Direct Methods in Surface Crystallography

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(Received 15 August 1988)

Direct methods have been studied for many years in the context of x-ray diffraction and it is the heavy atom technique of x-ray crystallography that inspires our approach to the surface problem. The idea is that we know the bulk structure lying behind the surface, and we can define a "reference surface" as near to the true surface structure as possible. It is subsequently treated as the "heavy atom" of the surface problem and all phases referred to the reference surface phases. The method is shown to work well for some simple examples. Future applications of greater sophistication are discussed.

PACS numbers: 68.35.−p, 61.14.Dc, 61.14.Hg

Several powerful techniques exist for the determination of surface structure. All of them rely to a greater or lesser extent on trial and error interpretation of experimental data. Surface extended x-ray absorption fine-structure spectroscopy has some limited possibilities for direct inversion by Fourier transform to give a radial distribution function, but the problem of determining the angular distribution of atoms, or their distribution between different environments must be solved by other means.

Low-energy electron diffraction has so far resisted attempts to use direct methods. Nevertheless, it is arguably the most successful technique with the majority of structures determined by this method. It owes this power to the very high density of information that the diffraction process produces: the coordinates of several independent surface atoms can be found by use of the information contained in diffraction data acquired over a range of a few hundred eV. Indeed, it is the very success of the technique that is forcing our attention back to the direct methods.

Consider a complex surface structure in which the x, y, and z coordinates of three atoms are to be determined, $n=9$ coordinates in all. For each coordinate we may wish to try $t=5$ different values to compare with experiment. This implies a very large number of different structures to try out,

$$N_{\text{trials}}=t^n=5^9=1.95\times 10^6 \text{ trials}. \qquad (1)$$

Of course things are not quite as bad as this: Some of the trial structures will correspond to chemically unrealistic situations, and once we are close to the true structure we can home in on the best agreement by a search strategy for the minimum in the R factor. Nevertheless, for very large systems we shall ultimately be defeated by the exponential growth of trials with the number of coordinates exhibited by Eq. (1), which is common to all trial and error strategies. The problem is formally classified as NP standing for a nonpolynomial dependence on n.

Direct methods have been studied for many years in the context of x-ray diffraction. The simple nature of x-ray diffraction theory means that a Fourier transform of experimental diffracted amplitudes will give the atomic coordinates directly. Only the intensities are known so the problem reduces to one of finding the phases. This can be done either by using sophisticated theorems which limit the volume of phase space which needs to be searched, or more traditionally by using the heavy atom method: A heavy atom is substituted into a complex unit cell and dominates the diffracted amplitudes, A_{0G}. Subsequently, coordinates of all other atoms are to be referred to the position of the heavy atom so that A_{0G} is chosen to be real. Since the other atoms produce a relatively small change in diffracted amplitude, δA_G, it follows that

$$|A_G|^2 \approx |A_{0G}|^2+2|A_{0G}|\,|\delta A_G|\cos(\theta), \qquad (2)$$

where θ is the phase of δA_G. Hence, apart from the usual ambiguity about centro-symmetric crystals, we know the amplitudes and we can Fourier transform to find the coordinates.

It is this heavy atom technique which inspires our approach to the surface problem. The idea is that we know the bulk structure lying behind the surface, and we can define a "reference surface" based on the same bulk structure, and as near to the true surface as our chemical intuition and other information enables us to guess. This reference surface is subsequently treated as the "heavy atom" of the surface problem and all phases referred to the reference surface phases.

What use are the phases? LEED is recognized as a multiple-scattering problem and a Fourier transformation, even of LEED amplitudes, generally giving a jumble of nonsense. Here we introduce the second important concept in our approach: Provided that the reference surface is reasonably close to the real structure the diffracted amplitudes will change by an amount that is first order in the atomic displacements. Suppose that we have a surface in which one of the top layer atoms in the unit cell is displaced by an amount δr from the reference surface. The changes in the amplitudes and the displacements will be connected by a tensor

$$\delta A_g = \sum_j T_{gj}\delta r_j , \tag{3}$$

so that the change of intensity is

$$|A_g|^2 = \left|A_{0g} + \sum_j T_{gj}\delta r_j\right|^2 \approx |A_{0g}|^2 + M_{gj}\delta r_j , \tag{4}$$

where

$$M_{gj} = A^*_{0g}\sum_j T_{gj} + A_{0g}\sum_j T^*_{gj} . \tag{5}$$

The accuracy of tensor LEED has been explored elsewhere, and several applications to structure determination have been made.[1-3] Hence we are working with a well proven concept. It does not take a great leap of the imagination to realize that if we know $|A_g|^2$ from experiment, and we can calculate A_{0g} and T_{gj} theoretically, then δr_j can be found by matrix inversion

$$\delta r_j = \sum_g (M^{-1})_{jg}(|A_g|^2 - |A_{0g}|^2) . \tag{6}$$

This is the simplest form of the theory and we have applied it to relaxation of the Rh(110) and W(100) surfaces.

For the Rh(110) surface LEED intensities, as conventionally measured and analyzed earlier,[4,5] were evaluated in the energy range 50 to 200 eV for seven beams symmetrically nonequivalent at normal incidence. Because of the surface roughness, theoretical and experimental intensities usually differ in their absolute level and so the experimental intensities were renormalized beam by beam according to

$$I'_g = I_g \frac{\int |A_g(\delta R)|^2 dE}{\int I_g(E)\, dE} , \tag{7}$$

whereby in a first-step approximation $A_g(\delta R) = A_g(0) = A_{0g}$ was used $[\delta R = (\delta r_1, \delta r_2)]$. We then used (6) to find δr_j, the displacements of the first two layers of atoms, assuming that the relaxation is entirely in the direction normal to the surface. The unrelaxed surface with the interlayer distance $D_0 = 1.345$ Å was used as a reference structure. Only a subset of the intensities is necessary to define a square matrix M, i.e., a 2×2 matrix for a two-layer relaxation δr_1 and δr_2. For different subsets of the measured intensities different values for $\delta r_1 = D_{12}$ and $\delta r_2 = D_{23}$ result in oscillations about the correct values known from the conventional full dynamical analysis.[4] The oscillating deviations from the correct result are largely due to the neglect of the quadratic term in δr_1 [see (4)], whose relative magnitude is energy dependent. Assuming that these errors are statistical, the error minimization,

$$[d/d(\delta r_j)] \sum_{g,E} [I'_g - |A_g(\delta R)|^2]^2 = 0 , \tag{8}$$

leads to a system of nonlinear equations

$$\sum_{g,E} [I'_g - |A_g(\delta R)^2|][d|A_g(\delta R)|^2/d(\delta r_j)] = 0 , \tag{9}$$

which by use of (4) is linearized to give

$$\sum_{g,E} [I'_g - |A_{0g}(\delta R)|^2 - M_{gj}\delta r_j]M_{gj} = 0 . \tag{10}$$

Additionally we took the quadratic term into consideration by iterating the solution of (10) using

$$A_{0g}^{(v+1)} = A_{0g}^{(v)} + \sum_j T_{gj}\delta r_j^{(v)} ,$$

when going from step v to $v+1$. Similarly, the renormalization procedure according to (7) was repeated. The minimization was also extended to find the proper value of the inner potential. The whole procedure eventually gives the final value

$$\delta r_j = \sum_v \delta r_j^{(v)} .$$

Figure 1 displays the result for this iterative process starting from the unrelaxed surface as the reference structure. Clearly the iteration converges after only a few steps to the surface relaxation

$$(D_{12}/D_0, D_{23}/D_0) = (-5.7\%, +1.6\%) .$$

This is close to the result,

$$(D_{12}/D_0, D_{23}/D_0) = (-6.9\%, +1.9\%) ,$$

of the conventional R-factor analysis[4] and approaches it within the usual error bar of LEED results.

We also applied the direct method to the hydrogen

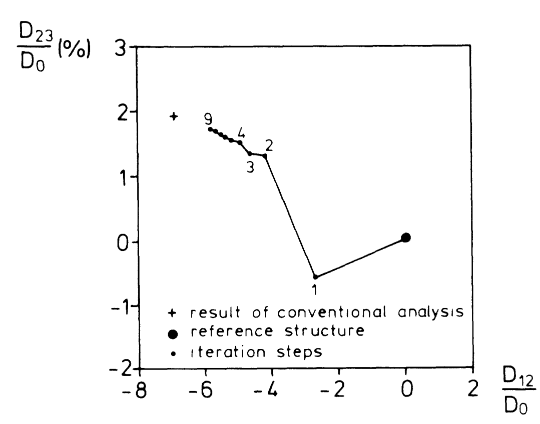

FIG. 1. Two-layer surface relaxation for Rh(110) as obtained by the direct method through iteration.

covered surface Rh(110) 1×1-2H. Recently it was shown that hydrogen removes the surface relaxation to (−1.3%, +0.2%) whereby neglect of hydrogen scattering only slightly affects the full dynamical analysis.[4,5] Again the direct method result calculated by neglecting hydrogen is near the exact result within the usual error limits as displayed in Table I. The same holds for the unreconstructed surface of W(100) for whose analysis measurements taken at 400 K were used.[3]

TABLE I. Comparison of two-layer relaxation results obtained by conventional and direct LEED analysis.

	Conventional method		Direct method	
Surface	$D_{12}/D_0(\%)$	$D_{23}/D_0(\%)$	$D_{12}/D_0(\%)$	$D_{23}/D_0(\%)$
Rh(110)	−6.9	+1.9	−5.7	+1.6
Rh(110) 1×1-2H	−1.3	+0.2	−0.8	+0.9
W(100)	−8.2	0.0	−6.3	+1.9

This straightforward application of the ideas and its success in predicting a simple structure gives us confidence to develop the method further. The problem is that the change in amplitude is not linear in the atomic displacement for large displacements, and the iteration used above with a constant tensor might hold for small displacements only. In an earlier paper we showed how it was much better to define a function of the atomic coordinates which then proved to be a more linear variable than the bare coordinates themselves. For example, if an atom has scattering factor,

$$t^{(0)}_{lm,l'm'} = \delta_{ll'}\delta_{mm'}[\exp(2i\delta_l) - 1]\,, \tag{11}$$

then translating the atom through a distance δr changes the scattering by

$$\delta t_{LL'} = \sum_{L''L'''} G_{LL''}(-\delta r)\, t^{(0)}_{L''L'''} G_{L'''L'}(+\delta r) - t^{(0)}_{LL'}\,, \tag{12}$$

where we have written L for the pair (lm) and

$$G_{LL'} = 4\pi \sum_{L''} (i)^{l-l'-l''}(-1)^{m'+m''} j_{l''}(K|\delta r|)\, Y_{l''-m''}[\Omega(\delta r)] \int Y_{lm} Y_{l''m''} Y_{l',-m'}\, d\Omega\,. \tag{13}$$

K is the complex wave vector of the electrons, the j's are spherical Bessel functions, and the Y's are the spherical harmonics, which in this instance we choose to be real functions.

If we regard δt as small we can use perturbation theory to write the change in diffracted amplitudes as

$$\delta A_g \approx \langle k_\parallel | \delta t | k_\parallel + g \rangle\,, \tag{14}$$

where the states $|k_\parallel\rangle$ and $|k_\parallel + g\rangle$ represent the incident and diffracted LEED states for the reference surface.

After substituting for δt and some considerable rearrangement we can write δA_g in the familiar tensor form,

$$\delta A_g \approx \sum_{LL'} T_{gLL'} B_{LL'}\,, \tag{15}$$

where

$$B_{LL'} = \sum_j \sigma_j j_l(K|\delta r_j|)\, Y_{lm}(\Omega(\delta r_j)) \times j_{l'}(K|\delta r_j|)\, Y_{l'm'}(\Omega(\delta r_j))\,. \tag{16}$$

σ_j is the probability of finding a displacement of type j in the unit cell of the reference surface. Since we have chosen to define the Y's to be real and the imaginary part of K is generally very small, then B is a real quantity. The number of values of L and L' that need to be considered is a function of how large the $|\delta r_j|$'s are: For large l or l' the Bessel function in (16) becomes very small and effectively cuts off the expansion.

Equation (15) constitutes a much more accurate tensor relationship than does Eq. (3). For the purposes of (15) we are to regard B as a vector which happens to be labeled by a double subscript. We can find B by taking a subset of our data points to make T into a square matrix which can be inverted. In practice we shall need to take large volumes of data to produce many estimates of B.

Having obtained the best estimate of B, now we can extract the atomic positions. To do this we change our viewpoint and now begin to regard B as a matrix. Note that B is a sum of separable terms, that is to say it has the form

$$B_{LL'} = \sum_j v_{jL} v_{jL'}\,, \tag{17}$$

where

$$v_{jL} = j_l(K|\delta r_j|)\, Y_{lm}(\Omega(\delta r_j))\,. \tag{18}$$

This implies that B has as many nonzero eigenvalues as there are different values of j. For example, by finding how many nonzero eigenvalues there are we discover the number of different types of atomic displacements. We can go further: Note that there is a sum rule,

$$\sin(K|\delta r_s - \delta r_t|)/(K|\delta r_s - \delta r_t|) = \sum_{lm} 4\pi j_l(K|\delta r_s|)\, Y_{lm}(\Omega(\delta r_s))\, j_l(K|\delta r_t|)\, Y_{lm}(\Omega(\delta r_t))\,. \tag{19}$$

The implication is that if the different values of δr are well separated compared with the wavelength of the electrons, the vectors v form an orthonormal set so that the eigenvectors of B are the vectors v_j, and the eigenvalues are σ_j. From the eigenvectors we easily infer the positions of the atoms.

What are the limitations? First, we do have to assume that the displacement from the reference structure produces small changes in scattering. In practice we have found through experience of the tensor LEED method that displacements of up to 0.4 Å can be tolerated without producing large errors. It is possible that some sort of iterative procedure could be used for larger displacements whereby an inaccurate estimate of the r_j's was used to define a new reference surface closer to the true structure. We are always free to check the structure we obtain by a conventional dynamical calculation and direct comparison with the data. The great virtue of the direct method is that it goes straight to an estimate of the structural coordinates without having to plod around parameter space.

Second, our method relies on differences in intensity between experimental spectra and those for a theoretical reference surface. Theory is good at predicting peak positions in LEED, but bad at absolute intensities. Ideally we should make two experiments: One on a known reference structure so that the differences could be found purely from experiment. Dynamical inputs such as the Debye-Waller factor, inelastic damping, etc., have nonlinear effects on the calculated intensities and some thought has to be given for each system to how the effect of intensity errors can be minimized.

Despite these limitations we are cautiously optimistic that direct methods have a valuable role to play in the future of surface crystallography, and that they will greatly extend the range of structures that can be studied.

K.H. and W.O. want to acknowledge financial support through Deutsche Forschungsgemeinschaft (DFG).

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