

THE THEORY OF TENSOR LEED

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We present a method for high-speed surface structure determination by low energy electron diffraction called tensor LEED. Tensor LEED is a perturbative approach to the calculation of LEED I - V spectra in which an initial reference surface is distorted to generate a particular trial structure. If these atomic displacements are small then we can use a first order perturbation theory to calculate the resultant changes in the LEED I - V spectra. This leads to a highly efficient calculational technique which can reduce the computational effort expended upon a typical structure determination by several orders of magnitude.

1. Introduction

Low energy electron diffraction (LEED) has developed into the foremost technique for surface structure determination and, within the last 10 to 15 years, LEED has been responsible for the elucidation of the atomic positions at several hundred solid surfaces [1,2]. Much of the success of LEED has been derived from its symbiotic combination of experimental and theoretical techniques. However as the emphasis in surface structure determination moves towards more complex, and industrially relevant surfaces, so the emphasis in LEED moves towards the development of new theoretical methods which make such systems accessible to the LEED technique.

In this paper we present a new theoretical method for the calculation of LEED I - V spectra from complex surfaces called tensor LEED, which we believe will make even the most complex surface structures available for structure determination by LEED. In this paper we shall set out the theory of tensor LEED. Results of the first applications of the method have been presented elsewhere [3,4] and will be published in more detail in a subsequent paper [5].

Although there now exist computer codes capable of calculating LEED I - V spectra from surfaces of almost arbitrary complexity [2,6,7] extreme calcula-

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tional difficulties are encountered as the LEED is applied to complex surfaces. Examples of such surfaces could be organic molecules adsorbed on catalyst substrates or extensively reconstructed surfaces but the common feature shared by such surfaces is a large number of atoms in the unit cell. The fundamental problem in the application of the LEED technique to such systems is that conventional LEED analysis consists of the application of a trial and error procedure in which calculated $I-V$ spectra are compared to the measured curves. Therefore it is necessary to repeat what is essentially a complete LEED calculation for each possible surface structure.

Consequently complex surfaces present two specific problems. Firstly, the computational effort expended to calculate a set of $I-V$ spectra from a single surface structure scales as N^3 , or at best N^2 , where N is the number of atoms in the surface unit cell. Secondly the time taken by a trial and error search to locate the positions of all N atoms in the unit cell scales exponentially with N . In other words, one must search through a $3N$ dimensional parameter space to determine the "best fit" surface structure. Thus one is often forced to make a compromise between the expenditure of computational resources and the reliability of the structure determination leaving some regions of parameter space unexplored.

To date much of the development of LEED theory has concentrated upon solving these problems by attempting to reduce the overall run-time for each LEED calculation. For certain incident beam directions symmetry among the scattered LEED beams can be exploited [7] and in many circumstances fast, iterative, perturbation schemes can be used. Most prominent among these in RFS [6] and, to a lesser extent, its intralayer analogue RSP [2,7-9] which have in common the fact that they are both iterative perturbation schemes and are therefore limited in accuracy only by the number of iterations taken (assuming absolute convergence). In contrast there are other, non-iterative, techniques such as a quasidynamical LEED [10-12], which neglects intralayer scattering, the beam-set-neglect method [13], which ignores coupling between certain beam sets and partially kinematic type calculations [14]. All these methods involve taking a sum over only a subset of all possible multiple scattering paths to evaluate an approximate LEED $I-V$ spectrum.

When dealing with complex surfaces not only are these approximations required but efficient search strategies are also needed, since we cannot explore all possible regions of parameter space. Most common among these techniques is the sequential optimisation of a set of structural parameters. This method involves optimising each structural parameter in turn which is then fixed at its best fit value before proceeding to the next parameter to be varied. Clearly, this type of search strategy does not necessarily lead to the global R -factor minimum since correlations exist between structural parameters. Therefore considerable care must be taken to avoid local R -factor minima by choosing the order in which the structural parameters are varied to reflect the

relative sensitivity of the I - V spectra to changes in these quantities. Therefore it is usual to vary first the positions of atoms which move the greatest distance upon reconstruction or are nearest to the surface [15]. Unfortunately even this procedure can lead to erroneous structural conclusions, as has been demonstrated for InSb by Cowell et al. [16].

An alternative approach, proposed by Adams [17], is to employ a systematic procedure in which the theory/experiment comparison is performed as the theoretical I - V spectra for each trial structure are calculated. The structural parameters for the next trial surface are then determined "a posteriori" from the results of the previous calculation using a minimisation algorithm. Unfortunately, this procedure is incompatible with conventional LEED computer programs which work most efficiently by performing calculations for a number of trial structures at each energy point (i.e. the loop over structures is inside the energy loop).

In this paper we propose a new perturbation scheme for the calculation of LEED I - V spectra, which, in many circumstances, goes some way to solving the problems outlined above. This technique differs from previous perturbation schemes in the way we aim to increase the efficiency of the entire structure determination as a whole, rather than reducing the run-time of each individual LEED calculation. We have also shown that tensor LEED is ideal for incorporation into an R -factor optimisation scheme [18], where it can be used to perform a directed search through the parameter space of unknown structural variables.

2. The theory of tensor LEED

2.1. Introduction

In order to introduce the theory of tensor LEED it is instructive to compare low energy electron diffraction to a simpler diffraction technique, that of X-ray scattering.

The fundamental physics pertaining to X-ray diffraction is that the atomic scattering of an X-ray photon is *weak* [19]. In fact the scattering cross-section of an atom seen by an X-ray photon is several orders of magnitude less than its physical cross-sectional area. Thus we can consider the crystal from which the X-rays diffract as a first order perturbation of the incident photon wavefield in vacuum. This leads to a direct relationship between the atomic positions \mathbf{R}_j and the scattered wavefield which can be expressed through a kinematic structure factor as just a sum of exponentials.

In contrast, the atomic scattering of low energy electrons is *strong* [6]. Indeed, the scattering cross-section of an atom as seen by a LEED electron is approximately its physical cross-sectional area. Thus we cannot consider the

crystal surface as a first order perturbation of the incident electron wavefield in vacuum. This leads to a complex relationship between the atomic positions and the scattered wavefield which can only be calculated by numerically summing the multiple scattering paths by which an electron propagates through the surface.

Tensor LEED represents an attempt to retrieve the simplicity of the X-ray diffraction in the LEED case. The trick is not to start with the electron wavefield in free space and consider the surface as a perturbation. Instead we use as the basis of our perturbation theory a particular surface structure, called the *reference structure* within which the electron wavefield can be calculated exactly by conventional means. We then distort this surface structure into another, "trial", surface by moving some of its constituent atoms and treat this distortion as a perturbation of the reference structure. Provided that these atomic displacements are small (in some sense) then the effect of this distortion on the LEED $I-V$ spectra can be calculated by a first order perturbation theory. This is the essence of the theory of tensor LEED; a first order perturbation approach which begins with a complete LEED calculation for a reference surface structure.

Of crucial importance to the application of tensor LEED is the question of how far can atoms be displaced from their position in the reference structure whilst retaining the accuracy of the perturbation approach upon which our theory is based. Extensive trial calculations and comparison with full dynamical calculations indicate that atoms can be displaced by as much as 0.4 Å. The results of such applications of tensor LEED have been briefly reported in a previous paper [3] and will be presented in more detail in the subsequent publication [5].

2.2. Basic principles

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

$$\delta V_j = \delta \mathbf{r}_j \cdot \nabla V_j(\mathbf{r} - \mathbf{r}_j). \quad (1)$$

Let $|\phi^+(\mathbf{k}_{\parallel})\rangle$ be the exact LEED state of the undistorted system produced by an incident beam of energy E and momentum \mathbf{k}_{\parallel} parallel to the surface. The distortion causes the amplitude of a scattered wave of energy E and parallel momentum \mathbf{k}'_{\parallel} , to be changed by an amount

$$\delta A = \sum_j \langle \phi^+(\mathbf{k}'_{\parallel}) | \delta V_j | \phi^+(\mathbf{k}_{\parallel}) \rangle \quad (2)$$

$$= \sum_{ij} T_{ij} \delta r_{ij}, \quad (3)$$

where the cartesian tensor, T , analogous to the form factor in X-ray diffraction, is defined by

$$T_{xj} = \sum_j \langle \phi^+(k_{\parallel}) | \nabla_x V_j | \phi^+(k_{\parallel}) \rangle, \quad (4)$$

and similarly for T_{yj} and T_{zj} . The sum of eq. (3) is taken over the three cartesian coordinates ($i = 1-3$) of each of the N displaced atoms ($j = 1-N$). The atomic displacements δr_j play the role of the "structure factors". Clearly $I-V$ spectra from a large number of distortions of the reference structure can be generated once T is known by simply resummation eq. (3) leading to vast increases in computational efficiency over conventional methods.

Note that the matrix element of eq. (2) is identical to that describing impact scattering in HREELS [20-22] in which two low energy LEED states are coupled together by the electron-phonon interaction. Eq. (2) also has similarities with photoemission theory in which two LEED states are coupled by the photon field [23,24].

The second level of sophistication recognises that if $2\pi\delta r_j$ becomes comparable with the electron's wavelength the approximation will break down so that eq. (1) is only valid for atomic displacements of less than 0.1-0.15 Å. Fortunately, for larger displacements, there is a better way to calculate the response of the scattered amplitude to the displacement of an atom. In an angular momentum basis we can use the translation theorem [25]. First we expand the atomic t matrix of a displaced atom as

$$t'' = t_j + \delta t_j(\delta r_j). \quad (5)$$

δt_j is the change in the t matrix of the j th atom produced by displacing it through δr_j referred to the position of that atom within the undistorted surface r_j . In an angular momentum basis we can use the translation theorem for spherical waves to calculate δt_j and replace eq. (2) by

$$\delta A = \sum_j \langle \phi^+(k_{\parallel}) | \delta t_j | \phi^+(k_{\parallel}) \rangle \quad (6)$$

$$= \sum_j \sum_{lm, l'm'} T_{j;lm,l'm'} \delta t_{j;lm,l'm'}, \quad (7)$$

$|r_j; lm\rangle$ being the state of angular momentum lm centred on r_j and $T_{j;lm,l'm'} \equiv \langle lm | T | l'm' \rangle$. Eq. (7) for the change in amplitude is still factorised into a form factor and a structure factor; the latter, δt , is a purely geometric quantity. This is our preferred formula and is almost as convenient as (3) to evaluate. The connection between the first and second versions of our theory can be established by substituting into eq. (6) the expression for δt_j evaluated in the first Born approximation; $\delta t_j = \delta V_j$, thereby yielding eq. (3).

The third level of approximation includes corrections to δt from scattering by atoms surrounding the one displaced. We do this by calculating the

reflection matrix S of a cluster of atoms around the displaced atom to define a renormalised δt matrix:

$$\delta t = \delta t + \delta t S \delta t + \dots \quad (8)$$

Although the calculation of S is a comparatively time consuming procedure [26] the advantages of this formulation of tensor LEED outweigh the additional computational effort required if the trial surfaces are sufficiently complex. However, extensive tests indicate that the second level of approximation seems to be adequate for many systems; we believe that this third version of our theory represents an unnecessary level of sophistication.

In the next section we formally develop the theory of tensor LEED. We shall consider the second version of the theory outlined in the previous section and therefore we aim to derive eq. (6) and a more computationally attractive version of eq. (7). The first, linear, version of the theory will be developed as a special case. To describe the multiple scattering of LEED electrons we shall use Green functions, originally applied to LEED by Beeby [27]. However, our approach has more in common with the theory of photoemission developed by Pendry [23,24].

2.3. Theory

2.3.1. The reference surface

Our first task is to evaluate the LEED states of the undistorted, reference, system which are coupled together by the perturbation introduced by moving some atoms into their position in the actual trial structure.

Consider a reference surface consisting of a lattice of atomic potentials V_j at positions r_j excited by a LEED beam of energy E and parallel wavevector k_{\parallel} . The incident LEED beam can be written as a plane wave:

$$\langle r | G_0^+ | \epsilon(k_{\parallel}) \rangle \equiv \exp(iK^+ \cdot r), \quad (9)$$

$$K^+ = (k_z^+, k_{\parallel}), \quad (10)$$

$$k_z^+ = +\sqrt{(2E - |k_{\parallel}|^2)}. \quad (11)$$

In eq. (9) we have defined a state $|\epsilon(k_{\parallel})\rangle$ which when acted upon by the free space Green function G_0^+ , generates a plane wave travelling in the positive z direction with parallel momentum k_{\parallel} .

These incident electrons interact with the reference surface and undergo multiple scattering to form a LEED state $|\phi^+(k_{\parallel})\rangle$. If the undistorted surface occupies the half space $z > 0$ then $|\phi^+(k_{\parallel})\rangle$ is generated by the full Green function for the undistorted surface:

$$|\phi^+(k_{\parallel})\rangle = G^+ |\epsilon(k_{\parallel})\rangle. \quad (12)$$

G^+ can be expressed as a Born series in the atomic potentials V_j and the free space Green function G_0^+ :

$$G^+ = G_0^+ + \sum_i G_0^+ V_i G_0^+ + \sum_{ij} G_0^+ V_i G_0^+ V_j G_0^+ + \dots, \quad (13)$$

where, in eq. (13) we assume that the surface potential is described by an assembly of identical muffin tin potentials:

$$\langle \mathbf{r}' | V_j | \mathbf{r} \rangle \equiv V(\mathbf{r} - \mathbf{r}_j) \delta(\mathbf{r} - \mathbf{r}'). \quad (14)$$

Alternatively we can write eq. (13) in terms of atomic t matrices t_j :

$$G^+ = G_0^+ + \sum_i G_0^+ t_i G_0^+ + \sum'_{ij} G_0^+ t_i G_0^+ t_j G_0^+ + \dots, \quad (15)$$

where the prime on the summation sign denotes that $i \neq j$. In an angular momentum representation the atomic t matrix of the j th atom can be expressed in terms of a set of phase shifts $\delta_{j,l}$:

$$\begin{aligned} t_{j;lm,l'm'} &\equiv t_{j;l} \\ &= \delta_{ll'} \delta_{mm'} (i/2\kappa) [\exp(2i\delta_{j;l}) - 1]. \end{aligned} \quad (16)$$

κ is the electron wavevector *within* the surface corrected for the jump in the crystal potential at the surface barrier V_{0r} :

$$\kappa = \sqrt{2(E - V_{0r})}. \quad (17)$$

Outside the surface the LEED state $|\phi^+(\mathbf{k}_{\parallel})\rangle$ consists of a set of plane waves leaving the surface:

$$\langle \mathbf{r} | \phi^+(\mathbf{k}_{\parallel}) \rangle = \langle \mathbf{r} | G^+ | \epsilon(\mathbf{k}_{\parallel}) \rangle = \sum_g A_g^- \exp(i\mathbf{K}_g^- \cdot \mathbf{r}), \quad (18)$$

each corresponding to a reciprocal lattice vector \mathbf{g} of the reference surface and where

$$\mathbf{K}_g^- = (k_{gz}^-, \mathbf{k}_{\parallel} + \mathbf{g}), \quad (19)$$

$$k_{gz}^- = -\sqrt{(2E - |\mathbf{k}_{\parallel} + \mathbf{g}|^2)}. \quad (20)$$

We can invert eq. (18) to establish the connection between the Green function for the reference surface G^+ and the diffracted plane wave amplitudes A_g^- :

$$A_g^- = \langle Z_0, \mathbf{k}_{\parallel} + \mathbf{g} | G^+ | \epsilon(\mathbf{k}_{\parallel}) \rangle, \quad (21)$$

where

$$\langle \mathbf{r} | Z_0, \mathbf{k}_{\parallel} \rangle = \exp(i\mathbf{k}_{\parallel} \cdot \mathbf{r}) \delta(z - Z_0). \quad (22)$$

The plane wave amplitudes A_g^- are what are usually evaluated by a standard LEED calculation in order to calculate the intensity reflected by the

reference surface into any LEED beam \mathbf{g} :

$$I_g = \frac{|k_{gz}^-|}{|k_z^+|} |A_g^-|^2. \quad (23)$$

2.3.2. The trial surface

Now let us distort this reference surface to generate a trial structure. We do this by moving the atoms at positions \mathbf{r}_j through displacements $\delta\mathbf{r}_j$ so that the new lattice is described by a set of lattice vectors $\mathbf{r}_j + \delta\mathbf{r}_j$.

In a conventional LEED calculation the I - V spectra from this trial structure would be evaluated by performing another full dynamical LEED calculation for the new geometry. Our approach is to consider the trial surface as a perturbation of the reference structure. The plane wave amplitudes reflected by this surface, \tilde{A} , are obtained by substituting the Green function for scattering by the distorted surface, \tilde{G}^+ , into eq. (21).

$$\tilde{A}_{g'}^- = \langle Z_0, \mathbf{k}_{\parallel} + \mathbf{g}' | \tilde{G}^+ | \epsilon(\mathbf{k}_{\parallel}) \rangle. \quad (24)$$

Since we allow the trial surface to have a different symmetry to that of the undistorted system we distinguish between the sets of reciprocal lattice vectors of the two structures \mathbf{g}' and \mathbf{g} respectively.

We now develop the perturbation theory required for tensor LEED. Our aim is to relate the plane wave amplitudes scattered by the trial and reference surfaces; \tilde{A} and A . We do this by expanding \tilde{G}^+ as a Born series in the Green function for the undistorted system G^+ :

$$\tilde{G}^+ = G^+ + \sum_i G^+ \delta\mathbf{t}_i G^+ + \sum_{ij} G^+ \delta\mathbf{t}_i G^+ \delta\mathbf{t}_j G^+ + \dots \quad (25)$$

where $\delta\mathbf{t}_j$ is the change in single site \mathbf{t} matrix of the j th atom produced by displacing it through $\delta\mathbf{r}_j$ referred to its position in the reference surface.

We now make the approximation which is central to the application of tensor LEED. We assume that for small atomic displacement $\delta\mathbf{r}_j$ the corresponding $\delta\mathbf{t}_j$'s are so small that terms in eq. (25) in which $\delta\mathbf{t}_j$ appear more than once can be neglected. In other words, we assume that $\delta\mathbf{t}_j$ is so small that scattering paths on which an incident LEED electron scatters from a $\delta\mathbf{t}$ more than once make a negligible contribution to the detected intensity. Thus we assume that it is a good approximation to write:

$$\tilde{G}^+ \approx G^+ + \sum_i G^+ \delta\mathbf{t}_i G^+, \quad (26)$$

and substituting this expression for \tilde{G}^+ into eq. (24) we find that the distortion of the reference structure specified by the atomic displacements $\delta\mathbf{r}_j$ changes the amplitude of electrons diffracted in beam \mathbf{g}' by:

$$\delta\tilde{A}_{g'}^- = \sum_j \langle Z_0, \mathbf{k}_{\parallel} + \mathbf{g}' | G^+ \delta\mathbf{t}_j G^+ | \epsilon(\mathbf{k}_{\parallel}) \rangle. \quad (27)$$

It now remains to remove the Green functions G^+ from eq. (27) and re-express δA in terms of LEED states of the reference structure $|\phi^+(\mathbf{k}_\parallel)\rangle$. From eq. (12) we know that

$$G^+ |\epsilon(\mathbf{k}_\parallel)\rangle = |\phi^+(\mathbf{k}_\parallel)\rangle. \quad (28)$$

To identify $\langle Z_0, \mathbf{k}_\parallel + \mathbf{g}' | G^+$ we note that

$$\langle (\mathbf{k}_\parallel + \mathbf{g}') | G^+ \quad (29)$$

is the electron wavefunction generated by multiple scattering of some initial wavefield

$$\langle (\mathbf{k}_\parallel + \mathbf{g}') | G_0^+ \quad (30)$$

among the atoms of the undistorted surface. Substituting the integral expression for G_0^+ into (30) and evaluating the resulting contour integral we find that

$$\langle (\mathbf{k}_\parallel + \mathbf{g}') | G^+ | \mathbf{r} \rangle = (1/i k_{g'z}^+ \Omega) \exp[i \mathbf{K}_{g'}^+ \cdot (\mathbf{r} - \mathbf{Z}_0)]. \quad (31)$$

From eq. (31) it immediately follows that eq. (29) represents nothing other than the conjugate of the LEED state generated by exciting the reference surface with a plane wave of amplitude $1/(i k_{g'z}^+ \Omega)$ and parallel wavevector $(\mathbf{k}_\parallel + \mathbf{g}')$. Thus

$$\delta A_{g'} = (1/i k_{g'z}^+ \Omega) \langle \phi^+(\mathbf{k}_\parallel + \mathbf{g}') | \delta t_j | \phi^+(\mathbf{k}_\parallel) \rangle. \quad (32)$$

We see from eq. (32) that the change in amplitude of LEED beam \mathbf{g}' , generated by moving the j th atom in the reference surface from \mathbf{r}_j to $\mathbf{r}_j + \delta \mathbf{r}_j$, is simply the matrix element of the corresponding change in the single site t matrix between the LEED state of the undistorted structure for an incident beam \mathbf{k}_\parallel and a "time-reversed" LEED state for an incident beam $(\mathbf{k}_\parallel + \mathbf{g}')$.

2.3.3. The tensor

In order to evaluate the matrix element of eq. (32) we must determine both the change in the t matrix, δt , and the explicit form of the LEED states $\langle \phi^+(\mathbf{k}_\parallel + \mathbf{g}') |$ and $|\phi^+(\mathbf{k}_\parallel)\rangle$ in the vicinity of each displaced atom.

Let us first consider δt . δt_j is the change in the t matrix of the j th atom produced by displacing it through $\delta \mathbf{r}_j$ referred to the position of that atom within the undistorted surface \mathbf{r}_j . In an angular momentum basis

$$\delta t_{j;lm,l'm'} = -t_{j,l} \delta t_{l'} \delta_{mm'} + \sum_{l''m''} G_{lm,l''m''}(-\delta \mathbf{r}_j) t_{j;l''} G_{l''m'',l'm'}(+\delta \mathbf{r}_j). \quad (33)$$

where $G(\delta \mathbf{r}_j)$ is a free particle propagator to $\delta \mathbf{r}_j$ [25]

$$G_{lm,l'm'}(\delta \mathbf{r}_j) = 4\pi \sum_{l''m''} i^{(l-l'-l'')} (-1)^{(m'+m'')} \times j_{l''}(\kappa |\delta \mathbf{r}_j|) Y_{l''-m''}(\delta \mathbf{r}_j) C_{lm,l''m'',l'-m'}. \quad (34)$$

j_l is a spherical Bessel function, Y_{lm} is a spherical harmonic and $C_{lm,l'm',l''-m''}$ is a Gaunt coefficient:

$$C_{lm,l'm',l''-m''} \equiv \int Y_{lm}(\Omega) Y_{l'm'}(\Omega) Y_{l''-m''}(\Omega) d\Omega. \quad (35)$$

We can see that δt_j depends only upon the atomic phase shifts of the j th atom and the corresponding displacement $\delta \mathbf{r}_j$. In other words δt_j is a purely geometrical quantity and is independent of the complex dynamical processes within the reference surface.

Now let us express the LEED states $\langle \phi^+(\mathbf{k}_{\parallel} + \mathbf{g}) |$ and $|\phi^+(\mathbf{k}_{\parallel})\rangle$ in terms of quantities which can be evaluated from a standard LEED computer program. To do this we switch to an angular momentum basis and expand these wavefunctions in spherical partial waves about \mathbf{r}_j .

$$|\phi(\mathbf{k}_{\parallel})\rangle = \sum_{lm} \langle \mathbf{r}_j; lm | \phi(\mathbf{k}_{\parallel}) \rangle | \mathbf{r}_j; lm \rangle. \quad (36)$$

Outside the muffin-tin of the j th atom $|\phi(\mathbf{k}_{\parallel})\rangle$ takes the form of

$$\begin{aligned} \langle \mathbf{r} | \phi(\mathbf{k}_{\parallel}) \rangle &= \sum_{lm} A_{j;lm}(\mathbf{k}_{\parallel}) \left[j_l(\kappa |\mathbf{r} - \mathbf{r}_j|) \right. \\ &\quad \left. + i \exp(i\delta_{j;l}) \sin \delta_{j;l} h_l^1(\kappa |\mathbf{r} - \mathbf{r}_j|) \right] Y_{lm}(\mathbf{r} - \mathbf{r}_j), \end{aligned} \quad (37)$$

so that

$$\langle \mathbf{r}_j; lm | \phi(\mathbf{k}_{\parallel}) \rangle = A_{j;lm}(\mathbf{k}_{\parallel}) \quad (38)$$

is the amplitude of the spherical partial wave (l, m) incident upon the atom at \mathbf{r}_j produced by exciting the reference surface with a LEED beam of parallel momentum \mathbf{k}_{\parallel} . Later, we shall demonstrate that these amplitudes can be evaluated by performing what is essentially a LEED calculation for the undistorted surface.

Substituting (36) into (35)

$$\delta A_{g'}^- = \sum_{j;lm,l'm'} \langle \phi^+(\mathbf{k}_{\parallel} + \mathbf{g}') | \mathbf{r}_j; lm \rangle \langle lm | \delta t_j | l'm' \rangle \langle \mathbf{r}_j; l'm' | \phi^+(\mathbf{k}_{\parallel}) \rangle. \quad (39)$$

We can now make use of the reciprocity theorem [28,29] to write:

$$\langle \phi^+(\mathbf{k}_{\parallel} + \mathbf{g}) | \mathbf{r}_j; lm \rangle = (1/2i\Omega\kappa k_{gz}^+) (-1)^m \langle \mathbf{r}_j; l-m | \phi^+(-\mathbf{k}_{\parallel} - \mathbf{g}) \rangle, \quad (40)$$

where Ω is the area of the reference surface unit cell. Substituting (40) into (39) and utilising (38):

$$\delta A_{g'}^- = (1/2i\Omega\kappa k_{gz}^+) \sum_{j;lm,l'm'} (-1)^m A_{j;l-m}(-\mathbf{k}_{\parallel} - \mathbf{g}) \delta t_{j;lm,l'm'} A_{j;l'm'}(\mathbf{k}_{\parallel}). \quad (41)$$

We now substitute into (41) the explicit expression for δt obtained from (31) and (32) and rewrite the change in amplitude δA_g^- as

$$\delta A_g^- = \sum_{j;lm,l'm'} F_{j;lm,l'm'} S_{j;lm,l'm'} - F_{j;00,00}/(4\pi), \quad (42)$$

where N_s is the number of atoms in the trial structure surface unit cell and the dependence of both S_j and F_j upon the exit beam \mathbf{g} is implied. S_j takes the form of a "structure factor"

$$S_{j;lm,l'm'} = i^{-(l+l')} j_l(\kappa|\delta\mathbf{r}_j|) Y_{l-m}(\delta\mathbf{r}_j) j_{l'}(\kappa|\delta\mathbf{r}_j|) Y_{l'-m'}(\delta\mathbf{r}_j) \exp(i\mathbf{g} \cdot \mathbf{r}_j). \quad (43)$$

F_j can be considered as a "form factor":

$$F_{j;lm,l'm'} = (1/2i\Omega\kappa k_{gz}^+) \sum_{l''m''} f_{j;lm,l''m''}^- (-1)^{(m''+l'')} t_{j;l''} f_{j;l''m'',l'm'}^+, \quad (44)$$

where the partial form factors f_j^+ and f_j^- are defined as:

$$f_{j;lm,l'm'}^- = \sum_{j;l''m''} i^{l''} C_{l''m'',lm,l'-m'} A_{j;l''-m''}(\mathbf{k}_{\parallel} - \mathbf{g}), \quad (45)$$

$$f_{j;lm,l'm'}^+ = \sum_{j;l''m''} i^{l''} C_{lm,l'm',l''-m''} A_{j;l''-m''}(\mathbf{k}_{\parallel}). \quad (46)$$

S_j is a purely geometrical quantity depending solely upon the atomic displacements $\delta\mathbf{r}_j$ and the electron energy. In particular S_j is independent of the structure of the reference surface. In contrast the tensor F_j depends only upon the scattering properties of the reference surface and is independent of the structure of the trial surface for which LEED beam intensities are to be evaluated.

The single centre expansion eq. (32) contained within the definition of δt implies that the sums over (l', m') and (l, m) can extend between l values of 0 and twice the largest l value needed to describe atomic scattering ($l = l_{\max}$). However the properties of the spherical Bessel functions of eq. (34) and in particular their dependence upon the order l implies that

$$S_{j;lm,l'm'} \approx 0 \quad \text{for } (l \text{ or } l') \geq \kappa|\delta\mathbf{R}_j|, \quad (47)$$

whilst for scattering by the full atomic potential:

$$t_{j;l} \approx 0 \quad \text{for } 1 \geq \kappa|\mathbf{R}_{j;\text{mt}}|, \quad (48)$$

where $R_{j;\text{mt}}$ is the muffin tin radius of the j th atom. Since for all trial surfaces for which eq. (35) applies $|\delta\mathbf{R}_j| \ll |\mathbf{R}_{j;\text{mt}}|$ we see that the rank of S_j and F_j are both less, and often considerably less, than that of the (diagonal) atomic t matrix. This aspect of eq. (42) leads to considerable computational savings over alternative methods of evaluating the change in amplitude as will be discussed later.

Eqs. (42)–(46) are the fundamental formulae of tensor LEED since they express the tensor F_j in terms of quantities that can be easily evaluated using conventional LEED programs. It can be seen that once F_j is known I – V spectra from an arbitrary trial surface can be rapidly evaluated simply by calculating the structure factor S_j for each displaced atom and resummation (42) to yield the intensity reflected by the trial surface:

$$I_{g'} = \frac{|k_{g'z}^-|}{|k_z^+|} |A_g^- \delta_{gg'} + \delta A_g^-|^2. \quad (49)$$

2.4. Constructing the tensor

It remains for us to show how the spherical wave amplitudes $A_{j;lm}$ needed to construct the tensor F_j can be obtained from a conventional LEED calculation. The method we present here is based on the dynamical approach of Pendry and is therefore applicable to both the CAVLEED [30] and the Van Hove and Tong [7] program packages or any program in which the multiple scattering paths are summed in real space. For simplicity we assume that the reference surface for which the amplitudes are calculated has only one atom in the surface unit cell, although the method can be generalised.

Suppose we wish to calculate the spherical wave amplitudes $A_{j;lm}(\mathbf{k}_\parallel)$ of the final electron wavefield about the j th atom generated by exciting the undistorted surface with a LEED beam of parallel wavevector \mathbf{k}_\parallel .

$$\langle \mathbf{r} | \phi_0^+ \rangle \equiv \exp(i\mathbf{K}^+ \cdot \mathbf{r}). \quad (50)$$

The multiple scattering of $|\phi_0^+\rangle$ among the surface gives rise to the total LEED wavefunction $|\phi^+(\mathbf{k}_\parallel)\rangle$. If the j th atom at \mathbf{r}_j is located in the i th atomic plane of the surface with origin \mathbf{c}_i then, on either side of this plane, the wavefunction consists of plane waves:

$$\langle \mathbf{r} | \phi^+(\mathbf{k}_\parallel) \rangle \equiv \sum_g B_g^+ \exp[i\mathbf{K}_g^+ \cdot (\mathbf{r} - \mathbf{c}_i)] + B_g^- \exp[i\mathbf{K}_g^- \cdot (\mathbf{r} - \mathbf{c}_i)]. \quad (51)$$

If renormalised forward scattering (RFS) is used to evaluate the interlayer scattering, the amplitudes B^+ and B^- are calculated during the RFS iteration loop and can be extracted from the RFS subroutines after convergence [6,7]. These incident plane waves produced an initial wavefield about the j th atom:

$$\sum_{lm} A_{j;lm}^0 j_l(\kappa |\mathbf{r} - \mathbf{b}_{ji}|) Y_{lm}(\mathbf{r} - \mathbf{b}_{ji}), \quad (52)$$

$$\mathbf{b}_{ji} = \mathbf{r}_j - \mathbf{c}_i, \quad (53)$$

$$A_{j;lm}^0 = 4\pi i^l \sum_g B_g^+ Y_{lm}^*(\mathbf{K}_g^+) + B_g^- Y_{lm}^*(\mathbf{K}_g^-). \quad (54)$$

To evaluate the total wavefield about \mathbf{r}_j , $|\phi_s(\mathbf{k}_\parallel)\rangle$, we must include scattering

by the atom at \mathbf{r}_j and contributions from the multiple scattering of (51) by other atoms in the i th layer:

$$\langle \mathbf{r} | \phi_s(\mathbf{k}_{\parallel}) \rangle = \sum_{lm} A_{j;lm}(\mathbf{k}_{\parallel}) \left[j_l(\kappa |\mathbf{r} - \mathbf{b}_{ji}|) + i \exp(i\delta_{j;l}) \sin \delta_{j;l} h_l^1(\kappa |\mathbf{r} - \mathbf{b}_{ji}|) \right] Y_{lm}(\mathbf{r} - \mathbf{b}_{ji}). \quad (55)$$

$$A_{j;lm}(\mathbf{k}_{\parallel}) = \sum_{l'm'} A_{j;l'm'}^0(\mathbf{k}_{\parallel}) (1 - X)^{-1}_{l'm',lm}. \quad (56)$$

The X matrix summarises the effect of the intralayer scattering and is identical to that which must be calculated to evaluate the layer scattering matrices [6,7]. Since it is always necessary to evaluate the spherical harmonics $Y_{lm}(\mathbf{K}_g)$, B_g and X in any conventional LEED calculation for the reference surface, modifying such a program to evaluate $A_{j;lm}(\mathbf{k}_{\parallel})$ is simply a matter of collecting these quantities from the appropriate subroutines and adding short routines to evaluate (54) and (56). Once these spherical wave amplitudes for the incident and each time reversed exit beam are known the tensor F_j can be evaluated from (42)–(46).

3. Linear tensor LEED

Earlier in this paper we pointed out that if the distortion required to generate the trial structure were small enough then we could derive an expression for the change in amplitude of each scattered LEED beam which is linear in the atomic displacements. Therefore in this section we shall set out this version of our theory which we call linear tensor LEED.

In the previous section we indicated how δt can be evaluated using spherical wave propagators. Here, however, we present a simpler, alternative, derivation which leads directly to eq. (3). We begin in a linear momentum representation where the displacement, $\delta \mathbf{r}_j$, of the j th atom introduces a simple phase factor into the atomic scattering factor, t :

$$\langle \mathbf{k}' | \delta t_j | \mathbf{k} \rangle = \langle \mathbf{k}' | t_j | \mathbf{k} \rangle (\exp[i(\mathbf{k}' - \mathbf{k}) \cdot \delta \mathbf{r}_j] - 1). \quad (57)$$

If the magnitude of the displacement is small compared to the electron wavelength then

$$\kappa |\delta \mathbf{r}_j| \ll 1, \quad (58)$$

so that

$$\langle \mathbf{k}' | \delta t_j | \mathbf{k} \rangle \simeq \langle \mathbf{k}' | t_j | \mathbf{k} \rangle (i[\mathbf{k}' - \mathbf{k}] \cdot \delta \mathbf{r}_j). \quad (59)$$

We require $\delta \mathbf{r}_j$ in an angular momentum basis:

$$\begin{aligned} \langle \mathbf{r}_j; l''m'' | \delta \mathbf{r}_j | lm; \mathbf{r}_j \rangle &= i \sum_{l'm'} t_{j;l'} \int \langle \mathbf{r}_j; l''m'' | \mathbf{k}' \rangle \langle \mathbf{k}' | \mathbf{r}_j; l'm' \rangle \langle \mathbf{r}_j; l'm' | \mathbf{k} \rangle \\ &\quad \times \langle \mathbf{k} | \mathbf{r}_j; lm \rangle (\mathbf{k}' - \mathbf{k}) \cdot \delta \mathbf{r}_j d\Omega_k d\Omega_{k'}, \end{aligned} \quad (60)$$

$d\Omega_k$ denotes an integral over the angular coordinates of \mathbf{k} and,

$$\langle \mathbf{r}_j; lm | \mathbf{k} \rangle = Y_{lm}(\mathbf{k}). \quad (61)$$

We can write eq. (60) as a scalar product

$$\langle \mathbf{r}_j; l''m'' | \delta \mathbf{r}_j | lm; \mathbf{r}_j \rangle = \alpha_{j;l''m'',lm} \cdot \delta \mathbf{r}_j, \quad (62)$$

where the cartesian components of the vector α are

$$\alpha_{j;l''m'',lm}^x = i(t_{j;l'} - t_{j;l}) \int \langle l''m'' | \mathbf{k} \rangle \mathbf{k} \cdot \hat{\mathbf{x}} \langle \mathbf{k} | lm \rangle d\Omega_k, \quad (63)$$

and similarly for $\alpha_{j;l'm',lm}^y$ and $\alpha_{j;l'm',lm}^z$. The matrix element in eq. (63) can be evaluated giving:

$$\alpha_{j;l''m'',lm}^z = (-1)^{m''} V_{l''l} C_{lm,10,l'm''}, \quad (64)$$

$$\alpha_{j;l''m'',lm}^x = i2\sqrt{2} (-1)^{m''} V_{l''l} (C_{lm,11,l'm''} + C_{lm,1-1,l'm''}), \quad (65)$$

$$\alpha_{j;l''m'',lm}^y = 2\sqrt{2} (-1)^{m''} V_{l''l} (C_{lm,11,l'm''} - C_{lm,1-1,l'm''}), \quad (66)$$

$$V_{l''l} = i\sqrt{4\pi/3} \kappa (t_{j;l''} - t_{j;l}),$$

We wish to derive an expression for the tensor T such that the change in amplitude of the LEED beam \mathbf{g} produced by the set of displacements $\delta \mathbf{r}_j$ is (from eq. (3))

$$= \sum_{ij} T_{ij} \delta r_{ij} \quad (67)$$

Substituting eq. (62) into (41) we find that the elements of the tensor T are:

$$T_{ij} = 1/(2i\kappa k_{g^+z}) \sum_{lm,l'm'} (-1)^m A_{j;l-m}(-\mathbf{k}_{\parallel} - \mathbf{g}') \alpha'_{j;lm,l'm'} A_{j;l'm'}(\mathbf{k}_{\parallel}), \quad (68)$$

where $A_{j;lm}$ are the spherical wave amplitudes described in eq. (38).

4. The implementation of tensor LEED

From eq. (42) it is apparent that the calculation of $I-V$ spectra from the trial surface involves two stages:

(i) Firstly we must evaluate the spherical wave amplitudes A_{lm} incident upon each displaced atom in the reference surface produced by the incident LEED beam $A_{j,lm}(\mathbf{k}_{\parallel})$ and a time-reversed exit beam corresponding to each observed LEED beam $A_{j,lm}(-\mathbf{k}_{\parallel} - \mathbf{q})$. In reality it is not necessary to repeat the calculation for each time-reversed exit beam, only for each time-reversed beam set. A beam set is defined as a set of exit beams related to one another by a reciprocal lattice vector of the reference surface. If we choose the reference structure to have the same symmetry as the trial surfaces then there is only one exit beam set: all exit beams are related to one another by a reciprocal lattice vector of the undistorted structure. If we choose a reference structure which has higher symmetry than the trial structures then we need more than one beam set, for instance if we use tensor LEED to distort a $p(1 \times 1)$ surface into a $c(2 \times 2)$ then we must perform time reversed calculations for two beam sets. This point is discussed in more detail elsewhere [31,32].

These amplitudes are used to construct the tensor F_j . This part of the calculation we call the *reference calculation* since all the structural parameters required for the calculation of these quantities are defined by the atomic geometry of the reference surface and are independent of any particular trial structure for which we may wish to evaluate $I-V$ spectra.

(ii) Secondly we evaluate the structure factor S_j for each trial surface and form the product of (42) with the previously calculated tensor F_j to find change in amplitude of each exit beam. This is the *trial structure calculation*. By repeating this part of the calculation we can evaluate the $I-V$ spectra from any number of trial structures.

This natural division of the complete calculation into two essentially self-contained units is reflected in the organisation of the computer code used to implement this method which consists of two distinct programs. This allows us to separate the comparatively time consuming reference calculation, which would have to be performed on a mainframe computer, from the highly efficient tensor LEED calculation which can be performed on even a quite modest microcomputer. The first program performs the reference calculation to evaluate the tensors F_j which are written to a disc or tape transfer file. The remaining part of the calculation is performed by the second program which reads the tensors F_j and then generates the $I-V$ spectra for each requested trial structure. Detailed documentation of the computer codes which implement tensor LEED can be found elsewhere [31,32].

5. The efficiency of tensor LEED

By using tensor LEED we can expect to obtain large gains in computational efficiency over conventional methods. Either version of our theory requires a

reference structure calculation to evaluate the tensor T (linear tensor LEED) or F (Tensor LEED). The computer time consuming for this part of the calculation is similar to that required for a complete full dynamical calculation for the reference structure. Additional time is needed to construct the tensor and this increases the CPU time for this part of the calculation by approximately 30%. Note, however, that the reference structure calculation only has to be performed for a very few structures, often only one. Furthermore, we decrease the computational effort expended on this part of the calculation by choosing a reference structure which has a smaller or more symmetrical unit cell than the actual surface being investigated. This surface can then be distorted into a series of more complex trial structures. For example, when investigating a reconstructed surface we can often use the unreconstructed surface as the reference structure.

However, the real gains in efficiency are obtained in the trial structure calculation. Here we must evaluate either (3) (linear tensor LEED) or (42) (tensor LEED) for each trial structure. If we examine these equations we see that (3) is a trivial scalar product whilst (42) is simply a pair of vector multiplications. In particular there are no matrix inversions or multiplications which give rise to the problematic N^3 and N^2 scaling with the number of atoms in the surface unit cell encountered in conventional LEED. In fact it is immediately apparent that the time taken to evaluate either eq. (3) or eq. (42) scales *linearly* with N ; the optimum scaling for LEED calculations [33,34].

Tensor LEED theory can be applied to many complex surface structures. The only limitation is that the atomic motions required to generate the trial structure from the reference surface be less than the limit of 0.4 Å in the case of tensor LEED or 0.1 Å in the case of linear Tensor LEED. We can consider disordered surfaces since tensor LEED does not require order: for example we can consider disordered adsorbate systems such as those investigated in diffuse LEED. We can also develop a similar theory to treat cases in which the perturbation in the crystal potential is not caused by atomic displacements. For example, we can consider substitutional alloys in which the difference between the scattering potential of each atomic species can be regarded as the perturbation in eq. (1). One limitation of tensor LEED is, however, that the trial structure cannot be generated by the removal or addition of entire atoms from the reference structure unit cell. This represents a substantial perturbation of the crystal potential beyond the validity of the approximations upon which tensor LEED is based. For these cases we must employ a reference structure which has the correct number of atoms in the surface and distort this structure by tensor LEED. The exception to this limitation arises in the case of light adsorbate atoms, such as hydrogen. The scattering of LEED electrons by hydrogen is so weak that it will permit the application of tensor LEED in which the reference structure is the substrate and the trial structure contains an adsorbed hydrogen overlayer.

More concrete examples of the time savings which can be obtained by tensor LEED will be presented in the following paper [5].

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