CALCULATION OF VLEED SPECTRA WITH THE EXTENDED LINEAR AUGMENTED PLANE WAVE **kp** METHOD*

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November 6, 1999

Abstract

We describe a new method to calculate the VLEED (very low energy electron diffraction) spectra within the Bloch waves approach. The method is based on the variational solution of the Schrödinger equation for a semi-infinite crystal. Inside the solid the trial LEED function Φ is a linear combination of propagating and evanescent Bloch waves, which are generated by the inverse ELAPW (extended linear augmented plane waves) -**kp** method. The trial function is smoothly continuous over the whole space, and it satisfies by construction the equation $(\hat{H} - E)\Phi = 0$ both in the crystal and in the vacuum half-spaces. In the surface layer the equation $\delta||(\hat{H} - E)\Phi|| = 0$ is solved. To illustrate the properties of the method we discuss its application to the 1D case. We have performed a self-consistent band structure calculation of the $1T$ chalcogenide VSe_2 and obtained from the first principles the normal-incidence target current spectrum (TCS) for its (0001) surface.

78.20.-e, 73.20.At, 76.60.-i

1 Introduction

Computational methods to treat the LEED problem can be divided into two groups depending on whether the crystal is represented as a finite number of monolayers or is treated as a half-space. The former approach is adopted in the multiple-scattering layer KKR technique [1] and in purely direct-space methods, [2] and the latter one gives rise to Bloch-waves based methods. [3] The Bloch waves approach is advantageous in the case of weak electron absorption because

*Czechoslovak Journal of Physics, **49**, N11, 1575-1582 (1999)

the computational effort does not depend upon the value of the optical potential. Inside the bulk half-space the LEED wave function is a linear combination of the Bloch wave functions Ψ_n (propagating and evanescent) that are solutions of the complex band-structure problem and thereby take into account all multiple scattering in the crystal. [3] This linear combination is matched at a plane parallel to the surface to the solution in the surface region (a slab inside which the crystal potential changes from its bulk distribution to a constant value in the vacuum). The latter in turn must be matched to the wave function in the vacuum half-space, where it is a linear combination of the incident and the reflected plane waves. The method we describe in this paper unites the matching and the construction of the solution in the surface region into a single variational procedure.

The Bloch solutions are generated by the inverse ELAPW-**kp** method. [4] The ELAPW-**kp** is a variational band-structure method to solve the Schrödinger equation for a realistic singular crystal potential. In a **kp** method the matrix elements of the crystal potential are **k**-vector independent. This feature makes the method advantageous in solving the inverse band-structure problem, i.e., given two real cartesian components of the Bloch vector, $\mathbf{k}_{||} = (k_x, k_y)$, and the energy, E, to find the values of $k_\perp$ that satisfy the Schrödinger equation

$$\hat{H}\Psi(E, \mathbf{k}_{||}, k_\perp; \mathbf{r}) = E\Psi(E, \mathbf{k}_{||}, k_\perp; \mathbf{r}) \tag{1}$$

with the complex Bloch vector $\mathbf{k} = (\mathbf{k}_{||}, k_\perp)$. Similar to the plane-wave pseudopotential method, [3] the problem is reduced to a generalized nonhermitian matrix eigenvalue problem,

$$\begin{pmatrix} 0 & \hat{H} - E\hat{O} \\ \hat{I} & 2\hat{P}_\perp \end{pmatrix} \begin{pmatrix} \vec{D} \\ \vec{C} \end{pmatrix} = (k_\perp - k_\perp^0) \begin{pmatrix} \hat{I} & 0 \\ 0 & -\hat{O} \end{pmatrix} \begin{pmatrix} \vec{D} \\ \vec{C} \end{pmatrix}. \tag{2}$$

Here $\vec{C}$ is the eigenvector in the APW representation. The difference from the plane wave approach [3] is that the overlap matrix $\hat{O}$ and the momentum matrix $\hat{P}_\perp$ in the ELAPW representation are nondiagonal. The matrices are evaluated in terms of the basis functions (energy-independent APWs) at a reference Bloch vector $\mathbf{k}^0 = (\mathbf{k}_{||}, k_\perp^0)$.

We have shown in Ref. ikp that even for a step-like potential barrier (the thickness of the surface layer is zero) the matching problem is not trivial. With a finite set of solutions Ψ_n of Eq. 1 exact matching of function and derivative at the crystal boundary is not, in general, possible, and the calculated LEED intensities depend upon the definition of the mismatch to be minimized. In Ref. new we have proposed a new method of constructing the LEED function: for a given set of functions Ψ_n we construct a smoothly continuous function Φ that minimizes the energy deviation $\|(\hat{H} - E)\Phi\|$ under the constraint that the incident current is unity. In Ref. new the method was applied to the TCS spectra of (111) surfaces of fcc metals. There the barrier was assumed to be step-like, in other words, the technique was used only to solve the "matching" problem and not to obtain the wave function in the surface region.

In the present paper, using the 1D case as an example, we show that the method is capable of solving the complete problem. We also present an *ab initio* TCS spectrum of the $1T$ chalcogenide VSe_2 and compare it with the experiment.

2 Formalism

Consider a semi-infinite crystal that comprises the bulk half-space, $z < 0$, the vacuum region, $z > L$, and the surface region, $0 < z < L$. In the bulk the crystal potential does not change from layer to layer, in the vacuum the potential is constant, and in the surface layer the potential has a 2D periodicity. The LEED state $\Phi(\vec{\rho}, z)$ is defined by its energy E and the surface projection of the Bloch vector $\vec{k}_{||}$. In the bulk the LEED state is a linear combination of propagating and evanescent Bloch states, Ψ_n,

$$\Psi_n(\vec{\rho}, z) = \sum_{s=0}^{N_F-1} f_{sn}(z) \exp[i\vec{K}_s\vec{\rho}], \quad z < 0. \tag{3}$$

Here $\vec{K}_s = \vec{k}_{||} + \vec{G}_s$, $\vec{G}_s$ being the surface reciprocal lattice vectors; $\vec{G}_0 = 0$. We now analytically continue the functions Ψ_n to the half-space $z > 0$. The functions $f_{sn}(z)$ with $G_s \neq 0$ are extended by attaching a linear combination of two tails: a "physical" tail $p_s(\vec{\rho}, z)$, which has a correct asymptotics at $z \to +\infty$, and an auxiliary tail $a_s(\vec{\rho}, z)$, which decays rapidly with the distance from the surface and is negligible for $z > L$. The "physical" tail

$$p_s(\vec{\rho}, z) = \exp[i\vec{K}_s\vec{\rho} + ik_s z], \quad K_s^2 + k_s^2 = E, \tag{4}$$

may be a propagating wave, $Im\, k_s = 0$, or an evanescent wave, $Im\, k_s > 0$, depending on E and K_s^2. This formalism enables us to formulate the matching problem in terms of smoothly continuous functions. For $G_s = 0$ the physical part, $p_0(z)$, is always propagating: it is a linear combination of the incoming and the outgoing (central beam) plane wave. Thus any linear combination of the extended functions (denoted by X_n) satisfies the Schrödinger equation both in the vacuum half-space and (with a certain accuracy) in the bulk. On the other hand, in the surface region any linear combination of X_n differs from the exact wave function by a function which has zero value and zero slope both at $z = 0$ and at $z = L$. The idea of the method is to expand the difference function in terms of plane waves having period L in z direction. Then the wave function can be obtained by minimizing $\|(\hat{H} - E)\Phi\|$ under the constraint that the incident current is equal to unity, which leads to a system of linear equations. The variational parameters of the procedure are the coefficients of the functions X_n

and of the plane waves; the former include the parameters that determine the functions a_s.

In Ref. new we have considered the case of a step-like potential. There the auxiliary tail was taken as a single evanescent plane wave $a_s(\vec{\rho}, z) = \exp[i\vec{K}_s\vec{\rho} + iq_s z]$, $Im\, q_s > 0$. However, for the procedure to be applicable to the case of the barrier of arbitrary shape the functions a_s must have certain variational freedom.

3 The 1D case

We now focus on getting the wave function in the surface region with the variational method. Let the potential inside the "crystal" be constant, $V(z) = -V_0$ for $z < 0$. In the surface region the potential changes smoothly to reach the vacuum value $V(z) = 0$ for $z > L$. There exists only one solution Ψ for each energy, the transmitted wave $\Psi(z) = \exp[ik^T z]$, $k^T = -\sqrt{E + V_0}$. The function

$$X_0(z) = \exp[ik^I z] + \mu_0 \exp[q_0 z], \quad q_0 < 0, \qquad \mu_0 = \frac{k^I - k^T}{k^T + iq_0}, \tag{5}$$

carries the incident wave with the wave vector $k^I = -\sqrt{E}$, and matches the transmitted wave $(1 + \mu_0)\exp[ik^T z]$ at $z = 0$. We shall also need a set of functions that carry the same reflected wave.

$$X_j(z) = \exp[ik^R z] + \mu_j \exp[q_j z], \qquad k^R = -k^I, \quad \mu_j = \frac{k^R - k^T}{k^T + iq_j}, \qquad j \geq 1, \quad q_1 = q_0 > q_2 > q_3 \ldots q_j > q_{j+1} \ldots \tag{6}$$

It is evident that the solution for the step-like barrier is such combination of two functions X_0 and X_1 that the auxiliary tails $\exp[q_0 z]$ cancel. For the potential of arbitrary shape we need more than one function X_j in order to satisfy the following conditions. First of all, the linear combination $T = X_0 + \sum_{j=1}^{N} u_j X_j$ must have correct values of function and derivative at the surface boundaries, $z = 0$ and $z = L$. Note that for $z > 0$ all derivatives of T are continuous, but higher derivatives may have a break at $z = 0$. The difference function $\Phi - T$ is expanded in terms of linear combinations of plane waves that go to zero with zero derivative at the surface boundaries. The quality of such expansion will be the better the higher is the order of the highest continuous derivative of the difference function. Thus, additional functions X_j are necessary to minimize the nonperiodicity of higher derivatives of the function $\Phi - T$.

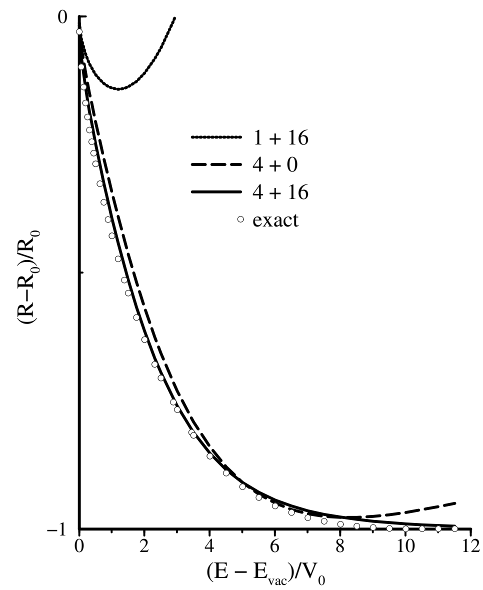

Figure 1: Electron reflectance in a 1D case referenced to the reflectance of a step-like barrier. The exact result is shown by open circles. The lines show the results obtained with the variational method.

If the potential in the surface region grows continuously, the electron reflectance $R(E)$ is reduced with respect to the step-like-barrier value $R_0(E)$. Thus, in terms of observables, the shape of the potential can be characterized by the function $\delta R(E) = (R(E) - R_0(E))/R_0(E)$. In Fig. 1 we compare the function $\delta R(E)$ obtained by the variational method and the exact function. The potential in the surface region was chosen to be $V(z) = -V_0(1 + \cos(\pi z/L))/2$. The exact function was calculated by solving the Schrödinger equation in the surface region with the Runge-Kutta method and matching the solutions at the surface boundaries.

As is seen from the figure, the quality of the reflectance curve is much more sensitive to the number of functions X_j (1 or 4), i.e., to the variational freedom of the decaying tail, than to the number of the plane waves (0 or 16) in which we expand the periodic function $\Phi - T$. To illustrate the effect of the plane waves we show in Fig. 2 the electron density distribution in the LEED state, $|\Phi|^2$, as reproduced by the variational method.

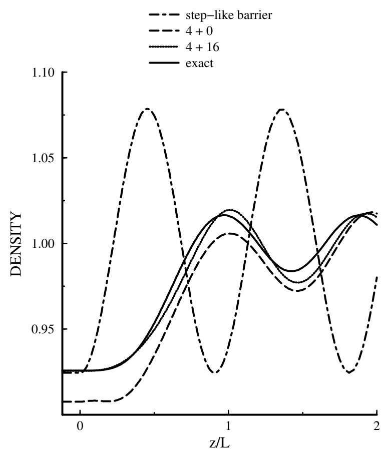

Figure 2: Density distribution in a LEED state. The exact function (solid line) is compared to the functions calculated with the variational method (dashed and dotted lines). The dot-dashed line shows the result for a step-like potential.

4 Target current spectrum of VSe_2

In this section we show the application of the above formalism to the simplified case of a step-like potential barrier, but to a realistic crystal.

In Fig. 3 a normal-incidence TCS spectrum of the (0001) surface of the $1T$ chalcogenide VSe_2 is compared to the VLEED experiment of Ref. str. The structures in the theoretical spectrum can be easily understood in terms of the ΓA-projected real band structure of the crystal. The method rejects propagating Bloch states that do not connect to the wave function in the vacuum (nonconducting states). Thereby we obtain a "conducting" band structure, the energy gaps of which correspond to the minima in the TCS curve. Below $E - E_F = 30$ eV the evanescent part of the complex band structure does not strongly affect the spectrum, but it is responsible for the structure at 34 eV. Above 15 eV the experimental structures are much less pronounced than the theoretical ones because of the strong effect of the electron absorption not included in the present calculation. Gross features of the experimental spectrum are well reproduced by the present calculation, however, to understand the fine structure a more detailed study is required, which would include a more accurate treatment of the surface and take into account the electron absorption.

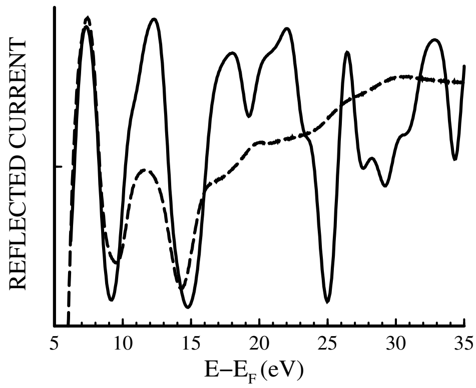

Figure 3: Theoretical (solid curve) and experimental [6] (dashed curve) TCS spectra of VSe_2. The onset of the theoretical spectrum is adjusted by shifting the curve by 0.7 eV to higher energies.

Acknowledgment

One of the authors (E.E.K.) gratefully acknowledges the support by a grant of the Alexander von Humboldt-Stiftung.

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