Reliability factors for LEED calculations

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Abstract. A new R-factor is defined which is insensitive to intensity discrepancies between theory and experiment but retains a simple functional form. An error analysis of R introduces another new quantity, the 'double-R' reliability factor, RR, where $R \times RR$ is the variance of R. This enables quantitative statements to be made about the significance of minima in R.

1. Introduction

The main technique of determining atomic geometry at surfaces is dynamical analysis of LEED data (Jona 1978, Marcus 1976, Pendry 1974, Tong 1977); experimental LEED intensities are compared with calculations for a series of trial structures. The procedure requires very careful experiments and, for the more complicated systems, a long and tedious series of computations. Even though current theory can produce 'good' agreement with experiment the agreement is never perfect. Curves consist typically of a series of peaks characterised chiefly by an energy and an intensity. The energies at which peaks occur are dictated by the phase of waves diffracted from the atoms in the surface and are directly related to the geometry, these energies are quite well reproduced by theory (i.e. to within much less than the peak width). Intensities are less well accounted for because they are influenced by many effects that are not well understood—by thermal vibrations, by inelastic losses, and sometimes by data collection techniques.

Where the parameters to be determined are very simple, such as a choice between sites 'A' and 'B' for the location of an adsorbate atom, or a uniform dilation of the spacing between the last two layers of atoms, visual inspection of the curves is often adequate. The eye is well equipped to neglect the relatively poor correlation of intensities and to concentrate on peak positions. In more complicated instances the quantity of data to be assimilated and evaluated rapidly becomes much too large and this procedure fails. In recent analysis of a diatomic molecule on a transition-metal surface, more than 2000 separate graphs were generated to be compared with experiments, each one containing many peaks. Some automated criterion is required to summarise overall quality of agreement. Preferably this would be contained in a single number, the reliability or R-factor.

The requirements of a good R-factor are that it is chiefly sensitive to peak positions. It should not be at all sensitive to absolute intensities, but should pay some attention to relative intensities especially of features that are close in energy. It should also be a very simple function of the intensities not involving higher than the first derivative with

respect to energy. Otherwise, calculations must be made at closely spaced energies to ensure numerical accuracy, with a consequent increase in computing times.

Many suggestions have already been made (Legg *et al* 1977, Van Hove *et al* 1977, Zanazzi and Jona 1977) of which the most sophisticated is that of Zanazzi and Jona. They propose

$$R_{ZJ} = \frac{A}{\delta E} \int \omega(E) |cI'_{th} - I'_{expt}| dE$$

where

$$c = \int I_{expt} / \int I_{th}, \qquad \omega = \frac{|cI''_{th} - I''_{expt}|}{|I'_{expt}| + \epsilon}, \qquad \epsilon = |I'_{expt}|_{max}$$

where the integrals extend over a range δE. A is chosen to normalise R_{ZJ} to unity for uncorrelated curves

$$A = \delta E \Big/ \left(0.027 \int I_{expt} \right).$$

Zanazzi and Jona say that empirically $R = 0.2$ is good agreement, $R = 0.35$ mediocre and $R = 0.5$ is bad agreement.

This function has proved useful in several determinations but is clearly empirically based and has the disadvantage of involving the second derivatives of the intensities. In this paper I try to construct an R-factor starting from the logical premise of insensitivity to intensity. The R-factor is then analysed statistically, and a more precise meaning given to its value in terms of levels of confidence. In particular the way the significance levels of R depend on the size of the database is considered. This leads to the definition of the double reliability factor, RR, which determines, amongst other things, the level at which a minimum in R becomes significant. It will be shown that RR varies as the square root of the size of the database.

2. What should be compared?

LEED curves consist for the main part of a series of Lorentzian peaks

$$I \simeq \sum \frac{a_j}{(E - E_j)^2 + V_{oi}^2}. \tag{1}$$

Their widths are dictated by the imaginary part of the electron self energy, V_{oi},

$$\Delta E = 2|V_{oi}| \tag{2}$$

and in most materials V_{oi} is approximately independent of energy, above say 30 eV, and takes a value of around -4 eV. Other features can sometimes appear in the curves. For example multiple scattering can induce a zero in the curves. In fact these zeros contain much structural information because the phase of the diffracted wave changes rapidly in their vicinity. They should not be suppressed in a comparison of theory and experiment. Occasionally sharp features due to surface resonances appear. Electrons trapped in surface states sometimes have long lifetimes if the state sits mainly outside the surface, and produce narrow resonances.

For a series of widely spaced peaks, the criterion of insensitivity to the amplitudes is

met by the logarithmic derivative

$$L(E) = I'/I \tag{3}$$

which in the case of equation (1) reduces to

$$L \simeq \sum_j \frac{-2(E - E_j)}{(E - E_j)^2 + V_{oi}^2}.$$

In place of each peak in the intensity L, shows a $\pm$ excursion of amplitude:

$$L = \pm 1/|V_{oi}| \qquad \text{at } E = E_j \mp |V_{oi}|. \tag{4}$$

This completely eliminates the amplitudes if the peaks are well separated. If the peaks overlap to some extent, the relative intensities do affect L but, as we described, the relative intensities of closely spaced peaks are quite well reproduced and it is desirable to have some sensitivity to this correlation. Comparison of L_{th} and L_{expt} works well except when I is zero, as it can be when multiple scattering is present. The infinity in L gives too high emphasis to zeros. We prefer to use instead of L a function which gives similar emphasis to zeroes and Lorentzian peaks,

$$Y(E) = L^{-1}/(L^{-2} + V_{oi}^2). \tag{5}$$

It can be shown that Y takes a maximum value of

$$Y_{max} = \pm\tfrac{1}{2}|V_{oi}| \qquad \text{when } L = \pm 1/|V_{oi}| \tag{6}$$

which for a series of Lorentzians defined in equation (3) occurs when

$$E = E_j \mp |V_{oi}|. \tag{7}$$

Two warnings are needed when calculating Y for experimental data. Noise in the data can be dangerous in giving spurious variations in I'. Some smoothing of curves should then be attempted, e.g.

$$\tilde{I} = \frac{1}{\pi} \int \frac{I(E')\Sigma \, dE'}{(E - E')^2 + \Sigma^2} \tag{8}$$

where we choose $\Sigma < |V_{oi}|$ to avoid losing real information from $\tilde{I}$. The second warning concerns the background that occurs in all LEED curves. Y is specifically designed to pick up small peaks well separated from large ones, and the presence of background noise will severely interfere with this process. Either the background must be carefully subtracted experimentally, or the theory must have an equivalent background added (but at the price of losing information in the weak peaks) or the background can be fitted by a smoothly varying curve whose parameters are adjusted to optimise the final R-factor.

We shall use as an example a LEED calculation for a molecule adsorbed on a noble metal surface. We shall vary the distance, d, of the molecule from the surface. Experiments will be simulated by taking the theory curves for $d = 2 \cdot 0$ Å and distorting them as follows

$$I_{expt} = \sin(0 \cdot 22 \, E) \exp(-E/108) \times I_{th}. \tag{9}$$

The first factor is designed to simulate errors in intensities of peaks, the second to describe the strong decrease of intensity at high energies due to thermal effects. We show the resulting 'experiment' in figure 1(a). Figure 1(b) shows the corresponding Y_{expt}. Note that despite the wide variations of peak intensity in I, Y gives equal emphasis to the peaks. Y is a function which oscillates between $\pm\tfrac{1}{2}|V_{oi}|^{-1}$.
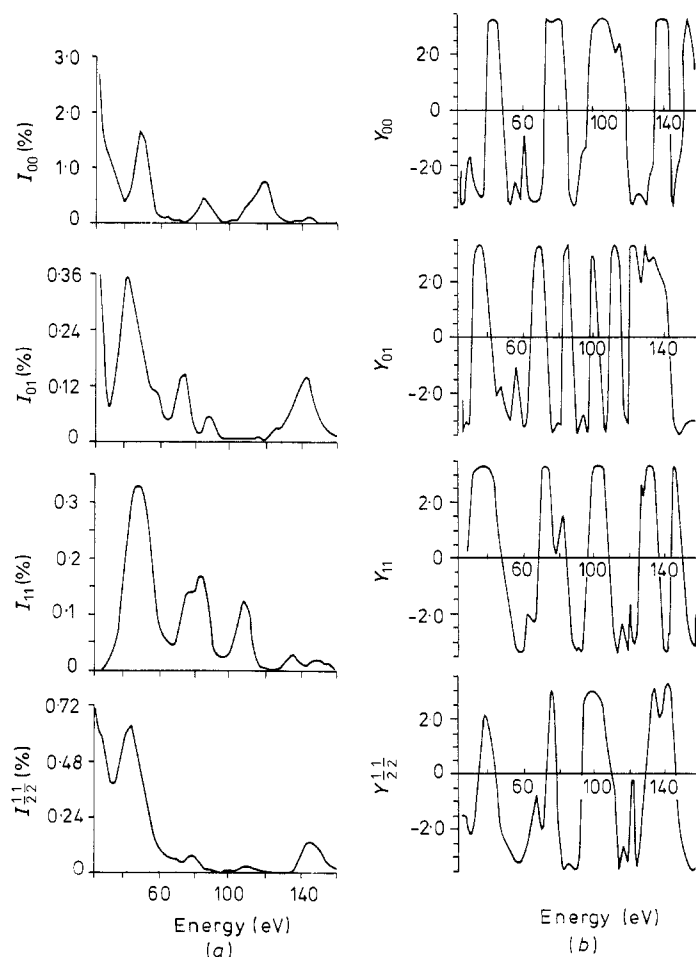
Figure 1. (a) Simulated experimental LEED curves for a molecule adsorbed on a noble metal surface; (b) The Y-function corresponding to the experimental curves in (a).

The new reliability factor is defined in terms of the Y functions

$$R = \sum_g \int (Y_{g\text{th}} - Y_{g\text{expt}})^2 dE \bigg/ \sum_g (Y_{g\text{th}}^2 + Y_{g\text{exp}}^2) \, dE. \tag{10}$$

The denominator normalises R to unity when there is no correlation between theory and experiment. This can easily be seen, because in the absence of correlation the average of the product

$$\overline{Y_{\text{th}} Y_{\text{expt}}} = \overline{Y_{\text{th}}} \times \overline{Y_{\text{expt}}} \tag{11}$$

reduces to zero as a result of the oscillatory nature of Y. Thus

$$\overline{(Y_{\text{th}} - Y_{\text{expt}})^2} = \overline{Y_{\text{th}}^2} + \overline{Y_{\text{expt}}^2} \tag{12}$$

and the normalisation follows.

Figure 2 shows the reliability factor of equation (10) computed for our model 'experimental' data plotted for various displacements of the molecule normal to the surface.
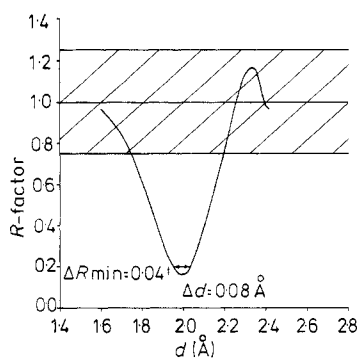
Figure 2. The reliability factor calculated for various spacings, d, between the molecule and the surface. The shaded region indicates the variance of R about unity.
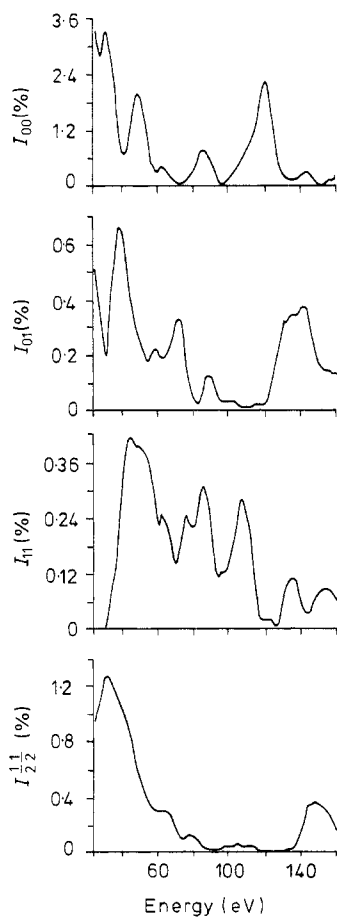

Figure 3. Theoretical intensity curves corresponding to the optimum spacing of $d = 2\cdot0\,\text{Å}$, to be compared with figure 1(a).

As we expect, a sharp minimum in R is seen at $d = 2.0$ Å, the value of R returning to approximately unity far from the minimum.

Figure 3 shows the theoretical intensity curves for the optimum spacing of 2.0 Å. Comparison with figure 1(a) shows that there is very good agreement by conventional standards of LEED comparisons.

3. Reliability of reliability factors

The great difficulty in using R-factors, especially a new one. is knowing how deep a minimum is significant. There will be fluctuations in R even for uncorrelated data producing spurious minima, and a level of significance must be established either through experience or preferably through a proper theory. Fortunately the new reliability factor is a simple quadratic function of the discrepancy and so is easily analysed statistically.

We consider all possible comparisons between theory and experiment made for different modes of data collection, using different presciptions to construct the theoretical potential, and ask for the statistical variation in the R-factor that the different errors encountered will produce.

We consider again our single isolated Lorentzian peak. Only its energy affects the comparison of Y_{th} and Y_{expt} and we assume that the error in energy, Δ, follows a normal distribution

$$P(\Delta) = (1/\sigma\sqrt{2}\pi) \exp(-\Delta^2/2\sigma^2). \tag{13}$$

Many assumptions are made here, not least of which is the assumption of random errors. In practice many of the errors will be, at least partly, systematic. Our working here is intended as a guide rather than a rigorous analysis.

For an error in locating this single Lorentzian of Δ, assumed smaller than the peak width, we have

$$\int_{-\infty}^{+\infty} (Y_{th} - Y_{expt})^2 \, dE \bigg/ \int_{-\infty}^{+\infty} (Y_{th} + Y_{expt}) \, dE \simeq \alpha\Delta^2. \tag{14}$$

From equations (13) and (14) we can calculate the mean R factor

$$\bar{R}_1 = \alpha\overline{\Delta^2} = \left(\alpha\int \Delta^2 \exp(-\Delta^2/2\sigma^2) \, d\Delta\right)\bigg/\int \exp(-\Delta^2/2\sigma^2) \, d\Delta = \alpha\sigma^2 \tag{15}$$

and the variance of R is

$$\left[\int (\alpha\Delta^2 - \alpha\sigma^2)^2 P(\Delta) \, d\Delta\right]^{1/2} = \sqrt{2}\alpha\sigma^2 \tag{16}$$

therefore

$$\text{var } R_1/\bar{R}_1 = \sqrt{2} \tag{17}$$

Suppose that there are N well separated peaks in the curve. From elementary statistical theory

$$\text{var } R_N/\bar{R}_N = \sqrt{(2/N)} \tag{18}$$

In an extended range of data many peaks will occur. Indeed the multiple scattering equations contain such a rich variety of structure that peaks are usually packed as

tightly together as they can be, i.e. in a total range of data δE, we will encounter approximately N well resolved peaks, where

$$N = \delta E/(4|V_{oi}|). \tag{19}$$

For the instance we have here

$$V_{oi} = -4\,eV, \tag{20}$$

$$\delta E = 490\,eV, \tag{21}$$

thus

$$N = 30 \cdot 6 \tag{22}$$

is the number of possible pieces of structure.

We can make a very quick estimate to check if this formula for N is a good one. Each Lorentzian contributes to $\int Y^2$ approximately $\pi/(2|V_{oi}|)$. Therefore

$$\int Y^2 \, dE \simeq N\pi/2|V_{oi}| = 12 \cdot 0.$$

This compares with a value of $16 \cdot 2$ obtained by integrating Y^2_{expt}, which indicates that we have made a conservative estimate of N.

We now define the double reliability factor

$$RR = \operatorname{var} R/\bar{R} \simeq (8V_{oi}/\delta E)^{1/2} = 0 \cdot 26. \tag{23}$$

For uncorrelated data in a finite sample we can expect deviations from $\bar{R} = 1 \cdot 0$ of the order of $RR = 0 \cdot 26$ for our example. We can be more precise if we wish and say that if

$$R < (1 \cdot 0 - 1 \cdot 96\, RR) \tag{24}$$

there is only a 5 % chance of this being a random fluctuation. Figure 2 shows a shaded area within which statistical fluctuations of R from unity will lie with 68 % probability, i.e. $R = 1 \pm RR$. In fact the R factor does not convey the statistical significance very well. We can define instead a *significance* factor which depends both on R and the size of sample

$$S = 1 - \frac{1}{\sqrt{2\pi}} \int_{-T}^{\infty} \exp(-\tfrac{1}{2}t^2)\, dt, \tag{25}$$

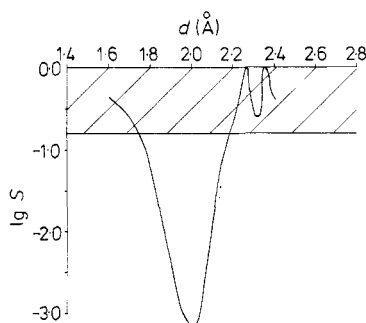$$T = (1 - R)/RR. \tag{26}$$

Figure 4. Logarithmic plot of the significance of the R-factor as a function of d. The shaded region lies within the variance of R about unity.

The significance factor is the probability of a random fluctuation to a value less than R. As S grows smaller the more significant the fluctuation. Figure 4 shows lg S. It is clear that for the data-set we take the dip of $R = 0.16$ at $d = 2.0$ is very significant indeed. There is only a one in a thousand chance that it is a statistical fluctuation.

A further application of the RR factor is to estimation of errors in d. If we assume that the residual value of R at the minimum is due to random fluctuations, we deduce that the variance in the minimum is

$$\text{var } R_{min} \simeq RR \times R_{min} \simeq 0.04. \tag{27}$$

From figure 2 we can deduce from this number, and the curvature in R near the minimum, that the accuracy of d is $d = 2.00 \pm 0.04\,\text{Å}$.

4. Conclusions

The simple R-factor, and statistical analysis that followed, will help to maximise the efficiency of extracting information from LEED curves. The general level of significance for a conventional size of data-set, such as that used as an example here, correlates well with the conclusions of Zanazzi and Jona about their R-factor. The moral is that high-statistical accuracy is very hard to achieve through sheer size of data set because of the square root variation. It is more rewarding to concentrate on high-quality data and calculations which reduce R_{min}.

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