Tensor LEED: A Technique for High-Speed Surface-Structure Determination

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A fundamental limitation of LEED as a surface-structure probe is the complexity of the theory compared with x-ray scattering from solids. By making one full dynamical calculation for a reference structure we express diffraction from modifications of this structure in first-order perturbation theory. This gives a theory analogous to the x-ray case in that it can be separated into a structure factor and a form factor which is a tensor in the dynamical regime. In many cases the linear dependence on the structure factor gives computational savings approaching 10^3 over conventional methods.

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Although LEED is one of the most successful surface-structure techniques, the present theory cannot interpret the most complex of diffraction patterns. To progress further we need a scheme of interpretation that avoids the disastrous N^3 scaling of computational effort with the number of atoms in the surface unit cell and which can then be used to explore very quickly large volumes of parameter space. Surprisingly enough this goal can be achieved for a large class of systems.

Our inspiration lies in x-ray scattering theory where an atom scatters x rays from state $\mathbf{K}$ to state $\mathbf{K}'$ with form factor $f_j(|\mathbf{K}'-\mathbf{K}|)$. The beauty of this weak-scattering theory is that the total scattered amplitude in state $\mathbf{K}'$, $A(\mathbf{K}')$, is calculated by first-order perturbation theory and is therefore a linear function of the individual atomic scattering amplitudes:

$$A(\mathbf{K}')=\sum_j f_j(|\mathbf{K}'-\mathbf{K}|)\exp[i(\mathbf{K}'-\mathbf{K})\cdot\mathbf{R}_j]. \quad (1)$$

This linear property leads to a complete factorization of the problem into form factors and structure factors. The latter contain all the geometric information we desire in a simple form, in fact as a sum of exponentials. In contrast, LEED theory[1] involves complex dynamical processes that weave the form factors and the structure factors together in an inseparable way. Thus, the comparative power of the x-ray technique resides in its essential simplicity which allows the rapid calculation of the scattering from a trial structure and the more direct inversion of experimental data. In this paper we seek this simplicity in the LEED case by attempting to find as close a parallel with the x-ray theory as we can.

The first step is to define a reference structure the scattering from which we shall treat from a full dynamical standpoint. In the x-ray case our starting point was empty space in which x rays propagate as plane waves, and the atoms introduce a weak perturbation. In the LEED case we start from the reference structure. The crucial point is that having made this investment in a time-consuming calculation, if we then move the atoms only a small amount the perturbation will be a weak one and can be calculated by first-order perturbation theory as for the x-ray case.

The theory comes in three levels of sophistication. At the simplest level, which treats the smallest displacements, a displacement of the jth atom by $\delta\mathbf{R}_j$ changes the potential in the surface by

$$\delta V_j=\delta\mathbf{R}_j\cdot\nabla V_j(\mathbf{r}-\mathbf{R}_j). \quad (2)$$

Let $|\mathbf{k}_p\rangle$ be the exact LEED state of the undistorted system produced by an incident beam of energy E and momentum $\mathbf{k}_p$ parallel to the surface. Then in the presence of a distortion the amplitude of the diffracted wave, with energy E and momentum $\mathbf{k}_p'$ parallel to the surface, is increased by

$$\delta A(\mathbf{k}_p')\approx\sum_j\langle\mathbf{k}_p'|\delta V_j|\mathbf{k}_p\rangle=\sum_{i,j}T_{ij}\,\delta R_{ij}, \quad (3)$$

where the tensor T, analogous to the form factor in x-ray scattering, is defined by

$$T_{xj}=\langle\mathbf{k}_p'|\nabla_x V_j(\mathbf{r}-\mathbf{R}_j)|\mathbf{k}_p\rangle, \quad (4)$$

and similarly for T_{yj} and T_{zj}. The $\delta\mathbf{R}_j$ play the role of the "structure factors." I-V spectra from a large number of distortions of the reference structure can be generated once T is known by a simple resumming of Eq. (3), leading to vast increases in computational efficiency over conventional methods.

The second level of sophistication recognizes that if $\delta\mathbf{R}_j$ becomes comparable with the electron's wavelength the approximation will break down. However, there is a better way to calculate the change in the scattering power of a displaced atom. Consider the t matrix of the

atom displaced by $\delta\mathbf{R}_j$, $t_j(\delta\mathbf{R})$, referred to the original position of the atom at $\mathbf{R}_j$,

$$t_j(\delta\mathbf{R}) = G(-\delta\mathbf{R})t_j G(\delta\mathbf{R}), \tag{5}$$

where $G(\delta\mathbf{R})$ is the free-particle propagator[2] to $\delta\mathbf{R}$. In an angular momentum basis we define

$$\delta t_{j;lm,l'm'}(\delta\mathbf{R}) = \sum_{LM,L'M'} G_{lm,LM}(-\delta\mathbf{R}) t_{j;LM,L'M'} \times G_{l'm',L'M'}(\delta\mathbf{R}) - t_{j;lm,l'm'}. \tag{6}$$

We can now develop a renormalized perturbation theory in δt_j which takes account of the change in the atomic scattering factor exactly. Equation (3) is replaced by

$$\delta A(\mathbf{k}'_p) \approx \sum_j \langle \mathbf{k}'_p | \delta t_j | \mathbf{k}_p \rangle = \sum_{j;lm,l'm'} \tilde{T}_{j;lm,l'm'} \delta t_{j;lm,l'm'}, \tag{7}$$

where

$$\tilde{T}_{j;lm,l'm'} = \langle \mathbf{k}'_p | \mathbf{R}_j;lm \rangle \langle \mathbf{R}_j;l'm' | \mathbf{k}_p \rangle, \tag{8}$$

$|\mathbf{R}_j;lm\rangle$ being the state of angular momentum lm centered on $\mathbf{R}_j$. Equation (7) for the change in amplitude is still factorized into a form factor and a structure factor; the latter, the pair of G's in (6), is a purely geometric quantity. This is our preferred formula and is almost as convenient as (3) to evaluate. The third level of approximation includes corrections to δt from scattering by atoms surrounding the one displaced: We believe that it represents an unnecessary level of sophistication.

The utility of this new approach depends on how far atoms can be displaced while maintaining the validity of first-order perturbation theory upon which tensor LEED (TL) is based. Therefore we have implemented the TL technique as a modification of the standard Van Hove and Tong[1] package of computer codes and performed a direct comparison of I-V spectra generated by full dynamical calculations (FDC) and TL for the three model surfaces.

The first system we considered was a hypothetical $p(2\times2)$ reconstruction of Ni(100) in which one in every four of the top-layer atoms was displaced by a distance d along the surface normal. I-V spectra for six beams,

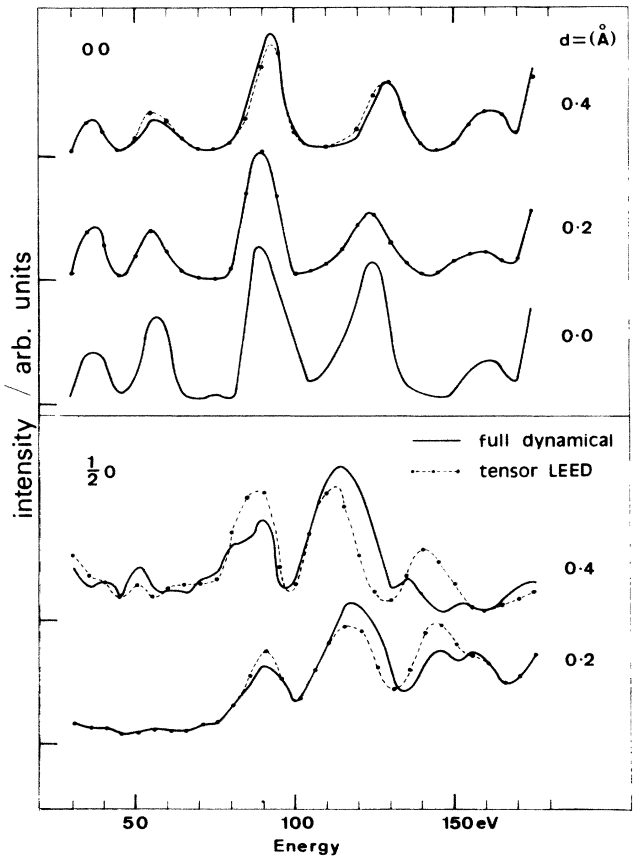


FIG. 1. I-V spectra of (0,0) and $(\frac{1}{2},0)$ beams for Ni(100)-$p(2\times2)$ generated by tensor LEED and by full dynamical calculations.

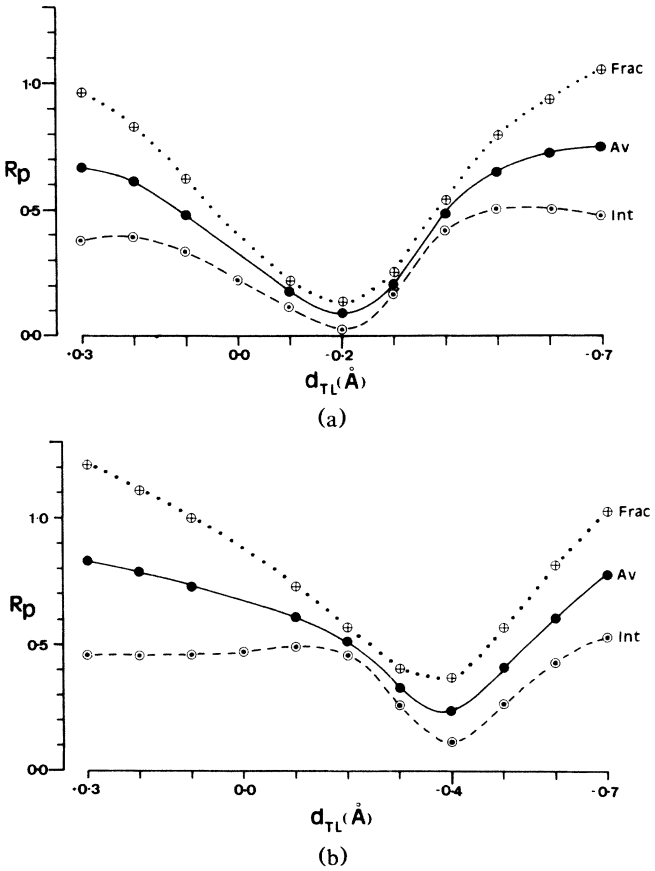


FIG. 2. Beam-averaged Pendry R factor between Ni(100)-$p(2\times2)$ I-V spectra generated by tensor LEED and by full dynamical calculations showing the R factor between the FD spectra for (a) $d = -0.2$ Å and (b) $d = -0.4$ Å and TL spectra for $0.3\text{ Å} \le d \le -0.7$ Å.

$0.3 \leq d \leq 0.7$ Å (negative displacements are out of the surface), were generated by TL for which the starting calculations were for the unreconstructed surface. The corresponding FDC's are extremely time consuming and were therefore performed only for $d = -0.2$ and $d = -0.4$ Å. From Fig. 1, we see that agreement is highly satisfactory at $d = -0.2$ Å, although at $d = -0.4$ Å some peaks and minima in the $(\frac{1}{2},0)$ beam are displaced. The integer-order beam spectra are, however, exceptionally well reproduced.

A quantitative measure of the agreement between the two methods is given in Fig. 2 which shows the Pendry R factor,[3] R_P, between the two sets of spectra. The beam-averaged R factor is 0.08 at $d = -0.2$ Å and 0.23 at $d = -0.4$ Å, the increase of R_P with increasing d reflecting the gradual failure of perturbation theory for large displacements. From these results we estimate that, used alone, our method would lead to essentially the same structural conclusions for $|d| \leq 0.2$ Å. For $0.2 \leq |d| \leq 0.4$ Å we believe that TL would locate the actual structure to within 0.1 Å. This is confirmed by Fig. 2 which demonstrates that there is significant disagreement between the two methods for $d = 0.4$ Å, yet TL is sufficiently accurate to produce a clear minimum at $d = -0.4$ Å. For larger displacements we envisage using TL to perform an initial structure search to locate regions of parameter space containing probable structures which would then be investigated thoroughly with a FDC. A comparison of central-processing-unit times for these calculations indicates that for a standard structure search, during which 10 to 100 trial structures are investigated, we achieve a time saving of greater than 2 orders of magnitude over conventional methods.

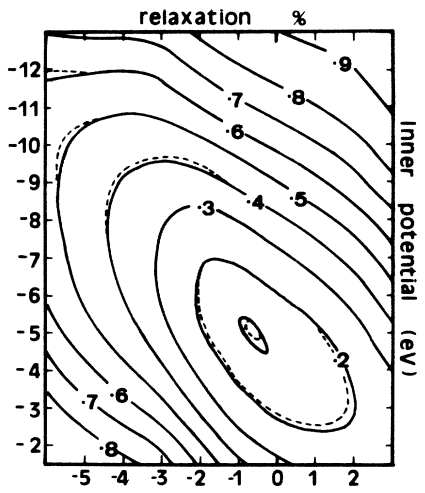


FIG. 3. Pendry-R-factor contour plot comparing experimental Cu(100) I-V spectra to FD (solid lines) and TL (dashed lines) calculations. The innermost contour is at $R_P = 0.15$. The inner potential is expressed with respect to the Fermi energy.

As a second test of TL we considered the top-layer relaxation of Cu(100). Previous LEED studies have found

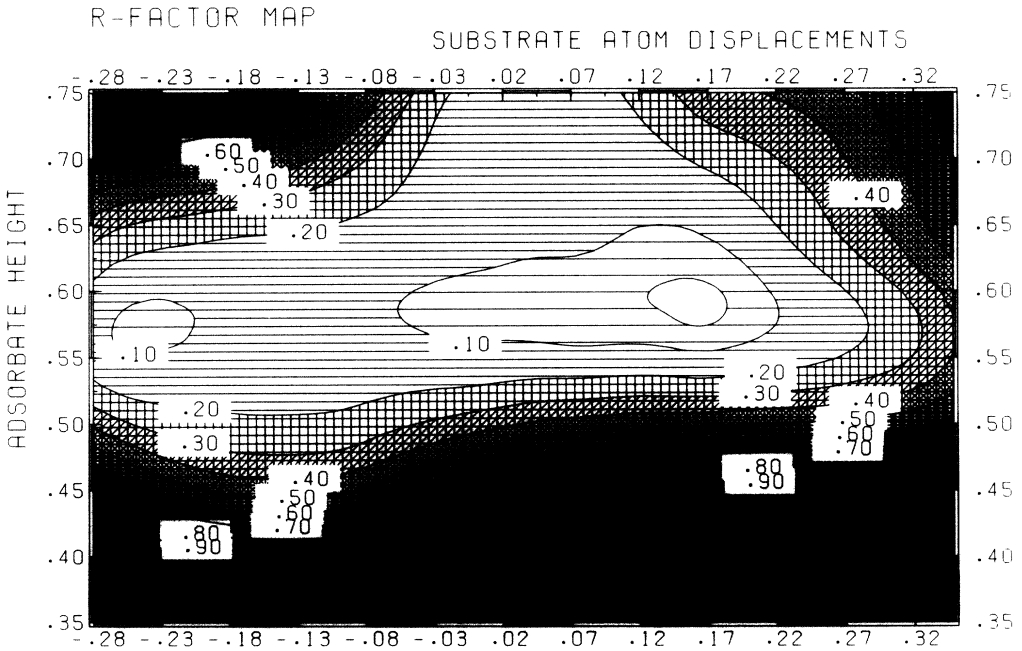


FIG. 4. Theory-experiment comparison of the diffuse intensity pattern from a disordered O overlayer on W(100) at 120 K displayed as a Pendry-R-factor contour plot of adsorption height (d_{WO}) against displacement (d_W) of the four W atoms surrounding the O atom. The minimum is at $d_{WO} = 0.59$ Å and $d_W = \sqrt{2} \times 0.15$ Å $= 0.21$ Å.

that this surface shows a small relaxation of the top layer into the surface by 1% to 2% of the bulk interlayer spacing.[4,5] We attempted to determine this relaxation from previously published experimental I-V spectra by both TL and FD methods. I-V spectra were evaluated for top-layer relaxations between 3% and -6% (positive out of the surface) and the Pendry R factor calculated between the experimental curves and both sets of theoretical spectra. From Fig. 3, we see that the R-factor minima for both the FD and TL calculations lie at the same value of the first-layer relaxation of -1% and have minima of 0.140 and 0.143, respectively. This result is consistent with previous studies in which multilayer relaxations were not considered. Note that the contour shapes are virtually identical for relaxations of up to 6%, implying that the perturbation theory used holds for displacements of all the atoms in the top layer of at least 0.11 Å.

Tensor LEED is not confined to conventional LEED. Any system involving the multiple scattering of electrons in the LEED energy range is accessible to the technique. To emphasize this point we have applied TL to the recently developed method of structure determination, diffuse LEED.[6,7]

Diffuse LEED has been used with striking success to determine the local absorption geometry of a disordered oxygen overlayer on W(100).[8,9] In this previous study it was assumed that the substrate was unreconstructed so that only the oxygen adsorption height was varied during the structure search. The oxygen atom was found to occupy a fourfold hollow site a vertical distance of 0.55 Å above the W plane. However, W(100) shows complex reconstructions,[10] and, therefore, we have used TL to extend the previous analysis to include substrate reconstruction. Displacements of the substrate produce an additional contribution to the diffuse intensity which can be evaluated by TL. We find a best-fit structure for an adsorption height of 0.59 ± 0.1 Å, with the four tungsten atoms adjacent to the oxygen atoms puckered inwards in the plane of the top layer by 0.21 Å. An R-factor map showing the plane of parameter space containing the best-fit structure is shown in Fig. 4. The R-factor minimum at $R_P = 0.05$ represents a 50% reduction of the R factor from its value for the unreconstructured substrate[8]—a very significant improvement by any measure.

In conclusion, we have shown that the new perturbation scheme, which we call tensor LEED, allows the accurate calculation of I-V spectra for distortions of a simple reference structure starting from a dynamical calculation as a basis for a perturbation theory. The method can be applied over a useful range of atomic displacements. TL can offer substantial savings of computer time over conventional methods, in many circumstances approaching 3 orders of magnitude, although not for simple cases such as Cu(100). Therefore we believe that TL will make some of the most complex reconstructed surfaces accessible to the LEED technique.

[1]J. B. Pendry, *Low Energy Electron Diffraction* (Academic, London, 1974); M. A. Van Hove and S. Y. Tong, *Surface Crystallography by LEED* (Springer, Berlin, 1979).

[2]P. J. Durham, J. B. Pendry, and C. H. Hodges, Comput. Phys. Commun. **25**, 193 (1982).

[3]J. B. Pendry, J. Phys. C **13**, 937 (1980).

[4]K. Heinz, N. Bickel, G. Besold, and K. Muller, J. Phys. C **18**, 933 (1985).

[5]H. L. Davis and J. R. Noonan, Surf. Sci. **126**, 245 (1983).

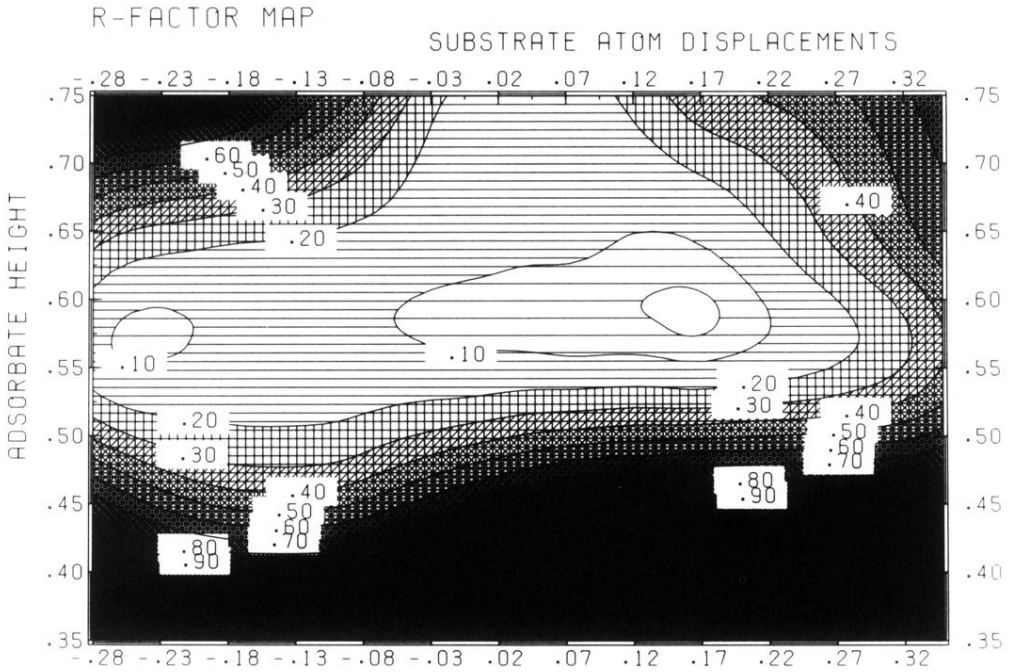
[6]J. B. Pendry and D. K. Saldin, Surf. Sci. **145**, 33 (1984).

[7]D. K. Saldin, J. B. Pendry, M. A. Van Hove, and G. A. Somorjai, Phys. Rev. B **31**, 1216 (1985).

[8]K. Heinz, D. K. Saldin, and J. B. Pendry, Phys. Rev. Lett. **55**, 2312 (1985).

[9]K. Heinz, K. Müller, W. Popp, and H. Lindner, Surf. Sci. (to be published).

[10]M. K. Debe and D. A. King, Surf. Sci. **81**, 193 (1979); R. T. Tung, W. R. Graham, and A. J. Helmed, Surf. Sci. **115**, 576 (1982); L. D. Roelofs and S. C. Ying, Surf. Sci. **147**, 203 (1984).



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