

**John Pendry: His Contributions to the Development of LEED Surface
Crystallography**

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Abstract

In this paper we discuss the pivotal role played by Sir John Pendry in the development of Low Energy Electron Diffraction (LEED) during the past three decades; the earliest understanding on the physics of LEED to the development of sophisticated methods for the structural solution of complex surfaces.

Introduction

Over the past several decades, the field of surface crystallography has seen the continual development of techniques for retrieving surface structural information [1-3]. The pursuit novel structural and imaging methods has occurred in parallel with the steady experimental and theoretical development of the oldest surface structural technique; low-energy electron diffraction (LEED) [4-8]. It is in this field that John Pendry played a pivotal role from the earliest understanding on the theory of LEED to the development of sophisticated methods for the structural solution of complex surfaces.

The phenomenon of electron diffraction was first postulated by de Broglie in 1924 [9] and it arose as a natural consequence of the theory of wave-particle duality. Three years later the diffraction of electrons was observed in the famous experiment performed by Davisson and Germer [10]; a well-collimated beam of electrons incident on a nickel sample that was accidentally recrystallized by heating resulted in the formation of a diffraction pattern. Although the contemporary importance of this experiment was the validation of the wave nature of the electron there was another remarkable aspect to this observation: unlike the diffraction of X-rays from a solid, the electron diffraction pattern was two-dimensional. This suggested that the interaction of low energy electrons with a solid is confined to the first few atomic layers at the surface of the material.

In the next issue of *Nature*, Thompson and Reid [11] reported the observation of electron diffraction occurring for incident electrons with higher kinetic energy. High energy electron diffraction developed very rapidly and became the foundation of Electron Microscopy [12].

However, the development of low energy electron diffraction as a structural tool did not occur until 40 years after the Davisson and Germer experiment. This long hiatus occurred for two reasons. The first was the necessity of understanding the behavior of electrons in an infinite 3D crystal and this was the primary focus of solid state physics during the intervening period. This was the foundation on which the understanding of electron-surface interactions was to be built. The second reason was experimental in nature. Davisson and Germer's experiment was fortuitous because a laboratory "accident" resulted in the creation of (111) microfacets on their Ni sample. In order to employ LEED for reproducible and quantitative surfaces studies it was crucial to create clean surfaces of fixed orientation and maintain the sample in this state for the duration of the LEED measurement. This required the development of Ultra-High-Vacuum technology together with methods for preparing clean surfaces and monitoring their cleanliness.

The Birth of LEED Crystallography

I first met John Pendry in Cambridge where he was working on the theory to explain low energy electron diffraction (LEED). Experimental LEED underwent a renaissance by applying the postacceleration technique whereby the diffracted electrons were separated from the inelastically scattered electrons by a single metal wire mesh grid system and then accelerated onto a light emitting phosphor covered screen that displayed the diffraction pattern. The rapid retrieval of the diffraction information (microseconds) permitted one to obtain diffraction from clean surfaces in a vacuum before contamination by ambient gases occurred and the monitoring the formation of surface structures of adsorbed molecules that were deliberately introduced as a function of time. As long as the ambient gas pressures remained below the mean free path of the scattered electrons in the diffraction chamber, the orderings of adsorbed atoms or molecules could be readily

monitored on surfaces. Single crystals of well-defined orientation were used in most of the LEED experiments as substrates and when adsorbed species ordered on those surfaces their orientation could be monitored with respect to the single crystal substrate. Evolution of the experimental LEED technique included determination of the size of the ordered domains on the surface from the coherence length of the incident monoenergetic electron beam, the mean square displacement of surface atoms from the surface temperature dependence of the diffraction beam intensities (Debye-Waller factor), ion bombardment cleaning of the single crystal surface to remove contamination and detection of the surface composition by the development and use of Auger electron spectroscopy.

Many studies of clean surfaces and adsorbed atoms and molecules on single crystal surfaces were carried out under well-controlled experimental conditions. Surfaces of clean group IV, III-V and II-VI semiconductors were found to reconstruct, surface atoms occupying atomic positions that were different than that expected from the projection of the bulk unit cell. Metal surfaces and oxides also exhibited reconstructions. Adsorbed atoms and molecules in these surfaces formed many ordered surface structures that changed with coverage and with temperature. Theory, however, was missing to interpret the diffraction beam intensities to determine the precise location of surface atoms.

The completion of the development of valence band structure calculations and UHV techniques converged in the mid 1960s and set the scene for the development LEED theory and experiment. At this time John Pendry, a student of Volker Heine, turned his attention to this problem. This time marked the beginning of John's remarkable career as a seminal figure in the development of LEED crystallography over the next three decades.

The experimental and theoretical advances in LEED surface crystallography came to fruition with the first reports of surface structures solved by Low-Energy Electron Diffraction (LEED) that appeared in the literature in the early 1970s [13-15]. These first applications of LEED theory were preceded by a time of fruitful debate and study of the fundamental nature of the interaction of low energy electrons with the surface of solids. The key physical features of the theory were: the importance strong elastic interaction of low energy electron with the surface atoms, the inclusion of multiple scattering processes and the proper description of inelastic processes by an inner potential.

Given the constraints of this paper, it would be unfair to John to attempt a complete historical review of John's extensive contributions to field surface science. Instead we shall highlight his key contributions to LEED. To understand John's influence on the field there is no better place to start than with his monograph "Low Energy Electron Diffraction" which was first published in 1974 [4]. This book contains the first comprehensive description of the basic physical ingredients of LEED presented in a clear manner that is characteristic of John's intuitive way of understanding the physics of a problem: the springboard for his creative approach. In addition, this book is remarkable in clearly articulating John's utilitarian direction: the goal of finding out where atoms are at surfaces [4]. A particularly notable aspect of John's book were the appendices which included the complete Fortran computer codes developed by John. Although not recognized explicitly, John's willingness to publish computer codes was very influential among the LEED community which continues to publish and make freely available it's codes.

Contained within this book are descriptions of two methods that revolutionized the calculation of LEED I-V spectra for comparison with experimental data. Both are efficient computational strategies for describing the interaction of electrons with surfaces. Prior to John's work, LEED calculations were largely built upon 3D bulk methods where the presence of the surface broke the symmetry of the problem adding much complexity to the calculation [16]. John's approach was different in that it exploited the broken symmetry to make the calculation easier and more efficient. The first application was the so-called layer-doubling method [4,17] where the surface is represented as a stack of identical 2D atomic planes. The basic idea is that once one has computed the transmission (t) and reflection (r) coefficients for single atomic layer the transmission (t_2) of reflection coefficients (r_2) of two atomic layers is obtained by the following operation:

$$r_2 = r_1 + t_1 r_1 t_1 + t_1 r_1 r_1 t_1 + \dots = r_1 + t_1 (1 - r_1 r_1)^{-1} r_1 t_1,$$

$$t_2 = t_1 t_1 + t_1 r_1 r_1 t_1 + \dots = t_1 (1 - r_1 r_1)^{-1} t_1 \quad [1]$$

Now one can obtain the transmission (t_4) of reflection coefficients (r_4) of a stack of four atomic layers but simply replacing t_1 and r_1 in equation 1 with t_2 and r_2 . For example,

$$r_4 = r_2 + t_2 (1 - r_2 r_2)^{-1} r_2 t_2 \quad [2]$$

By repeating this process one can generate the reflection and transmission coefficients for an arbitrary number of layers in the binary sequence $N=1, 2, 4, 8, 16$, etc. This approach has two virtues. Firstly, the amount of computer time required to stack M layers scales in a sub-linear fashion as M increases. This can be compared to stacking algorithms where the atomic layers are added one at a time to generate a stack that scale linearly with M . As a consequence layer-

doubling is a highly efficient method. Secondly, this is a recursive algorithm that is ideally suited to a computer calculation with the corresponding minimal amount of coding.

There is one remaining bottleneck in the calculation which was removed by John when he developed the so-called Renormalized Forward Scattering Method (RFS) [4]. The bottleneck in the layer doubling method is represented by equation 2 that requires the inversion of matrices. Matrix inversion is a computationally expensive process and scales as the dimension of the matrix cubed. Since the dimension of the reflection and transmission matrices of a single atomic layer scale roughly as the area of the unit cell the layer doubling method becomes very demanding when applied to surfaces where the unit cell is large (such as chemisorption systems).

John proposed a method to get around this bottleneck based on a perturbation expansion, recognizing that the physics of the strong forward scattering of LEED electrons by atoms means that $|r_1| \ll 1$. Therefore the expansion should be in order of powers of the (small) parameter r_1 , while flux conservation implies that $|t_1| \approx 1$. Unfortunately the naïve approach of replacing everywhere the inverses with a simple power series expansion yields a power series for the reflection matrix of the stack that is not a uniformly convergent power series r_1 . This means that in order to converge the stack reflectivity, one must include much higher powers of r_1 than is necessary so that the expansion quickly more computationally demanding than the layer-doubling method. There is also no straightforward way to monitor convergence in order to terminate the power series as it is evaluated.

Instead, John proposed an algorithm in which the LEED state in the surface was estimated through a series of sweeps through the stack of atomic layers, with each sweep picking up contributions to R which consisted of sequentially higher powers of r_1 . In effect, the RFS method automatically computes R as a uniformly convergent series in powers of r_1 . Not only is this highly efficient, but it also permits the monitoring of convergence through each sweep and termination of the calculation once a predetermined accuracy is reached.

These methods were applied by John to perform the first detailed structural analysis an adsorption structure Ni(100)-c(2x2)Na using the beautiful LEED I-V spectra measured by Stig Andersson [18]. Their results offered the first tantalizing glimpse of the ability of LEED to elucidate the nature of chemical bonding at surfaces. Throughout the 1970s LEED was used to determine the structures of many clean surface and simple adsorption systems until, by the mid 1980s, several hundred surface structures were known. John was the motivating force behind producing the first electronic catalog of known surface structures, the so-called SCIS catalog [19] which resulted from the close collaboration between the Imperial and Berkeley groups.

A New Dawn

The availability of a multiple scattering LEED theory [4,20] made it possible for us to solve the surface structure of molecules adsorbed on single crystal metal surfaces. The first surface structure of adsorbed organic molecule, ethylene on the (111) crystal face of platinum we reported in 1979. We could determine the locations of five surface atoms per unit cell and thus ethyldiyne $-C-CH_3$ surface structure on it forms from ethylene C_2H_2 on the platinum surface was discovered [21]. This was followed by the surface structure determination of ethylene on the rhodium (111)

crystal face [22]. The same multiple scattering LEED theory could be used to revisit the surface reconstruction of clean metal surfaces that was discovered in 1965 [23]. The surface structural model for the reconstruction of the clean (100) surfaces of platinum, gold and iridium could be developed [24].

This fruitful period of time evenly revealed a new set of problems in the application LEED crystallography. As the complexity of the surfaces increased so did the computational resources required to perform both the LEED calculations and the fitting of the calculated IV spectra to the experimental measurements. In the early 1980s, state of the art LEED structural analyses required the investment of several man-years. The only computers capable of running LEED codes within practical amount of time were shared supercomputers housed at national centers. For example, the calculation IV spectra for just a few hundred trial structures would take several hours of CPU time on a Cray-1S. Of course advances in computer technology would lead to the realization of the predictions of Moore's Law so that by the mid to late 1980s it was possible to perform a similar calculation on a powerful personal computer. Yet, as John recognized, such advances would have relatively little impact on the structural solution of more complex surface structure. This is because the standard trial and error method of comparing calculated IV spectra from all likely structures represents, in mathematical terms, a NP-complete problem. This is because the computational resources/time needed to determine N structural parameters by trial and error scales in a decidedly non-polynomial fashion. In fact, the time to solution scales exponentially as the Nth power. Such scaling could never be beaten by advances in computer speed, even at the rate of growth predicted by Moore's Law.

Diffuse LEED

John's first shot across the bows of these problems was to develop a method of computing dynamical LEED patterns from disordered adsorption structures. This development in LEED theory by the Pendry and Berkeley group to solve the surface structures of disordered monolayers led to what is called Diffuse LEED [25]. In Berkeley, we solved the surface structures of disordered layer of benzene and ethylene on the platinum (111) crystal face [26-28] and working with the Erlangen group the oxygen adsorption structures of oxygen on W(100) were solved [25].

The difficulty of this problem arises from the fact that a disordered surface has a surface unit cell that has effectively infinite area. This means that the reflection and transmission matrices of layers or stacks of atoms belong to the infinite dimensional vector space of C^{22} rather than the finite dimensional space of the ordered surface problem. The Berkeley group pioneered a clever approximate solution to this problem: the beam-set-neglect method. The basic idea was to model the disordered surface as an ordered surface with a very large (but not infinite) unit cell and then use approximate methods to handle the calculation of the intensities in the LEED diffraction pattern. When a surface has a very large unit cell the LEED diffraction pattern consists of numerous closely spaced diffraction spots and, in the limit of an infinite surface unit cell these discrete spots merge to form a diffuse pattern. In this limit the diffraction spots of the ordered surface are simply discrete samples of the diffuse pattern. The key question then becomes: how large of a unit cell is needed to obtain convergence onto the true diffuse pattern of the disordered surface.

Michel Van Hove recognized that the answer to this question lies in the basic physics of the interaction of low energy electrons with solids. Strong inelastic interactions result in a LEED electron having a relatively short mean free path, λ , while it is inside the solid. Typically $\lambda \approx 10 - 100 \text{ \AA}$. This implies that an electron can only contribute to the diffraction pattern if it has traveled a distance of less than the mean free path while interacting with the surface. This suggests that the area of the surface unit cell in the ordered model of a disordered structure must be approximately λ^2 or larger. This led to the development of the so-called Beam Set Neglect method [8].

John took a somewhat more direct approach in his development of a theory of DLEED. John understood that if one is dealing with a disordered overlayer of atoms adsorbed on an ordered surface then any electron contributing to the diffuse component of the pattern must have interacted with at least one adsorbed atom. Electrons that interacted only with the ordered substrate would end up in the Bragg spots instead. Thus the adsorbed atom must be the locus of all scattering paths contributing to the diffuse pattern. Thus the computation of each multiple scattering path and be broken into three pieces, each of which could be computed using either conventional LEED theory or methods borrowed from the theory of SEXAFS.

Tensor LEED

In 1985 John initiated a revolution in LEED Surface Crystallography, one that to all intents and purposes solved the NP-complete problem mentioned earlier. John combined his experience and knowledge of the theory of DLEED, SEXAFS and HREELS to propose a new perturbative method which could rapidly compute the IV spectra from structural distortions of a so-called reference structure.

In 1985 I was one of John's Ph.D. students at Imperial College and I had just finished working on the extension of DLEED theory to surface defects such as vacancies and steps. John sketched out the theory of tensor LEED at one of our morning meetings where John would often serve proper brewed coffee. John's notes occupied about half a sheet of paper he explained the idea very simply and intuitively.

Tensor LEED is a perturbative approach to the calculation of LEED intensities [29]. One starts by defining a reference structure: a particular surface structure that we guess to be as close as possible to the actual surface structure. We then distort this surface by moving some of the atoms to new positions. In this way we generate a trial structure that is a structural distortion of the reference structure related by a set of atomic displacements.

To first order, the difference between the amplitudes of a LEED beam scattered from the reference and trial surface, δA can be written as an expression which is linear in the atomic displacements which generate the trial structure. Thus, if we move N atoms through δr_{ij} ($i=1..N, j=1,2,3$):

$$\delta A = \sum_{i=1}^N \sum_{j=1}^3 T_{ij} \delta r_{ij}. \quad [3]$$

The quantity T is the tensor which depends only upon the scattering properties of the reference surface and can be calculated by performing what is essentially a full dynamical calculation for this surface. Once T is known then the diffracted intensities for many trial surfaces can be evaluated extremely efficiently by summing eqn. T1 after substituting the appropriate set of atomic displacements. This linear version of tensor LEED is limited to atomic displacements of less than 0.1Å beyond which becomes a poor approximation. In this case we can appeal to a more sophisticated version of the theory, one which allows displacements of up to 0.4Å, by reformulating eqn. T1 as:

$$\delta A = \sum_{i=1}^N \sum_{L,L'} T_{L'L} R_{LL'}(\delta r_{ij}) \quad [4]$$

where

$$R_{LL'}(\delta r_{ij}) = j_{\ell}(\kappa \delta r_{ij}) j_{\ell'}(\kappa \delta r_{ij}) Y_{\ell'm'}(\delta r_{ij}) Y_{\ell m}(\delta r_{ij})$$

In eqn. 4 we have replaced the sum over the three cartesian coordinates with a sum over angular momenta L=(l,m) and L'=(l',m'), the actual displacements of eq[1] being replaced by a function R of those displacements consisting of the product of spherical Bessel functions and spherical harmonics. For small argument the decrease of the magnitude of the Bessel functions with order effectively cuts off the expansion. This, and the fact that \$R\$ is a symmetric matrix limits, the number of terms on the left side of eqn. 4 to around 37 for the magnitude of atomic displacements

for which this equation remains valid. Consequently eqn. 4 is almost as straightforward as eqn. 3 to evaluate and is our preferred formula for most situations.

The relative simplicity of the mathematical operations required to evaluate equations [3] or [4] and thus intensities from many trial surfaces has important computational implications. Firstly, the calculation is extremely fast compared to conventional full dynamical methods. By using Tensor LEED theory, the computational time per trial structure can be reduced by a factor of 50 for a simple surface such as Cu(100) to 10,000 for a p(2x2) overlayer system. Secondly the time taken to evaluate intensities by Tensor LEED is independent of the presence or lack of symmetry within any given trial surface. Therefore we can consider highly asymmetric systems, such as off-center adsorption sites, with no loss of efficiency. These surfaces were largely inaccessible to conventional methods due to the large volume of parameter space associated with such systems and the inability to exploit symmetries.

I made a most foolish promise to implement the method within two weeks, just in time to coincide with a visit of Klaus Heinz who would be bringing new set of DLEED data from Erlangen. I had not left his office for more than 5 minutes when my skepticism began to grow. The folklore of the LEED community that I had absorbed the previous two years and always seem to emphasize the failure of perturbation techniques for the strong scattering of LEED electrons John's idea also involved the concept of a pair of time-reversed LEED states coupled by the perturbation. My lack of experience with Green's function methods, lead me to believe that was impossible to compute a time reversed state when inelastic scattering was present because

inelastic scattering would break any time reversal symmetry in the problem. So, rather than leaping forward into the calculation I spent my two weeks convincing myself that in the presence of inelastic scattering a LEED state could be time reversed. Unfortunately, John was not so convinced by my lack of progress when we met with Klaus Heinz two weeks later!

Nevertheless, I moved forward and wrote out the complete theory of Tensor LEED which I then implemented as a computer code, using the Van Hove and Tong LEED package to compute the time reversed LEED states. The theory was tested against fully dynamical calculations and showed a remarkable level of agreement for atomic displacements far larger than I had expected. One could use TLEED to seek out the correct structure by moving atoms by up to 0.4Å. At 0.2Å the IV spectra were virtually indistinguishable from those obtained from a full multiple scattering calculation. The range of the perturbation approximation was critical to its future utility since a basic understanding of chemical bonding reconstruction at surface allowed one, in most cases, to select a reference structure for which the actual surface structure lay within the TLEED radius of convergence. The method was also ideally suited to iterative refinement where TLEED led the way for fully dynamical calculations to close in on the correct structure.

I was fortunate to be able to incorporate the TLEED method into the computer codes used in Erlangen and Berkeley; groups that were performing structural studies of the most complex surface structures. I also was able to exploit the iterative nature of TLEED analysis to write some of the first LEED codes to perform automated structural refinement using optimization algorithms. This is especially important if we are to use an automated structure search since we

cannot predict in advance that the path to be taken through parameter space by the optimization procedure will pass through only symmetrical trial surfaces.

My basic codes were greatly enhanced by numerous individuals in Berkeley and Erlangen who created a suite of highly automated symmetrized codes. These codes were widely adopted by numerous groups around the world and are now the primary means of structural solution through LEED IV analysis.

Tensor LEED represented a revolution in structural surface chemistry. As surface structure analysis could include the possible rearrangement of surface atoms as molecules adsorb, we found that the surface atoms undergo adsorbate induced restructuring in every case when adsorption occurs to form strong surface chemical bonds. The restructuring of rhodium and platinum surfaces under the influence of ethylene adsorption was discovered [28,30]. Several surface restructurings of rhenium with varying concentrations of sulfur were uncovered. The concept of the “flexible surface” could be proposed that restructures under the influence of chemisorption that changed our static view of surface structure to a dynamic one [31-33].

The structural rearrangements of coadsorbed systems could be determined [34-36]. The complex surface structures of stepped metal surfaces could be analyzed [37,38]. These surfaces show exceptional chemical activity to break strong H-H, C-H, O=O and C=O chemical bonds and therefore are active sites for catalytic reactions. Tensor LEED permitted us to determine the clear

surface structures of more complex solids such as magnetite (Fe_3O_4) [39], ice [40] and sodium chloride [41] and lithium fluoride [42].

It is perhaps fitting to end this paper by reflecting upon John's utilitarian vision of using LEED of finding out where atoms are at surfaces. Today it is possible for an experimentalist to take LEED IV data and then analyze it using publicly available computer codes without the assistance of a LEED theorist. While to some this might seem like a rather delicious irony, I cannot help but think that this was what John wanted all along.

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