Finite-Difference Method for the Calculation of Low-Energy-Electron Diffraction

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A new scheme of calculation avoiding the muffin-tin approximation is presented for low-energy-electron diffraction. The finite-difference method is then used to solve the Schrödinger equation. A simple superposition potential and a nonuniform three-dimensional grid of points yields satisfactory experiment-theory agreement for the Cr(100)-(1 × 1)N surface, with geometrical parameter values close to the ones found in a standard study. An optimization of the charge exchange gives a 1.3 electron transfer from chromium to nitrogen.

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Up to now, all methods for low-energy-electron-diffraction (LEED) intensity calculations have been based on the muffin-tin approximation [1]. The largest possible nonoverlapping spheres are drawn about each nucleus, the potential inside is spherically symmetric, and the interstitial potential is constant. Then, the calculation is divided into three steps. First, the scattering by a single atom is described by phase shifts and partial spherical waves. Second, the scattering by an atomic plane parallel to the surface is calculated taking into account the intralayer multiple scattering. Third, the scattering by the whole crystal is obtained by computing the interlayer multiple scattering.

A large number of surface structures have been determined by this method, including adsorbate systems as well as ordered or substitutional alloys [2–4]. Nevertheless, the muffin-tin approximation is not appropriate at very low energy, in the presence of strong dipoles at the surface, or for semiconductors. In these cases the agreement between theory and experiment can probably be improved by using a more general computation scheme.

Some works, which could be applied to LEED, have already tried to go beyond the muffin-tin approximation for energy band problems. In particular, the discrete variational method (DVM) [5] uses a discretization of the potential to calculate matrix elements but keeps the usual expansion in plane waves in its Koringa-Kohn-Rostoker version [6]. More recently, Gonis, Zhang, and Nicholson [7] showed that the equations of multiple-scattering theory remain valid in the case of arbitrary-shaped potential cells.

Numerical methods, such as the finite-difference method (FDM), are extensively used in mechanics and hydraulics but less often in solid-state physics. The first presentation in this area was made in 1934 by Kimball and Shortley [8]. It was used later, for example, by Puska and Nieminen [9]. Both studies dealt with binding states. The FDM is based on the elaboration of a three-dimensional grid in the volume of interest, and a discrete form of the Schrödinger equation is given on the node points of this 3D grid. The unknowns are the values of the wave function at the grid points. This does not require any geometrical modeling of the potential such as the muffin-tin approximation, and therefore no particular basis of expansion (spherical or plane waves) is necessary. The advantages of the FDM are the mathematical simplicity and the flexibility coming from its direct derivation from the Schrödinger equation, which allows for an easy extension to more complicated situations such as nonlocal phenomena. A technical limitation of the FDM is that the grid has to be very dense in the vicinity of the atomic nuclei. However, the technique is now of practical use, thanks to the rapid improvements in computer capabilities. The purpose of the present paper is to develop the FDM to LEED applications.

The first thing is to build a potential describing the electron-crystal interaction as well as possible. As a first try, a simple superposition of spherical atomic electron densities is performed. Using Slater orbitals, it is always possible to attribute an electric charge to the atoms, and so, define a charge transfer that is just the number of charges passing from the valence orbitals of one atom to those of another atom. This charge transfer is an input parameter to be fitted in this study. This must be done keeping the surface cluster globally neutral. The potential is then divided into two contributions: the classical Hartree potential and the exchange-correlation potential as suggested by Hedin and Lundqvist [10]. The excited-state potential is calculated using the table given in Ref. [10]. The surface barrier is automatically taken into account including the three-dimensional corrugation. One just has to make the calculation sufficiently far outside the crystal.

This simple superposition is illustrated by looking at the dependence of the total potential on the energy at the mean distance between atoms in clusters of Cr_nN. A curve in excellent agreement with the one used for the real part of the optical potential in standard LEED is found. Note that the difficult and artificial choice of the muffin-tin radius is avoided. This eliminates nonphysical parameters such as potential shifts or a step between the "inside" and the "outside" of the muffin tin. The potential varies smoothly and without spherical symmetry in this area.

The imaginary part of the potential used to simulate the damping, mainly due to the plasmons, is assumed to be uniform in the solid and smoothly energy dependent as is usual in standard LEED computations. Note, however, that this assumption is not necessary, any periodic 3D dependence of the imaginary part of the potential being usable. At the surface, the imaginary barrier shape is chosen as proposed by Rundgren and Malmström [11].

The Schrödinger equation can then be solved in the whole zone of interest, namely, from the crystal-vacuum interface to deep enough in the bulk, where the electron wave field is widely damped out and a no-reflection boundary condition is used. Parallel to the surface, periodic boundary conditions are used. One takes advantage of all possible symmetries to divide as much as possible the number of grid points in the problem (see Fig. 1).

Considering the wave function as a second-order polynomial, the Laplacian in the Schrödinger equation $\Delta\psi + [E - V(\mathbf{x})]\psi_0 = 0$ can be written, for a cubic and uniform grid lattice with an interpoint distance h, in the form

$$\Delta\psi = \left(-6\psi_0 + \sum_{j,\varepsilon}\psi_j^\varepsilon\right)\Big/ h^2 ,$$

where ψ_0 is the wave function value on the central point where the potential is $V(\mathbf{x})$. The ψ_j^ε are the wave function values on the six nearest-neighbor points along the directions εj with $\varepsilon = +$ or $-$ and $j = x$, y, and z. For a quadratic uniform lattice with different interpoint distances h_j^ε along the six directions, one gets

$$\Delta\psi = \left(-\sum_j 2/h_j^\varepsilon h_j^{-\varepsilon}\right)\psi_0 + \sum_{j,\varepsilon}[2\psi_j^\varepsilon/h_j^\varepsilon(h_j^\varepsilon + h_j^{-\varepsilon})] . \qquad (1)$$

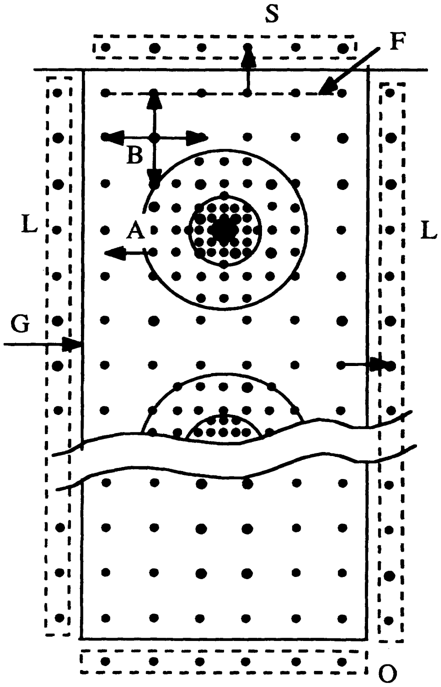

FIG. 1. General view of the meshing. G is the limit of the unit cell. Two atoms are represented with their concentric crowns and the corresponding division by two of the interpoint distance. In O, the wave function is close to zero. The neighboring points in L are deduced from symmetries or translation. In S, the wave function is calculated through the propagation of simple plane waves from the plane F where the Fourier transform is done. B is a point where formula (1) can be directly applied; at A, a neighboring point is missing and adjacent points must be considered in the Laplacian.

Close to an ion core, the kinetic energy of the electron is very high, whereas in the region between two ion cores, it is much lower. Consequently, it is necessary to use a nonuniform lattice of grid points in order to solve the Schrödinger equation. In this case, some nearest neighbors cannot be part of the grid points and a more complex Laplacian is deduced versus other wave function values on other points on the grid.

A set of n linear equations corresponding to the n points of the grid, with n unknowns, is obtained, the value of the wave function on a point depending on the values of the wave function on the neighboring points. At the vacuum-crystal interface, a Fourier transform is performed to get the values of the diffracted beam amplitudes, and so, it is possible to calculate by simple propagation the value of the wave function on the grid points outside the surface plane (see Fig. 1).

From this formulation it is easy to see that a nonlocal potential such as $V\psi(\mathbf{x}) = \sum U(\mathbf{x},\mathbf{x}')\psi(\mathbf{x}')d^3x'$ can be directly introduced in the discretized formula. For instance, it is in this way that the effect of temperature will be treated in the next step of the development of the method. Nevertheless, at this stage, a first crude approximation is to neglect the effect of multiple scattering on phonon damping. One then has just to multiply the diffracted intensity by a Debye-Waller factor. Anyway, temperature effects can cause different attenuations on the different peaks in a spectra, but never shift them in energy.

To determine the interpoint distance of the grid, the following convergence criterion is chosen:

$$h^2(E - V) = 6\beta , \qquad (2)$$

where β is a test parameter. In the crystal, the maximum interpoint distance value $h_{\max}$ is found between the atoms where $E - V$ is minimum. For simplicity, one can take an $h_{\max}$ value corresponding to the highest energy of incidence in the LEED study. Near the nucleus of an atom the potential is given by $-2Z/r$ and relation (2) cannot be used because h would have to converge to zero. Fortunately the oscillations of the wave function do not have infinite frequency. A first-order approximation to the wave function near the nucleus is given by the Hartree formula:

$$\psi_0 = \sum \psi_j^\varepsilon/(6 - 12Zh) .$$

To get the minimal interpoint distance around the nucleus the following convergence criterion is used:

$$h_{\min} = a/2Z ,$$

where a is another test parameter. Starting from $h = h_{\max}$ the interpoint distance is decreased by successive division by 2 when approaching a nucleus until the $h_{\min}$ value is reached. The grid between atoms is thus composed of successive concentric crowns. Between two of them, the point density is multiplied by 8 (Fig. 1).

Calculations are performed on Cr(100)-(1×1)N at normal incidence and compared with both experimental spectra and with previous standard LEED calculations. Chromium is a transition metal and such a material might not be the best choice to get an improvement with respect to conventional calculations. Indeed, the muffin-tin approximation is rather good in this case. Nevertheless, the goal is to prove the validity of the present method, and with the geometry of this surface already resolved by standard LEED [12], parameters can be reoptimized just around the values already found.

Trials were made to determine appropriate values of the test parameters a and β. With $a = \beta = 0.3$, a reasonable agreement between experiment and theory is obtained. With $a = \beta = 0.15$ convergence is achieved. In our case this means a maximum interpoint distance $h_{\max}$ around 0.11 Å and five grid divisions to reach $h_{\min} = 0.036$ Å for nitrogen and seven to reach $h_{\min} = 0.009$ Å for chromium because of its higher atomic number. The $p4m$ unit cell is seven layers deep and contains around 17000 points.

The structure has been optimized by the mean of metric distances [13]. The nitrogen atom was kept in the fourfold hollow sites. The rippling between nitrogen and chromium atoms and the two first chromium interlayer distances d_{12} and d_{23} are optimized in the present work: (i) d_{12} is found equal to 1.84 Å corresponding to 28% expansion, to be compared with 1.79 Å and 25%, respectively, in the previous study; (ii) the distance between the nitrogen and the second-layer chromium remains the same (2.01 Å), which implies a 0.16-Å rippling; (iii) d_{23} is found to be equal to 1.25 Å, slightly lower than the 1.40-Å value previously found. One can note that the discrepancy between the nitrogen local environment models due to standard and to FDM LEED is very small.

An optimization of the charge exchange between the nitrogen and the surrounding chromiums of the first atomic plane has been performed. Calculations with between 0 and 2 electron transfer from chromiums to nitrogen were tried. The best agreement is found for a 1.3 ±0.5 electron transfer. This is consistent with values given in bulk nitrides by band-structure calculations [14] or by x-ray diffraction [15].

The result is given in Fig. 2. The agreement obtained between FDM calculated and experimental I-V curves is quite good in spite of not taking the temperature into account.

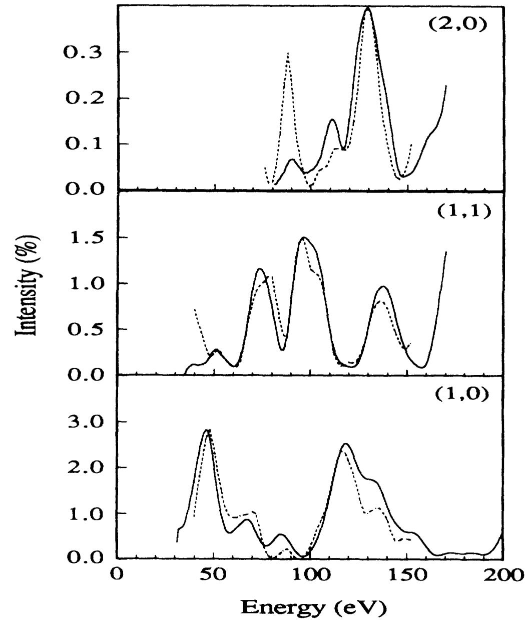

FIG. 2. The best agreement between the experimental (solid curve) and calculated (dotted curve) spectra. The incidence is normal.

Concerning computing requirements, the new method is more expensive than the traditional approach: (1) One needs between 5 and 10 times more memory, and (2) the computing time for one structural model is of the same order, but the present program cannot be easily optimized to loop over interlayer distances.

In conclusion, the finite-difference method works for LEED calculations. Being more expensive than the traditional approach, the interest of the method is not for making the standard analysis but the following: first, the possibility of studying situations difficult to reach with classical methods, such as evaluation of specific parameters or analysis of non-muffin-tin surfaces and, second, its possible extensions. The next step must be to consider the effect of temperature and to extend the formulation to nonspherical atomic orbitals permitting, thus, a real description of the surface atomic bondings. The method can be extended to band-structure calculations or electronic structure calculations in a cluster with the same kind of grid. A variational scheme would then have to be added for the energy calculation.

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