Calculation of surface states using a one-dimensional scattering model

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Abstract. The complex electronic band structure of a one-dimensional solid is described using a one-dimensional scattering approach. The method yields the value of the wave function and its derivative between the atomic layers. These values can be matched at the surface to the corresponding values of the wave function on the vacuum side. The method is compared to the two-band approximation of the nearly free electron model. Advantages of the proposed scheme are the easy adaption for layered systems and alloys.

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At the surfaces of solids the changed boundary conditions can lead to the development of new states. The wave functions of these surface states are localized near the surface and decay exponentially into the solid in contrast to the Bloch waves propagating in the bulk. Surface states often exist in the energy range near the Fermi level and have been detected by photo-emission and inverse photo-emission experiments [1]. A particular type of surface states is supported by the potential well created in front of a metal surface by the attractive force acting between an electron and its image charge in the metal [2]. The image states form a series of states converging towards the vacuum energy $E_{vac}$ and can be measured best by two-photon photo-electron spectroscopy [3]. Surface states can often be described very well by one-dimensional models [2, 4]. The most commonly used description of the band structure of a solid is the two-band approximation to the nearly free electron model using only one Fourier coefficient of the potential [4]. In Sect. 1 an alternate approach using a one-dimensional scattering model is developed. The matching of the wave function for the solid to the solution on the vacuum side at the surface will be discussed in Sect. 2. It will be shown in Sect. 3 that it reproduces the results of the two-band model, but has the advantage that it can be applied to overlayer systems and alloys (Sect. 4) or to the inclusion of a more realistic band structure (Sect. 5).

1 One-dimensional scattering model

The basic requirement for the existence of a surface state is that the wave function decays exponentially into the bulk and vanishes for large distances away from the surface. A convenient way to achieve this is to determine the solutions satisfying these boundary conditions in the bulk and the vacuum separately. One then has to find the energies where the wave function and its derivative for both solutions can be matched continuously at the surface. The main requirement is, therefore, the knowledge of the wave function and its derivative at the surface. In the one-dimensional scattering model this information is obtained for the bulk solution [5, 6]. As sketched in Fig. 1, the solid is composed of individual layers with a (possibly infinitely small) region between the layers with a constant potential $V_c$. In this region the wave function can be expanded into plane waves

$$\phi(z) = Ae^{-iks} + Ar e^{iks} + Br e^{iks}. \quad (1)$$

From Fig. 1 the interpretation of the various terms are a wave of amplitude $A$ travelling to the left which is reflected by the potential of the layer to the left with a reflection coefficient $r$ and a wave of amplitude $B$ which has been transmitted through the layer at the left with a transmission coefficient $t$. Without absorption, the transmission and reflection coefficients are connected by the requirement of continuity $|r|^2 + |t|^2 = 1$. The wave vector $K$ is given by the energy $E$ relative to the potential $V_c$ by $E - V_c = \hbar^2 K^2 / 2m$, where $m$ denotes the (effective) mass of the electron. According to Blochs theorem, the solutions in the periodic potential with period $a$ must obey

$$\phi(z + a) = e^{i\omega a} \phi(z) \quad (2)$$
The wave function between the atomic layers is described by a superposition of waves of amplitude $A$ and $B$ traveling to the left and right, respectively. The fraction $t$ is transmitted and the fraction $r$ is reflected. At the surface ($z = a/2$), the bulk wave function is matched to the wave of amplitude $C$ reflected (coefficient $r_B$) by the vacuum barrier.

The solutions for the Bloch wave vector $k$ can be found from inserting (1) and the plane wave expansion at $z = -3a/2$ from Fig. 1 into (2) and applying the same procedure to the derivatives of the wave functions. Introducing the abbreviations $\alpha = \exp(ik\alpha)$ and $\beta = \exp(ika)$, the following equation is obtained

$$\beta^2\beta + \beta(x^2r^2 - \alpha^2t^2 - 1) + \alpha t = 0. \quad (3)$$

The two solutions $\beta_1$ and $\beta_2$ are related by $\beta_2 = \beta_1^{-1}$ and give, in general, complex solutions for the Bloch wave vector $k$. Note that all equations are complex and permit the inclusion of an imaginary part of the potential $V_C$. For a real potential $V_C$, the wave vector can be real — corresponding to propagating solutions — or it can contain an imaginary part — indicating exponentially decaying or increasing solutions for energies in band gaps. The ratios of the amplitudes is given for the two solutions by

$$\frac{A/B_1}{A/B_2} = \frac{(\beta_1 - \alpha t)/\alpha r}{(B/A)}_2. \quad (4)$$

This relation guarantees that for the problem of surface states always a solution decaying into the bulk with $|B/A| < 1$ can be found. After these considerations the wave function at the surface can be written as

$$\varphi(a/2) = \alpha^{-1/2} A(1 + \omega r + B/A \alpha t) \quad (5)$$

and evaluated using (3) and (4). A similar equation holds for the derivative of the wave function.

For the practical evaluation of the one-dimensional scattering model the following assumptions are made: $t = |t|$ real and $r = (i^2 - 1)^{1/2}$ purely imaginary [7]. Equation (3) can then be rewritten as [5]

$$\cos(Ka) = t \cos(ka), \quad (6)$$

which has for $|\cos(Ka)| > t$ complex solutions $k$. This demonstrates the existence of band gaps with the edges given by $|\cos(ka)| = 1$. For low energies, the relevant parameters of the band structure are the lower and upper band edges, $E_l$ and $E_u$, and the bottom of the valence band $E_b$, (Fig. 2). The solutions of $|\cos(Ka)| = t$ with the lowest energies are given by the following three equations

$$E_g(\arccos t/\pi)^2 = E_b - V_c,$$

$$E_g(1 - \arccos t/\pi)^2 = E_l - V_c,$$

$$E_g(1 + \arccos t/\pi)^2 = E_u - V_c, \quad (7)$$

which can be solved for $V_c$, an (energy independent) $t$, and the factor $E_g = h^2 \pi^2/2ma^2$ relating energies and momenta. The resulting complex band structure is shown in Fig. 2 (solid lines). The parameters for Pd(111) are $E_b = -6.35$ eV, $E_l = 1.00$ eV, and $E_u = 7.60$ eV [3] yielding a transmission coefficient $t = 0.884$. Note that for most cases $V_c$ is only slightly below the bottom of the band and may be chosen equal to $E_b$. In this case, $t$ and $E_g$ are obtained from the last two equations of (7).

### 2 Calculation of surface states

The potential outside the solid is for large distances $z$ equal to the vacuum energy $E_{vac}$. In front of a metal surface, the interaction of the electron with its image charge yields an asymptotic behavior as

$$V(z) = E_{vac} - \frac{e^2}{4\pi\varepsilon_0} \frac{1}{z - z_0}. \quad (8)$$
This potential is modified near the surface $z_0$ and joins the potential of the solid. The simplest way to achieve this is the use of (8) only in the range $V(z) > V_C$ with an appropriate adjustment of the image plane $z_0$ (Fig. 1). The solutions for the wave functions in the truncated Coulomb potential on the vacuum side are then given by Whittaker functions [8]. Various other potentials have been proposed which require the numerical integration of the Schrödinger equation to obtain the wave function [9, 10].

For the application to image states which have energies close to $E_{vac}$, the details of the potential near $V_C$ are less important. A simple way of obtaining the wave function and its derivative at the surface uses a one-dimensional scattering approach on the vacuum side as well. The wave of amplitude $C$ is reflected by the vacuum barrier with a reflection amplitude $r_B$ (Fig. 1). If the electron energy is below $E_{vac}$, the transmission probability (in the absence of an external electric field) is zero and the reflection coefficient can be written as $r_B = \exp(i\Phi_B)$. For the wave function at the surface, the plane wave expansion is

$$\varphi(a/2) = C e^{iK_0z_0} + C e^{i\Phi_B} e^{-iK_0z_0}. \tag{9}$$

Here, the use of a continuous potential makes $K$ identical to the one used in (1). For the barrier phase $\Phi_B$, the following expression [11]

$$\Phi_B(E) = \pi[\sqrt{(3.4 \text{ eV})/(E_{vac} - E)} - 1] \tag{10}$$

is a good approximation to the solutions of (8). Equations (5) and (9) give as a necessary condition for the continuity of the wave function and its derivative at the surface a set of two homogeneous linear equations for the amplitudes $A$ and $C$. Nontrivial solutions are obtained only for certain energies where the determinant vanishes. One of the advantages of the method is that the coefficients entering the equations can be easily calculated as a function of energy with the use of (3, 4) and (10).

Instead of searching for the zeros of the determinant of the linear equation it is more convenient to find the maxima in the reciprocal value of the determinant as a function of energy. This procedure works also for energies outside the band gap and for a non-vanishing imaginary part of the potential $V_C$. In practical applications it actually requires always an imaginary part of $V_C$ to avoid complications by a division by zero. It can be chosen sufficiently small ($<10^{-3}$ eV) so that the results are not affected if calculations with a real potential $V_C$ are wanted.

Energies for image states on various surfaces have been calculated using the one-dimensional scattering model and the simple approximation (10) for the barrier phase [3]. Excellent agreement with the experimental values is found for most surfaces. An exception occurs for the ferromagnetic surfaces which is, however, not related to inadequacies of the model calculations [3, 12].

3 Two-band model

The usual way of representing the one-dimensional band structure of solids starts with the two-band approximation to the nearly free electron model (see, e.g., Chap. 9 of [5]). The dispersion is given by the solutions of the following equation

$$\left( \frac{\hbar^2 k^2}{2m} \right) \begin{pmatrix} V_{g} \\ V_{g} - \hbar^2 \omega^2/2m - E \end{pmatrix} \begin{pmatrix} c_k \\ c_{k-q} \end{pmatrix} = 0, \tag{11}$$

where $q = 2\pi/a$. The energy at the bottom of the band is obtained for $k = 0$ and the band edges are the solutions for $k = g/2$. Referencing the energy scale relative to the constant potential $V_0$ yields the following equations

$$E_b - V_0 = (2E_g - |V_{g}^2|/|V_{g}^2|),$$

$$E_i - V_0 = E_g - |V_{g}|,$$

$$E_s - V_0 = |V_{g}|,$$

which can be solved for the potential parameters $V_0$ and $V_g$ [13], and the factor $E_g$. Following this procedure gives for the two-band model a complex band structure (dashed lines in Fig. 2) almost identical to the one obtained from the one-dimensional scattering model (solid lines). The agreement is even better for other surfaces with a smaller ratio between the band gap and $E_g$. The slight differences at higher energies are due to the different values for $E_g$ in both cases, which would disappear if $V_{c} = V_{o} = E_b$ were chosen. In that case, the bottom of the bands would differ by $\approx 0.6$ eV. Note that for most cases, $E_b$ is slightly above the bottom of the band and can be set to a good approximation equal to $E_b$. The solutions for $V_{g}$ and $E_g$ are then obtained from the last two equations in (12).

The two-band approximation to the nearly free electron approximation is valid only near the zone boundary. Equation (11) can be evaluated for larger values of $k$ and $E$, but the higher band gaps are not obtained. In contrast, the one-dimensional scattering model gives band gaps for wave vectors $K = n\pi/a$. For a constant transmission coefficient the size of the band gap increases proportional to $n$.

From the derivation of the two-band approximation it is suggestive to write the wave function as [5, Chap. 9]

$$\varphi(z) = c_k e^{iKz} + c_{k-q} e^{i(k-q)z}. \tag{13}$$

This representation can then be used to evaluate the wave function and its derivative at the surface for the calculation of surface states as outlined in Sect. 2. However, this is not exact, since (11) is a submatrix cut out of an eigenvalue problem of infinite dimension. The wave function of the latter problem contains an infinite number of plane waves. In this context it might be helpful to note that the solutions of Schrödinger’s equation for the periodic potential $V(z) = 2V_c \cos(2\pi z)$ are the Mathieu functions and are not given by (13). The formulation of the band structure within the one-dimensional scattering model uses a plane-wave expansion of the wave function which only assumes a constant potential in an infinitely small region between the layers. The scattering by the layers is described by the transmission coefficient from which the band structure can be derived without explicit
knowledge of the scattering potential or the wave function in the layers. A wave function can be constructed in the one-dimensional scattering model from third-order polynomials with the appropriate boundary conditions. This yields a representation by continuously differentiable spline functions. The results [14, 15] are very similar to the wave function given by (13) in the two-band model. It should be remembered that these "pseudo" wave functions should be used with caution between the layers.

4 Overlayers and alloys

The one-dimensional scattering model can easily be extended to include the effects of additional overlayers on the surface. At the interface, the wave function of the substrate (5) has to be matched to the solution for the overlayer. The latter is given by a linear combination of both solutions of (3), since the condition that the wave function decays into the solid does not hold in the overlayer. The matching conditions can be obtained by evaluating (1) at the left-hand side of the overlayer \( z = -a/2 \) using (4) and different amplitudes \( A_1 \) and \( A_2 \) for the two solutions. The resulting set of linear equations is easily solved and with the help of Bloch's theorem (2), the wave function and its derivative can be evaluated at the surface of the overlayer [18]. This information is sufficient to add another overlayer or to determine the energy of surface states as described in Sect. 2.

This procedure has been used successfully for image states at Ag and Au overlayers on Pd(111), where excellent agreement with the experimental data was found [15, 19]. It should be emphasized that the one-dimensional scattering approach describes the behavior of the overlayer based on the band structure of the bulk material and introduces no additional parameters. The proper convergence behavior for thick layers is obtained. The properties of the individual layers are derived in a physically meaningful way by the transmission coefficient \( t \).

The one-dimensional scattering approach can be extended also to the case of an alloy surface. The transmission coefficient of a layer can be regarded as the effective sum of the scattering by all ion cores of the atoms in the layer. For an alloy consisting of elements \( X \) and \( Y \), the transmission coefficient is the result of a suitable average over all atoms in the layer. If the relative concentrations of the constituents are \( x \) and \( y = 1 - x \), a reasonable assumption for the transmission coefficient of the alloy layer is

\[
t(x) = xt_x + (1 - x)t_Y.
\]

Similar equations are used for the parameters \( V_c \) and \( E_v \). This ansatz ensures the proper behavior in the limiting cases \( x = 0 \) and \( x = 1 \). In LEED (Low-Energy Electron Diffraction) calculations, a similar approach is known as averaged \( t \)-matrix approximation [20]. It is obvious that for the one-dimensional case the layer structure has to be retained in the alloy. It should be emphasized that within the scattering model the properties of an alloy of given concentration are determined completely by the bandstructure parameters of the constituents.

The combination of the extensions to the one-dimensional scattering model to overlayers and alloys yields the solution to the otherwise almost intractable problem of a surface with a concentration gradient. Such a situation can occur for segregation at an alloy surface or for an intermixed interface of an overlayer system. Starting from the bulk (of constant concentration) individual layers are added until the surface is reached. The transmission of each layer is calculated using (14) with the appropriate concentration. In practical applications, the number of layers can become quite large. The structure of the equations permits easily the combination of several layers with similar concentration into superlayers.

For a mixed interface, a reasonable assumption for the concentration in the layers can be obtained from a diffusion model [21]. This introduces only one parameter \( D_t \), which is the diffusion constant \( D \) and the diffusion time \( t \). An application of the method is shown in Fig. 3 for Au on Ag(111), which is known to intermix already at room temperature [17, 22]. The experimental data are for an occupied surface state [17]. The calculation of the surface states requires the knowledge of the work function \( E_{\text{vac}} \) relative to the Fermi level, which was obtained from [16]. For the calculations, the band structure parameters \( E_{\text{sh}} = -7.80 \text{ eV}, \quad E_{\text{h}} = -0.30 \text{ eV}, \) and \( E_{\text{e}} = 3.99 \text{ eV} \) for Ag(111) [3] and \( E_{\text{sh}} = -9.00 \text{ eV}, \quad E_{\text{h}} = -0.96 \text{ eV}, \) and \( E_{\text{e}} = 3.60 \text{ eV} \) for Au(111) [23] were chosen. The lower band edges were adjusted by \( \leq 0.04 \text{ eV} \) to ensure the correct energies of the occupied surface states on the clean surfaces even with the ap-
proximation (10) for the barrier phase. The calculated energies for the energies of the surface states agree very well for $Dr=0.9 \pm 0.2 \times 10^{-14} \text{cm}^2$. With $D=0.9 \pm 0.4 \times 10^{-19} \text{cm}/\text{s}$ [22] a diffusion time of $10^8 \text{s}$ is obtained which seems somewhat large. A possible explanation could be that the deposition was done in the photo-emission experiments [17] at a slightly higher sample temperature than in the work of Eisenhut et al. [22]. This would give a larger diffusion constant and bring $\tau$ down to the time range of the experiments. For a clarification of this point measurements of the surface-state energies and work function should be performed on the same samples. The constant energy of the surface state for coverages below 3 MonoLayers (ML) has been attributed to a Ag-rich surface [17]. The calculation shows clearly that it is caused by two counteracting effects. The increasing Au coverage tends to pull down the surface-state energy which is compensated by the steep increase of the work function for low coverages.

5 Discussion and outlook

The method of calculating the complex band structure with a one-dimensional scattering approach presented in this paper is equivalent to the use of the two-band model. Both schemes can be carried out with little mathematical and numerical effort. Conceptual and practical advantages of the one-dimensional scattering model have been discussed in Sect. 3 and 4. A further development of the method would go towards a more realistic description of the band structure.

The complex band structure of the solid can be obtained from a parametrized calculation. Such schemes are the combined-interpolation scheme [24] and the Slater-Koster tight-binding scheme as implemented by Papaconstantopoulos [25]. Usually, the eigenvalue equation of these schemes is solved for the energies at a given (real) $k$, but it can also be solved at a given energy for the complex wave vector $k$. The symmetry of the surface-state wave function restricts the bulk bands to be considered to those of the same symmetry. For most cases including image states, the wave function is totally symmetric. This implies that the dimension of the eigenvalue problem can be reduced considerably [25] making the solution for the complex $k$ vectors easier. Equation (3) can be solved for $t$ if the relation between $k$ and $E-V_c = \hbar^2/2m$ is known. This procedure yields an energy-dependent and possibly complex transmission coefficient $t$ from which the wave function and its derivative between layers and at the surface can be determined (4, 5). It should be mentioned that a similar improvement might be possible by the introduction of a $k$- or energy-dependent complex pseudopotential $V_g$ in the two-band model.

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References

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7. The choice of a real value for $r$ yields reasonable results in the cases considered here [6] and avoids the introduction of an additional parameter for the complex phase of $t$ [5]
13. The choice of a real negative value for $V_g$ yields reasonable results in the cases considered here [4]. A complex phase of $V_g$ affects the coefficients $q_k$ in (11) but not the energies. The situation should be compared to the freedom in the choice of the phase of the transmission coefficient $r$ [7]