV, is by about 200 meV less than the measured value [17] and other theoretical values [17, 18]. This deviation is mostly caused by the atomic sphere approximation (ASA) and the angular momentum cut-off, \( \ell_{\text{max}} = 2 \), which resulted in some error for the determination of the Fermi level and the vacuum potential.

The nearly free-electron-like, parabolic shape of the dispersion as well as the Rashba splitting being remarkably different along the two directions is obvious from Fig. 2 and a detailed analysis confirms this impression: The numerical results are very well fitted by the dispersion relations. The obtained effective mass along the \( \bar{YS} \) direction is in satisfactory agreement with the measured value, \( m_y = 0.25 m_e \). The effective mass along \( \bar{Y} \), \( m_x \) is only about one third of \( m_y \), which is the consequence that the states at the lower bulk band edge are mainly of \( p_x \) and \( p_y \) character (see Eq. (4)). Note that the energy separation of the surface state at the \( \bar{Y} \) point is 0.8 and 3.4 eV with respect to the lower and upper bulk band edges, respectively, implying a strong admixture of “electron” states from the continuum below the surface state.

One of the most astonishing results of these numerical calculations is the remarkably large anisotropy of the Rashba parameters, \( \alpha_{R,x} \sim 5 \alpha_{R,y} \). In view of Eqs. (14), this observation can also be explained with the absence of \( p_y \) states at the lower bulk band edge. This result also correlates with the results of the effective mass: the smaller value of \( m_x \) indicates a stronger admixture of \( p_x \) states, also responsible for the stronger renormalization of \( \alpha_x \). We remark that \( \alpha_{R,x} \) is even larger than \( \alpha_R \) we calculated for the \( L \)-gap state of Au(111), 0.57 eV Å. This latter value is though considerably larger than the experimental one, 0.4 eV Å [22], which correlates with the theoretically computed effective mass, \( m^* \sim 0.19 m_e \), being too small as compared to the experimentally observed value, \( m^* \sim 0.25 m_e \). The computed Fermi wave numbers, \( k_F = 0.160 \) and \( 0.189 \) Å\(^{-1}\), on the other hand, are almost in perfect agreement with the measured values [23]. Nevertheless, based upon the discrepancy regarding the value of the effective masses, we expect that our theoretical calculations for Au(110) somewhat overestimate the Rashba parameters, \( \alpha_{R,x/y} \).

The anisotropic Rashba coupling together with the anisotropic effective mass gives rise to two Rashba-split Fermi surfaces for the surface states, as shown in Fig. 3. The Rashba splitting along \( \bar{YS} \), \( \Delta k_y \approx 0.017 \) Å\(^{-1}\) is in the order of the experimental resolution (0.01 Å\(^{-1}\)) [17], but the value \( \Delta k_x \approx 0.026 \) Å\(^{-1}\) implies that the Rashba splitting should be detectable experimentally along the \( \bar{Y} \) direction.

In Fig. 4 we also show the polar plot of the energy splitting, \( \Delta \varepsilon(k) = \varepsilon_+(k) - \varepsilon_-(k) \), between the two bands at the inner Fermi surface (\( \varepsilon_+(k) = \varepsilon_F \)). As a comparison, the same quantity is displayed for the surface state

\[
\Delta \varepsilon(k) = \varepsilon_+(k) - \varepsilon_-(k) .
\]
FIG. 4: (Color online) Energy differences, $\Delta \varepsilon(k) = \varepsilon_+(k) - \varepsilon_-(k)$, for the Rashba-split surface state of Au(110) (solid line) and Au(111) (dashed line) as a function of the polar angle $\varphi = \arctan \frac{k_y}{k_x}$, shown in units of degree around the graph. The magnitude of $k$ was fixed to satisfy $\varepsilon_+(k) = \varepsilon_F$. The energy scale is indicated by the axis on the left.

In summary, we constructed a $k \cdot p$ perturbation theory for surface states in the presence of SO coupling, and derived a generalized Rashba Hamiltonian for (nearly free) electrons on metal surfaces. We found that in case of $C_{2v}$ symmetry, the Rashba interaction gets an anisotropic part in first order of $k$, which for Au(110) is found to dominate over the additional, well-known symmetric term. The anisotropic Rashba term appears due to the mixing of the surface state with the bulk states for finite momenta. Even for surfaces of higher symmetry, this mechanism (i.e., the corresponding term in $k \cdot p$ perturbation theory) gives a large contribution to the isotropic part of the Rashba Hamiltonian. Based on fully relativistic first-principles electronic structure calculations, we also demonstrated that a strongly anisotropic Rashba coupling should be experimentally observable for Au(110) surfaces.

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* Electronic address: szunyogh@phy.bme.hu

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