Spin-orbit splitting of image states

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Abstract. We quantify the effect of the spin-orbit interaction on the Rydberg-like series of image state electrons at the (111) and (001) surface of Ir, Pt and Au. Using relativistic multiple-scattering methods we find Rashba-like dispersions with $\Delta E_{SO}(K) = \gamma K$ with values of $\gamma$ for $n = 1$ states in the range 38 – 88 meV Å. Extending the phase-accumulation model to include spin-orbit scattering we find that the splittings vary like $1/(n + a)^{3/2}$ where $a$ is the quantum defect and that they are related to the probability of spin-flip scattering at the surface. The splittings should be observable experimentally being larger in magnitude than some exchange-splittings that have been resolved by inverse photoemission, and are comparable to linewidths from inelastic lifetimes.

1. Introduction

Image states [1] are a special class of weakly bound surface electronic states in which an electron outside a dielectric or conductor polariases the surface and is then attracted to the resulting “image charge”. Asymptotically the potential varies like $V(r) \sim -(4z)^{-1}$ so that a band gap preventing penetration of electrons into the crystal leads to a Rydberg-like series of states which in the case of a purely Coulombic image force at a planar metal surface arise at energies $E_n(K) = -[0.85 \text{ eV}]n^2 + \hbar^2 K^2/2m$, $n = 1, 2, \ldots$ where $K$ is the electron wave vector parallel to the surface and $m$ the electron mass. Deviations from this behaviour reflect the influence and response of the surface-dependant electronic and atomic structure, which may therefore be investigated by studying image states. Examples of theoretical and experimental work include the systematics of image states binding and dispersion on clean surfaces [2], image state on overlayers [3, 4, 5], at stepped metal surfaces [6], exchange splitting of image states at ferromagnets [7, 8, 9], as well as image states at surface nanostructures [10, 11, 12, 13]. In recent years there has also been considerable interest in the dynamics of image state electron [14, 15, 16, 17] as model electronic excitations at surfaces.

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One aspect of the physics of image state electrons that has yet to be addressed is
the influence of the spin orbit interaction $H_{SO} = \frac{\hbar}{4m^2c^2}\sigma \cdot (\nabla V \times \mathbf{p})$ which has
recently been found to have a significant effect on other surface state electron levels at
the surfaces of conductors with high atomic number \[19, 20\]. At first sight the spin-orbit interaction might be expected to be negligible. The mathematical analogy that can be drawn between the Schrödinger equation describing the electrons moving in the Coulomb-like image potential and that of $s$-electrons in the hydrogen atom enable the image state wavefunctions to be written as

$$\psi_{n,K,s}(r) = \frac{1}{8} z R_{n0}(z/4) \exp(iK \cdot r_\parallel) \chi_s$$

where $R_{n\ell}(r)$ is the normalised radial hydrogenic wavefunction and $\chi_s$ a Pauli spinor: $\chi_\uparrow = (1,0)$, $\chi_\downarrow = (0,1)$. Using these wavefunctions to diagonalise the spin-orbit perturbation $H_{SO}$ in the subspace of degenerate image state levels gives a spin-orbit splitting of

$$\Delta E_{n}^{SO} = \frac{\alpha^2 e^2 K}{64(4\pi\epsilon_0)n^3} = [0.012 \text{ meV Å}] \frac{K}{n^3}$$

where $\alpha = e^2/4\pi\epsilon_0\hbar c$ is the fine structure constant. This is well below the current resolution of inverse photoemission, two-photon photoemission or scanning tunnelling spectroscopy. However, it has previously been recognised that a more significant contribution to the spin-orbit splitting of “crystal–derived” surface states arises from the brief time spent by the electron in the vicinity of the nuclei of the surface atoms, where the gradient contribution to the spin-orbit interaction is $|\nabla V| \sim Z/r^2$. In this paper we report on calculations that we have performed to quantify the magnitude of the spin-orbit splitting that arises from the penetration of the image state wave function into the crystal at surfaces of Ir, Pt and Au. These are described in section 2. In section 3 we describe the modification of the phase accumulation model for image state energetics to include the effects of the spin orbit interaction. Finally, we summarise and discuss our findings.

2. Relativistic electronic structure calculations

To calculate the spin-orbit splitting of image states we use a recently developed code
that implements relativistic multiple-scattering theory. The theory behind this method
is essentially that described by Halilov et al. \[21\] so we do not reproduce it in detail here.
The basic idea is that the electronic structure is found from the single-particle Green
function corresponding to the Dirac Hamiltonian $\hat{H} = c \sigma \cdot \mathbf{p} + \beta mc^2 + V$ \[18\]. Thus
spin-orbit effects are treated non-perturbatively. Using scattering techniques the Green
function is determined for the special case of semi-infinite crystals with two-dimensional
in-plane translational periodicity, treating intralayer scattering within an angular
momentum representation and interlayer scattering in a plane wave representation. Our
calculations use 25 and 19 two-dimensional reciprocal lattice vectors to describe the
intralayer scattering for the (001) and (111) surfaces respectively, and partial waves up
to $\ell_{\text{max}} = 4$ \[22\]. The semi-infinite substrate means that continuum and surface-localised
Figure 1. Calculated surface state dispersion curves. The shading indicates the presence of bulk or vacuum continuum states. (a) Pt(111) $n = 1$ and $n = 2$ image states. The inset demonstrates the splitting of the $n = 1$ state is linear in $K$. (b) Au(001) $n = 1$ and $n = 2$ image states. (c) Au(111) surface state (note the energy scale in this case is with reference to the Fermi level).

states are clearly distinguished in the wave vector resolved local density of states, found from the imaginary part of the Green function. As in the non-relativistic version of the code [23], the electronic structure is found self-consistently using the local density approximation to density functional theory. We use the atomic sphere approximation for the crystal potential (including dipole contributions), with the potential in the three outermost atomic layers allowed to vary in response to the presence of the surface. Since the local density approximation does not lead to an image-like surface barrier, and hence does not support image states, once self-consistency has been achieved we replace the self-consistent barrier with a parameterised model barrier, for which we use the “JJJ” potential [24]

$$V_B(z) = \begin{cases} 
(1 - e^{\lambda(z-z_0)})/4(z-z_0), & z < z_0 \\
-U/(1 + Ae^{-\beta(z-z_0)}), & z > z_0.
\end{cases} \tag{3}$$

The fitting parameters $\lambda$, $U$ and $z_0$ were fixed by starting with values quoted by Smith et al. [25], who fitted to first-principles slab calculations, and then adjusted slightly to place the $n = 1$ image state at $K = 0$, $E_1$, close to values found experimentally. The procedure does not uniquely fix the parameters, but we found that different combinations that gave the same value for $E_1$ resulted in almost identical image state dispersion curves. Note that our results are for the $1 \times 1$ unreconstructed surfaces of the materials studied. In several cases the surfaces undergo complex surface reconstructions (e.g. Au(001) and Pt(001) adopt a $5 \times 20$ reconstruction but may be prepared in the $1 \times 1$ structure – see [26]).

In figure 1 we illustrate the dispersion curves that we find. For both Pt(111) and Au(001) the spin-orbit interaction can clearly be seen to split the $n = 1$ image state,
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Table 1. Calculated image state energies including the spin-orbit interaction at (001) – 1 × 1 and (111) – 1 × 1 surfaces of Ir, Pt and Au: \( E_n(K) = E_n + \hbar^2 K^2 / 2m \pm (\gamma / 2)K \). \( E_n \) values in brackets are from experiment.

| surface   | n | \( E_n \) (eV) | \( m(m_e) \) | \( \gamma \) (meV Å) |
|-----------|---|----------------|---------------|----------------------|
| Ir(111)   | 1 | -0.65          | 0.95          | 56 ± 1               |
|           | 2 | -0.18          | 1.00          | 9 ± 1                |
| Ir(001)   | 1 | -0.61          | 0.94          | 38 ± 1               |
|           | 2 | -0.17          | 0.99          | 6 ± 1                |
| Pt(111)   | 1 | -0.69 (-0.65\(^a\), -0.78\(^b\)) | 1.05 | 50 ± 2               |
|           | 2 | -0.19 (-0.16\(^d\), -0.20\(^b\)) | 1.03 | 8 ± 1                |
| Pt(001)   | 1 | -0.60 (-0.60\(^c\)) | 0.96 | 47 ± 2               |
|           | 2 | -0.17          | 0.99          | 9 ± 1                |
| Au(111) SS|   | -0.50 (-0.41\(^d\), -0.49\(^c\)-0.51\(^f\)) | 0.23 | 800 ± 50             |
| Au(001)   | 1 | -0.66 (-0.69\(^g\), -0.63\(^h\)) | 1.05 | 88 ± 4               |
|           | 2 | -0.18          | 1.05          | 20 ± 2               |

\(^{a}\) See Ref. \[29\]  \(^{b}\) See Ref. \[30\]  \(^{c}\) See Ref. \[31\]  \(^{d}\) See Ref. \[19\]  \(^{e}\) See Ref. \[33\]  \(^{f}\) See Ref. \[34\]  \(^{g}\) See Ref. \[26\]  \(^{h}\) See Ref. \[35\]

and whilst a splitting exists for the \( n = 2 \) and higher states it is much smaller. The inset in the figure illustrates the variation of the splitting with wave vector \( K \), the near-linear variation corresponding to a Rashba-like dispersion \[27, 28\].

\[
E_n(K) \simeq E_n + \frac{\hbar^2 K^2}{2m} \pm (\gamma / 2)K. \quad (4)
\]

From curves such as these we extract Rashba-parameters \( \gamma \) by a least-square fit using wave vectors \( K \leq 0.2 \) Å\(^{-1}\). These values are tabulated in table for the image states at the (111) and (001) surfaces of Ir, Pt and Au. At Au(111) the vacuum level lies outside of the projected band gap so that the image states in this case exist as resonances. We have not therefore included results for this case, but instead give the results that we find for the spin orbit splitting of the occupied surface state that occurs within the band gap at this surface. The dispersion of this state is shown also in figure and agrees well with previous work, validating our procedure. We find the wave vector splitting at the Fermi energy is \( \Delta k = 0.023 \) Å\(^{-1}\), compared with experimental values of 0.023 Å\(^{-1}\) \[19\], 0.025 Å\(^{-1}\) \[31, 32\] and 0.027 Å\(^{-1}\) \[36\], and a theoretical value of 0.023 Å\(^{-1}\) \[37\] that have been reported previously.

The results in table indicate that the spin-orbit splitting of \( n = 1 \) image states at Ir, Pt and Au surfaces is an order of magnitude smaller than that of the Au(111) Shockley surface state, and that of the \( n = 2 \) states smaller still. These trends reflect the differing extents to which the corresponding wave functions penetrate the crystal and experience the spin-orbit interaction at the ion cores. At the (001) surfaces \( \Delta E_n^{Ir} < \Delta E_n^{Pt} < \Delta E_n^{Au} \) which might be expected given the increasing atomic number \((Z^{Ir} = 77, Z^{Pt} = 78, Z^{Au} = 79)\), but at the (111) surface \( \Delta E_n^{Ir} > \Delta E_n^{Pt} \), pointing to
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a more complicated “band-structure” effect. In figure 1 the splitting of the Au(001) 
n = 1 image state is also seen to be affected as it disperses towards the band edge of 
continuum levels. We return to this later.

3. Phase accumulation model

The “standard model” for understanding image state energies is the phase accumulation 
model \[1\] in which surface states are envisaged as one-dimensional waves trapped by 
multiple reflection from the surface barrier and the crystal. In a region of constant 
potential (see figure 2) between barrier and crystal (which may be infinitesimal in width) 
the electron wave function can be expressed in terms of forward and backward travelling 
plane waves

$$\psi(z) = A \exp(ikz) + B \exp(-ikz).$$ \hspace{1cm} (5)

The two components are related at the barrier reference plane \(z = z_B\) by the barrier 
reflection coefficient \(r_B\), \(\psi(z) \propto \exp(-ik(z - z_B)) + r_B \exp(ik(z - z_B))\) and at the crystal 
reference plane \(z = z_C\) by the crystal reflection coefficient \(r_C\), \(\psi(z) \propto \exp(ik(z - z_C)) + 
\left. r_C \exp(-ik(z - z_C))\right\text{ which together with (5)} \text{ give rise to the condition for a surface state to exist:}

$$r_B r_C \exp(2ikd) - 1 = 0, \quad \text{ } d = z_B - z_C.$$ \hspace{1cm} (6)

For energies below the vacuum level and coincident with the crystal band gap the 
reflection probability at both crystal and barrier are unity and the reflection coefficients 
may be written in terms of phases: \(r_B = \exp(\phi_B)\), \(r_C = \exp(\phi_C)\). The surface state 
condition then becomes

$$\phi_B + \phi_C + 2kd = 2\pi n \quad n = 0, 1, \ldots$$ \hspace{1cm} (7)

which is a condition on the round-trip phase accumulated by the electron wave. The 
phases in (7) increase with energy. The crystal phase increases from 0 to \(\pi\) as the energy 
sweeps across the band gap, changing most rapidly near the band edges. Towards the 
bottom of the gap it is this variation in \(\phi_C\) which will determine whether or not (7) is 
satisfied, so that any surface state that does arise is usually referred to as “crystal-
derived”. On the other hand, \(\phi_B\) increases more and more rapidly as the energy 
approaches the vacuum energy, varying to a good approximation as

$$\phi_B(E) = \pi \left( \sqrt{\frac{3.4 \text{ eV}}{-E}} - 1 \right).$$ \hspace{1cm} (8)

In combination with (7) this yields a Rydberg-like series of image states

$$E_n = -\frac{0.85 \text{ eV}}{(n + a)^2}, \quad n = 1, 2, \ldots$$ \hspace{1cm} (9)

where the quantum defect \(a = (1 - [\phi_C + 2kd]/\pi)/2\) may usually be considered constant 
over the range of energies at which the image states are found.
We now consider the extension of this model to include the spin orbit interaction. Introducing the electron spin into the wavefunction in (5)

$$\psi(z) = (\psi_\uparrow(z), \psi_\downarrow(z)) = (A_\uparrow, A_\downarrow) \exp(ikz) + (B_\uparrow, B_\downarrow) \exp(-ikz),$$  

and reflection from the crystal is now described by a matrix

$$R_C = \begin{pmatrix} r_{C\uparrow\uparrow} & r_{C\uparrow\downarrow} \\ r_{C\downarrow\uparrow} & r_{C\downarrow\downarrow} \end{pmatrix}$$

allowing for the possibility of spin-flip upon reflection. With a similar matrix used to describe scattering from the barrier, the condition for a surface state becomes

$$\det [R_B R_C \exp(2i kd) - 1] = 0.$$  

The four reflection coefficients in (11) are not independent – for example flux conservation requires that $|r_{C\uparrow\uparrow}|^2 + |r_{C\downarrow\uparrow}|^2 = 1$ within a gap, and for a non-magnetic crystal $r_{C\uparrow\uparrow} = r_{C\downarrow\downarrow}$. In the non-magnetic case and for a planar potential $V = V(z)$ the electron wave functions $\Psi_K(r) = \psi_K(z) \exp(iK \cdot r_\parallel)$ are found from the Hamiltonian

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V + \frac{\hbar^2}{4m^2c^2} \sigma \cdot (\nabla V \times K).$$

which may be diagonalised by a rotation in spin space

$$H' = U_\theta H U_\theta^{-1} = -\frac{\hbar^2}{2m} \nabla^2 + V + \frac{\hbar^2 K}{4m^2c^2} \frac{dV}{dz} \sigma_z$$

with

$$U_\theta = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -i \exp(-i\theta) \\ 1 & +i \exp(-i\theta) \end{pmatrix}$$
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where $\vartheta$ is the angle of the electron wave vector. The Hamiltonian $H'$ does not mix spin-up and spin-down channels and so in this representation the reflection matrix describing scattering from the crystal is diagonal:

$$R'_C = \begin{pmatrix} r^+_C & 0 \\ 0 & r^-_C \end{pmatrix}. \quad (16)$$

Since the spin-orbit interaction is negligible in the barrier the barrier reflection matrix is also diagonal, and for a non-magnetic surface $R'^\uparrow_B = R'^\downarrow_B = r^+_B = r^-_B$ so that the surface state condition \(12\) becomes $r^+_C r_B \exp(2ikd) = 1$ leading to the round-trip phase condition

$$\phi_C \pm \eta + \phi_B + 2kd = 2\pi n \quad n = 1, 2, \ldots \quad (17)$$

where we have introduced $r^+_C = \exp(i(\phi_C \pm \eta))$ appropriate to energies within a gap. The surface states now come in spin-split pairs, with spin orientations that may be deduced from the spinors that are obtained by rotating back into the original reference frame the spin-up and -down eigenspinors $\chi'^\uparrow = (\begin{pmatrix} 1 \\ 0 \end{pmatrix}, \chi'^\downarrow = (\begin{pmatrix} 0 \\ 1 \end{pmatrix})$ of the primed frame:

$$\chi^\pm = U^{-1}_\vartheta \chi'^\pm = \frac{1}{\sqrt{2}} \left( \pm i \exp(i\vartheta) \right). \quad (18)$$

Thus $\hat{S} = \pm(-\sin\vartheta, \cos\vartheta, 0) = \pm \hat{\vartheta} \times \hat{K}$ and we find that the spins lie in the surface plane and perpendicular to $K$, to the left (right) for $+$ ($-$).

Rotating back to the original spin frame gives the reflection matrix \(11\) as

$$R_C = U^{-1}_\vartheta R'_C U_\vartheta = \exp(i\phi_C) \begin{pmatrix} \cos\eta & \exp(-i\vartheta) \sin\eta \\ -\exp(i\vartheta) \sin\eta & \cos\eta \end{pmatrix}. \quad (19)$$

In figure 3 we illustrate the variation in $\tan\eta$ at the Au(001) surface calculated from the reflection matrix found using the relativistic multiple-scattering method of section 2. For $K$ along $\Gamma X$ (see inset in figure 3) equation \(19\) $\tan\eta = r'^\downarrow / r'^\uparrow$. The relativistic multiple-scattering calculations include the atomic structure of the surface and the crystal potential is not one-dimensional, but the reflection coefficient for specular reflection behaves in a very similar manner to that of a one-dimensional crystal, especially for small $K$ where the wave function varies only slowly across the surface. In particular we find that the angular variation predicted by equation \(19\) is satisfied to within a percent or so. It is evident from figure 3 that the magnitude of the spin-orbit induced phase change is small, and away from the band edges $\eta$ is approximately independent of energy at Au(001) and linear in $K$: $\eta^\text{Au}_{(001)}(E, K) \simeq [-0.25 \text{ Å}]K$.

To first order the round-trip phase condition \(17\) is satisfied at energies $E_n \pm \Delta E_n^{\text{SO}} / 2$ where

$$\Delta E_n^{\text{SO}} \simeq -2\eta \left( \frac{d}{dE} (\phi_B + \phi_C + 2kd) \right)^{-1}_{E_n}, \quad (20)$$

neglecting the energy dependence of $\eta$ which is small compared to the other phases. For all the surfaces that we have studied we have found that $\eta$ does not change sign across the band gap, and the denominator in \(20\) is positive. Hence the model predicts
a series of spin-orbit split states with identical spin orderings, which we have confirmed is also the case in the relativistic multiple scattering calculations described in section 2. In particular with $\eta < 0$ the surface states that exist are split with the lower of each pair of levels having the spin pointing to the right of $\mathbf{K}$, as shown in figure 4. This is in agreement with the spin assignments shown in Henk et al. [37] for the Au(111) surface state, but disagrees with those given in Ref. [31].

When the gap contains image states, over the narrow range of energies within which the image states are found the energy-dependence of the round-trip phase is dominated

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**Figure 3.** Variation of the spin-flip to non-spin-flip scattering ratio $r^{\uparrow\downarrow}/r^{\uparrow\uparrow}$ for Au(001) in the major band gap of the projected band structure. (a) as a function of energy at $\mathbf{K} = (0.2, 0.0) \text{Å}^{-1}$. (b) as a function of wave vector along $\Gamma X$ at the mid-gap energy. The inset shows the projected gaps across the Brillouin zone at the same energy.

**Figure 4.** Spin orientation of spin-orbit split surface states for $\eta < 0$. 
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by the variation in the barrier phase \( \Phi_B \) and then

\[
\Delta E_n^{\text{SO}} \simeq -2\eta \left( \frac{d\Phi_B}{dE} \right)_{E_n}^{-1} = -\frac{\eta \times 1.7 \text{ eV}}{\pi(n+a)^3} \tag{21}
\]

Thus the spin-splittings exhibit the same scaling as the lifetime broadening \([1]\), in each case the behaviour ultimately originating in the variation with \( n \) of the wave function overlap with the crystal. We also see from (21) that the linear-in-\( K \) behaviour of \( \Delta E_n^{\text{SO}} \) arises from similar behaviour in \( \eta \). Since \( \eta \) is small \( \tan \eta \simeq \sin \eta \simeq \eta \) to a good approximation, and hence \( \eta \simeq -|r^{\uparrow\downarrow}| \). Thus the spin-orbit splitting is directly related to the spin-flip scattering rate, which could therefore be determined from experimental values of image state splittings. At Au(001), \( E_1 \simeq -0.66 \text{ meV} \) (table [1]), so combining equations (9) and (21) gives

\[
\Delta E_1^{\text{SO}} \simeq -\eta \times \frac{1.7 \text{ eV}}{\pi} \left( \frac{0.66}{0.85} \right)^{3/2} = -\eta \times 0.37 \text{ eV}
\]

and a splitting of 22 meV (figure [1]) at \( K = 0.25 \text{ Å}^{-1} \) yields \( \eta \simeq 0.06 \), which agrees with the value found from the multiple-scattering calculations shown in figure [3]. Finally, we note that equation (21) will not hold near band edges where the energy-dependence of the crystal phase \( \phi_C \) cannot be neglected. This is the origin of the anomalous dispersion shown for the \( n = 1 \) state at Au(001) in figure [1].

4. Discussion

To summarise, we have investigated the effect of the spin-orbit interaction on image state electrons at the (111) and (001) surfaces of Ir, Pt, and Au. Non-perturbative calculations that use relativistic multiple-scattering theory with self-consistent potentials and a parameterised surface barrier predict Rashba-like dispersion of the image state bands with splittings for \( n = 1 \) that are a factor 10-20 times smaller than that of the Au(111) Shockley state, for which our results are in good agreement with experiment and previous theory. Extending the phase accumulation model to include spin-orbit scattering, we find that the splittings scale as \( 1/(n+a)^3 \), where \( a \) is the quantum defect, and are directly related to the spin-flip scattering rate at the surface. The largest image state splittings we find are at Au(001) for which \( \Delta E_1^{\text{SO}} = 22 \text{ meV} \) at \( K = 0.25 \text{ Å}^{-1} \). This is larger than some exchange splittings of image states that have previously been resolved (e.g. 18 ± 13 meV at Ni(111) \([7]\) and 13 ± 13 meV at Ni(001) \([38]\)) by exploiting the spin resolution available in spin-resolved inverse photoemission, suggesting that the spin-orbit splitting may also be observable with an appropriate experimental set-up. The splittings are comparable to lifetime broadenings of late-transition and noble metal image states \([14, 16]\), indicating that account of spin-orbit effects may be necessary when determining image state lifetimes from lineshape analysis for 5\( d \) metals.

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