# Structure analysis of solid surfaces

Discrepancies that had cast doubt on the value of low-energy electron diffraction as a tool for defining the positions of surface atoms have been resolved, and new techniques are enhancing its usefulness.

Thor N. Rhodin and David S. Y. Tong

An accident that occurred at Bell Laboratories in 1925 started Clinton Davisson and Lester Germer on an historical series of experiments. While studying the backscattering of slow electrons from a polycrystalline nickel target, they observed that the angular distribution of the electrons changed completely when the surface was inadvertently oxidized at a high temperature. The consequent study of diffraction phenomena in electrons scattered from the (111) face of a nickel crystal confirmed the de Broglie hypothesis of the wave nature of electrons.[1] But Davisson and Germer also predicted that this type of experiment would provide a valuable approach to the important problem of defining the precise position of atoms in the surfaces of crystalline solids. This suggestion has been pursued diligently by scientists both in the US and abroad. Now, fifty years after Davisson and Germer demonstrated the coherent scattering of electrons by a crystalline solid, the goal of studying surface structure with this technique is becoming a reality. In this article we will discuss some of the major advances of the past few years that are making this achievement possible.

The diffraction spectra obtained when a beam of incident low-energy electrons with well-defined energy and momentum is scattered by a solid contain important information on the positions of the surface atoms. Because strong inelastic absorption keeps the penetration of an incident electron to within a few atomic layers it has long been anticipated that analysis of curves of diffracted-electron intensity as a function of beam energy could lead to a determination of the crystallography of surfaces. With adequate theoretical models to describe the electron-diffraction process we can obtain structural information such as the chemisorption bond-lengths and the binding locations of adsorbed atoms and molecules. This goal has recently been achieved on a number of relatively simple systems of overlayers adsorbed on substrates.

Before discussing the present status of this work, let us summarize some of the specific landmarks that have resulted in critical advances of the field. Early formulations by Kyo Kambe, Eion McRae and John Beeby laid the frameworks of the theoretical methods now in use. In low-energy electron diffraction, "LEED," the incident electrons have energies of 10–500 eV, high enough to excite surface and bulk plasmons in a target material, so it is important to include inelastic damping in the electron propagation in a solid, as was pointed out by a number of early workers. Charles Duke and Charles Tucker, and independently Robert Jones and John Strozier, showed how such a damping factor can be included by assuming a finite mean free path for the electrons. Then came the recognition that significant agreement between theory and experiment can be achieved with phase shifts calculated from realistic ion-core potentials. The importance of using multiple phase shifts to obtain agreement between theory and experiment was shown by John Pendry, by us and by Donald Jepsen, Paul Marcus and Franco Jona. Acquisition of complete reliable intensity data both on clean surfaces and simple overlayer systems by experimental researchers played a central role in these advances. Among these, the data of Stig Andersson, Bengt Kasemo, Alex Ignatiev and Jona, Werner Berndt and Peter Büttner, Joseph Demuth and Rhodin, and Jean-Bernard Theeton among others made useful contributions to the early stages of overlayer-structure analysis.[2]

In this article we shall present an overview of some recent achievements of surface-structure analysis by LEED. In particular:

▸ We shall examine the reliability of current dynamical LEED calculations to extract accurate chemisorption bond-lengths of adsorbed atoms. It was pointed out recently[2] that certain structural results determined by different groups showed some rather large discrepancies. The reasons for these disagreements were not known at the time, and they resulted in some serious questions as to the usefulness of the methodology. As a result of significant new

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findings, the physical reasons for uncertainties in some of the original surface structures are now understood. We shall explore the sources of these uncertainties and attempt to clarify the earlier differences.

▸ Accurate dynamical LEED calculations in the energy range 10–200 eV for structure determination require seven to eight phase shifts. Exact calculations based on inclusion of all orders of multiple scattering events require considerable computation cost. As was pointed out by Peder Estrup,[3] such exact methods usually require computation facilities beyond the capacity available in all but a few laboratories. However, the alternative of fast perturbation approaches within the dynamical approach of LEED is now available. Extensive applications of these have demonstrated that this dynamical approach can be made economical. We shall review the reasons why convergent perturbation schemes achieve accurate results with less computation time.

▸ We shall make some predictions based on our present understanding as to the future prospects of surface crystallography and point out what we believe to be important and fruitful directions for the near-future development of the LEED technique. We shall also briefly review the current status of development in the use of data-reduction methods, which analyze LEED intensity data by methods analogous to those used in x-ray diffraction.

### The chalcogens on a nickel surface

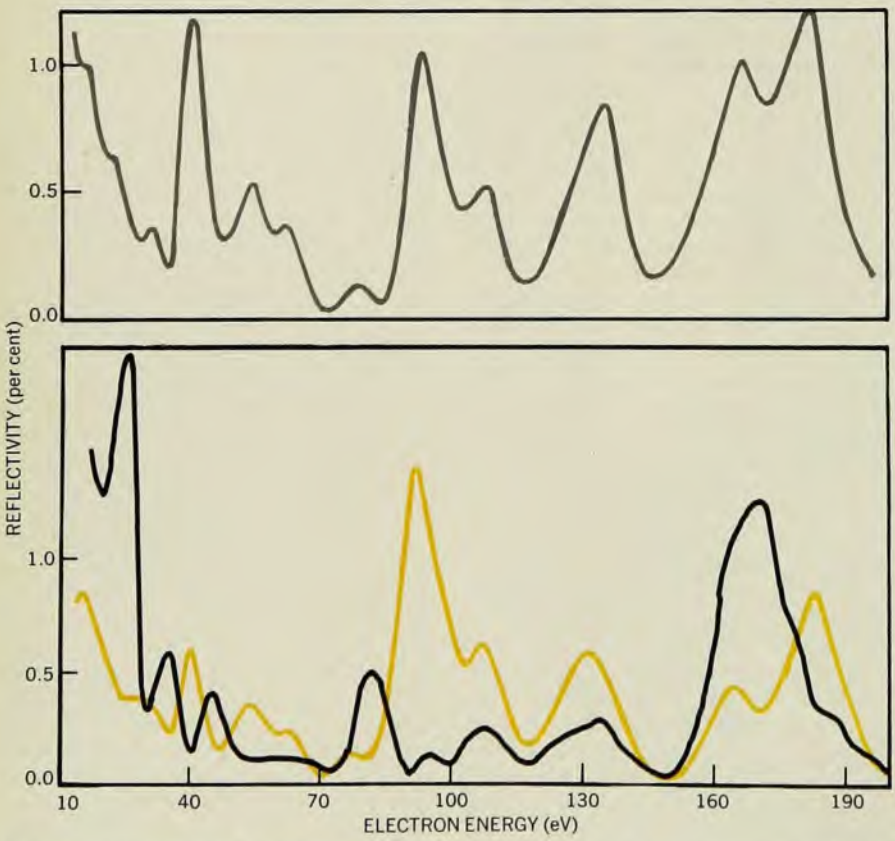
The recent success of the dynamical approach of LEED in extracting surface structure information from the experimental data is a major step in the development of the theoretical model of electron–solid scattering. Quantitative knowledge of chemisorption bond-lengths and the preferred coordination symmetry of adsorption sites provides valuable information on the chemical nature of chemisorption. A great deal of attention, and unfortunately also considerable uncertainty, were generated on the reliability of the theoretical interpretation of the centered chalcogen overlayers, with the surface cell spaced 2 × 2 relative to the substrate, on Ni(001). (The chalcogens are oxygen, sulfur, selenium and tellurium.)

The confusion was due to three roughly concurrent but independent calculations[4] that reported different sets of binding distances for two of the chalcogens, O and S. Andersson, Pendry, Kasemo and Michael Van Hove studied the c(2 × 2) oxygen chemisorption on Ni(001) and found that the oxygen sits at a four-fold coordinated binding site with a vertical interlayer spacing of 1.5 ± 0.1 Å. Demuth, Jepsen and Marcus studied the c(2 × 2) chemisorption for the four chalcogens on Ni(001) and for oxygen, they determined the same four-fold coordinated site but at the different interlayer spacing of 0.9 ± 0.1 Å.

The situation for c(2 × 2) sulfur on Ni(001) was also confusing. Duke, Nunzio Lipari, George Laramore and Theeton[4] determined a four-fold coordinated site with an interlayer spacing of 1.7 ± 0.1 A, whereas Demuth and his associates[4] obtained a spacing of 1.3 ± 0.1 A. Thus while all the calculations agreed on the coordination symmetry of the binding site (with an oxygen or sulfur atom sitting above four nearest-neighbor nickel atoms), they disagreed on the interlayer spacings, and hence the correct chemisorption bond-lengths.

Besides forming the c(2 × 2) overlayer structure, the chalcogens also form a p(2 × 2) overlayer structure on Ni(001) at a lower coverage. (The notation p(2 × 2) refers to a primitive surface cell with double the substrate lattice spacing; a c(2 × 2) cell contains a centered atom as well.) Demuth and Rhodin[5] have measured sets of LEED intensity data on both of these overlayer structures. Van Hove and Tong[6] recently calculated the interlayer spacings and adsorption sites for the complete set of p(2 × 2) chalcogen overlayers. For sulfur and oxygen, their results for the p(2 × 2) structure were identical with the c(2 × 2) results obtained by the Demuth group.[4] In view of the close resemblances in the data between c(2 × 2) and p(2 × 2) overlayers of oxygen and sulfur on Ni(001), it is reasonable to expect that the chemisorption bond-lengths would be very close to each other. Thus the results of Van Hove and Tong tend to confirm the calculated spacings of Demuth and his co-workers.

Why then did the Andersson group[4] obtain a substantially different interlayer spacing for oxygen and the Duke group[4] for sulfur on Ni(001)? Let us examine the factors that led them to these conclusions. In the calculation of Andersson and his colleagues, the source of uncertainty was mainly the specific choice of the scattering potential they used for the nickel substrate. In a successful structure determination, the phase shifts used for the scattering potential of the substrate must produce calculated LEED intensity curves that agree with the experimental data for the clean crystal. The scattering potential used in the Andersson group's calculation was a nonlocal Hartree–Fock nickel potential specifically constructed to treat electron scattering at very high energies. It has, however, since been shown[7] that in the energy range (10–200 eV) used for the structure analysis, the nonlocal Hartree–Fock potential produced intensity–en-



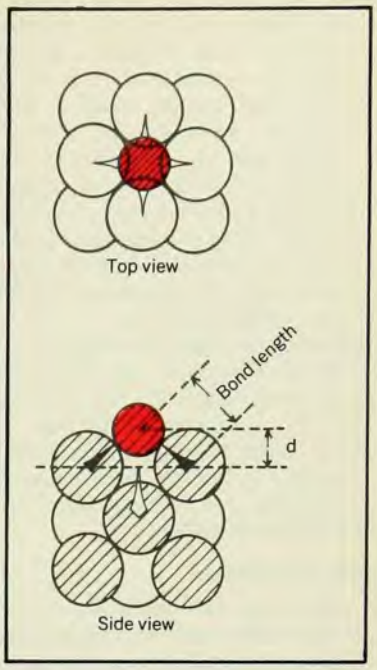

**Calculations based on two different potentials** are compared with experimental data (top curve) on the (001) face of a clean nickel crystal at 300 K, with the (0 0) beam at $\theta = 6°$, $\phi = 0°$. Pendry's Hartree-Fock potential yielded a curve (in black) that is in poor agreement but the curve (in color) from Wakoh's potential corresponds well with the data. Figure 1

## Overlayer structures

This Table summarizes results of structure analyses by the two groups named below on centered and primitive 2 × 2 overlayers of chalcogen atoms at a fourfold site. The substrate here is the (001) surface of nickel. The drawings on the right show the position of the overlayer atom (in color) and define the vertical spacing *d* and the bond length.

| | Theoretical | | | | Experimental |
|---|---|---|---|---|---|
| | c(2 × 2) structure[a] | | p(2 × 2) structure[b] | | |
| | *d* (Å) | Bond length (Å) | *d* (Å) | Bond length (Å) | Bond length (Å) |
| Ni–O | 0.90 ± 0.1 | 1.98 ± 0.05 | 0.90 ± 0.1 | 1.98 ± 0.05 | 1.84–2.06 Ni-chelate complexes |
| Ni–S | 1.30 ± 0.1 | 2.19 ± 0.06 | 1.30 ± 0.1 | 2.19 ± 0.06 | 2.10–2.23 Ni-chelate complexes |
| Ni–Se | 1.45 ± 0.1 | 2.28 ± 0.06 | 1.55 ± 0.1 | 2.34 ± 0.07 | 2.32 Ni-chelate complexes |
| Ni–Te | 1.90 ± 0.1 | 2.59 ± 0.07 | 1.80 ± 0.1 | 2.52 ± 0.07 | 2.64 Ni-Te bulk compounds |

[a] J. E. Demuth, D. W. Jepsen, P. M. Marcus, Ref. 4.
[b] M. Van Hove, S. Y. Tong, Ref. 6.




ergy spectra in poor agreement with the experiment on clean Ni(001). This fact can be readily seen in figure 1, where a comparison between experiment and calculation with the Hartree–Fock potential is shown. A calculation in which Tong, Pendry and Larry Kesmodel used a self-consistent nickel potential constructed by S. Wakoh[8] is also shown there for comparison.

Comparing the calculated curves with experiment we note that for the Hartree–Fock potential the agreement is rather poor. Shifts of more than 5 eV in major peak positions and substantial differences in peak shapes and relative intensities are evident from the figure. Such discrepancies between theory and experiment for the substrate are liable to produce serious errors in the structures obtained for overlayers. On the other hand, curves for clean Ni(001) calculated with Wakoh's potential correspond very well with the experiment, with every peak in the data reproduced in detail in the calculation. The Wakoh nickel potential was used in the overlayer calculations by Van Hove and Tong[6] for the p(2 × 2) structure and by Demuth and his colleagues[4] for the c(2 × 2) structure. Thus the different bond length originally obtained by Andersson and his associates[4] for oxygen on Ni(001) was due primarily to their choice of the substrate potential for nickel. Pendry told us that he had obtained the smaller value for the oxygen displacement, 0.9 Å, with a linear-superposition potential, which is similar to Wakoh's.[9]

Let us turn to the calculation of Duke and his co-workers[4] for sulfur on Ni(001). Since they used a linear superposition potential for nickel, these phase shifts are practically the same as those obtained from Wakoh's potential. Hence the uncertainty in their calculation was not in the dynamical inputs they chose; rather, it was in the accuracy of the computation. The theoretical model they used was based on Beeby's matrix-inversion method. This theory was developed to describe, in an exact formalism, the self-consistent solution of multiple scattering of an incident electron in a finite number of crystal layers. The method inverts a large matrix and requires a huge amount of computer core memory. The method is also time-consuming and hence not well suited for structure analysis of overlayers. In fact, because of the large core-storage demand and lengthy computation time, calculations for overlayer structure with this method were restricted to four phase shifts. The layer–Korringa–Kohn–Rostoker method used by the Demuth group[4] is more efficient by comparison.

We show in figure 2 the comparison between calculations done by different groups and the experimental data of c(2 × 2) sulfur overlayer on Ni(001) for the (½ ½) beam. For the experiments, the data of Theeten[4] were taken at 30 K and those of Demuth and Rhodin[5] at 300 K. Even with this temperature difference the two sets of experiments compare very well. Although there are small differences in peak shapes and relative intensities of some peaks, the number of peaks and the positions of major peaks agree very well in the two experiments. In Theeten's data, a 2.5-eV shift to lower energies should be added before it can be validly compared to the calculated spectra. This is required to account properly for a contact-potential difference in Theeten's definition of the vacuum level of energy.[10] With this shift—and bearing in mind that the two experiments were done at very different temperatures—all the small differences in the two experimental curves can be accounted for. Even without the 2.5-eV contact-potential correction for Theeten's data, the differences between the two experiments are small enough that they do not lead to different surface structures when analyzed by an accurate theoretical calculation.

Figure 2 shows the calculated curve for a c(2 × 2) sulfur layer on Ni(001) at a 1.3-Å interlayer spacing and T = 300 K by the Demuth group[4] using the layer–KKR method and the corresponding one by Van Hove and Tong using a convergent perturbation method. The two calculations used eight phase shifts and various dynamical inputs such as surface-vibration amplitudes and inelastic damping. However, they agree very well with both Demuth and Rhodin's[5] and Theeten's[4] data. Small differences in the details of peak shapes and heights in the two calculations are due to the different values of surface dynamical inputs used.

By way of comparison, the calculations[11] of Duke and his associates at T = 30 K are shown for interlayer spacings 1.3 Å and 1.7 Å (their choice of best fit with Theeten's experiment). We note distortions in peak shapes and shifts in peak positions. In addition,

the agreement with either experiment or with the other two calculations is limited. The lack of good agreement with experiment of the Duke group's calculation for either the 1.3-Å or the 1.7-Å interlayer spacing made it difficult to decide which spacing was correct. Duke and his colleagues[11] originally chose 1.7 Å as the interlayer spacing of best fit with Theeten's data without the shift. In a more recent article[12] they chose 1.3 Å for this fit with Theeten's experiment after including the 2.5-eV contact-potential shift.

In the Box on page 25 we list the now accepted interlayer spacings and chemisorption bond-lengths for c(2 × 2) and p(2 × 2) overlayer structures on Ni(001). These results provide a useful set of surface structures for the study of chemisorption of simple gas atoms on a transition-metal surface.

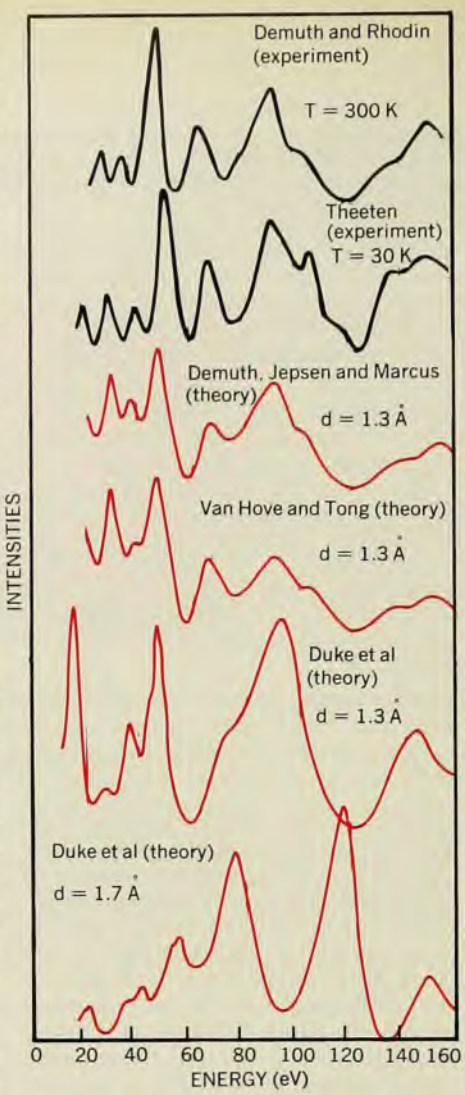
### Sodium on aluminum

We have seen how inadequate agreement between theory and experiment can lead to uncertainties in the surface structures determined. At the present stage in the development of the dynamical LEED approach for surface-structure analysis, it is important that theoretical models be accurate and well defined and that a detailed fit between theory and experiment be achieved. This would establish confidence that accurate and well defined dynamical calculations are independently able to predict the same surface structure from the same data.

Another such example is the sodium overlayer on the (001) surface of aluminum. The study of atomic chemisorption on a free-electron metal like aluminum is most relevant because *ab initio* binding calculations might be made on such a chemisorption system and hence provide a useful check of the LEED structure results. Sodium forms a c(2 × 2) ordered overlayer on Al(001). The data on this surface were taken by Bernard Hutchins and Rhodin. Two independent structure calculations were done simultaneously by Hutchins, Rhodin and Demuth and by Van Hove, Tong and Norman Stoner. Figures 3 and 4 compare these two calculations with the experiment. For the (½ ½) beam, the interlayer spacing of best fit is 1.96 ± 0.1 Å (the Rhodin group) and 1.98 ± 0.12 Å (the Van Hove group).

From this analysis it is possible to determine the bond lengths of both the aluminum–sodium and nickel–sodium[9] systems depicted in figure 5. The bond lengths are in reasonably good agreement with the covalent radii for substrate and overlayer.

These comparisons also illustrate a point of central importance in the LEED analysis of surface structure. In a dynamical LEED calculation, a set of input factors representative of various




**Comparison between theory** (colored curves) and experiment (black curves) for a centered 2 × 2 sulfur overlayer on Ni(001), the (½ ½) beam at $\theta = 0°$. Despite the difference in the temperatures, the experimental curves are quite similar. The calculations for the fourfold coordinated site are described in the text. Figure 2

electron interactions at the surface region must be used (for example, surface vibration amplitudes and surface inelastic damping). Because our present knowledge of these factors in most materials is at best semiquantitative (usually known only to within a 50% variance), a tool for surface crystallography, to be useful, must be able to extract structure information without the benefit of the exact knowledge of these dynamical quantities. Looking at the surface dynamical inputs used in the two calculations, we see that they are rather different. For example, the inelastic damping values used in the two calculations are 4.1 eV (the Van Hove group) *versus* 5.5 eV (the Rhodin group), a variance of 34%. The surface vibration temperatures of the sodium overlayer used are $\Theta_D(\mathrm{Na}) = 284$ K *versus* 150 K, a variance of 47.1%. The scattering potentials and inner potentials are also somewhat different although both produced good agreement with experiment on clean Al(001), a prerequisite for any valid surface-structure analysis. The large variances in the surface inputs indicate the present uncertainties in these surface quantities. However, the surface structures determined by the two calculations agree to better than 1.5%. The selective sensitivity of LEED spectra to the geometric positions of atoms over surface dynamical quantities is responsible for the capability of this technique to determine the surface crystallography of highly complicated materials (such as layered compounds and heavy transition metals) where the dynamical factors of the surface are not well known.

### Dynamical calculations

A low-energy electron undergoes multiple scattering among the atomic centers in a solid. Theoretical models that include all these events have come to be known as "exact" methods; two examples are Beeby's matrix-inversion method and the layer–KKR method. In these methods, all multiple scattering events are included by the inversion or diagonalization of large matrices. Exact calculations are therefore usually costly and require computers with a big core storage. However, there exist alternative methods within the dynamical approach that significantly reduce the cost (both in time and core storage) of computation; these are known as "perturbation methods" of LEED.

The idea behind the perturbation methods is simple. Because the incident electron penetrates only a few surface layers of a solid, only the first few scattering events can be large. Thus the electron-wave field inside a solid can be expanded in terms of perturbation theory, with each order including an additional set of multiple-scattering events.

McRae wrote the first perturbation expansion (to second order) in 1968. Perturbation calculations with realistic scattering potentials were carried out by Strozier and Jones for Be(0001) and by Tong and Rhodin for Al(001). Reasonable agreement with experiment was obtained for these "light" free-electron metals. Tong, Laramore and Rhodin[13] established the limits of finite-order perturbation methods in 1973. They showed that the direct expansion of multiple-scattering events to third order (including all possible combinations up to three scattering events) produced reasonably accurate results for free-electron metals such as aluminum, but failed to converge properly at some energies for transition metals such as nickel. The problem still remained and the search was on to find accurate per-

turbation schemes that would work well on transition metals as well as on free-electron metals.

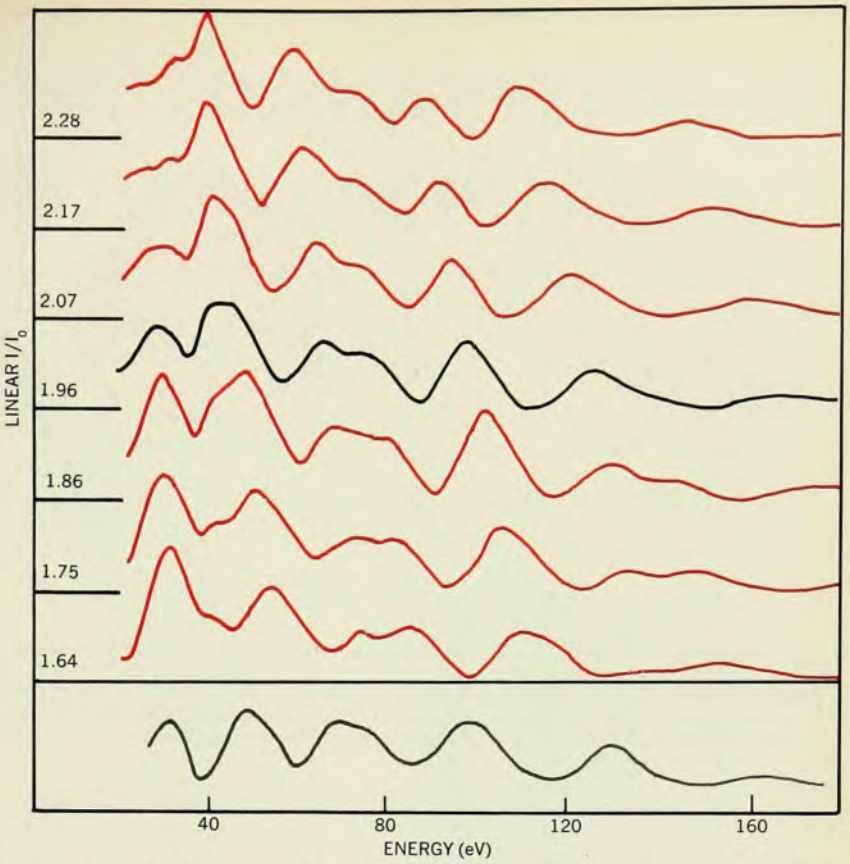
It is clear that a suitable scheme would be one that can be carried successfully to all orders required to achieve convergence. This can be done most easily if each order has exactly the same form as the one before. Then each order would take the same amount of computation time and have the same number of terms (as opposed to the exponentially increasing number of terms in the direct-perturbation expansions)—this is, in fact, the basic logic of an iteration process.

The problem, then, is to find an iteration scheme such that each iteration step takes a very small amount of computation time. If the time for each iteration is $t$, a calculation that requires $n$ iterations takes a total time $nt$; the computation time thus increases only linearly with $n$. If $t$ is small, the total time will be small compared to that for exact calculations.

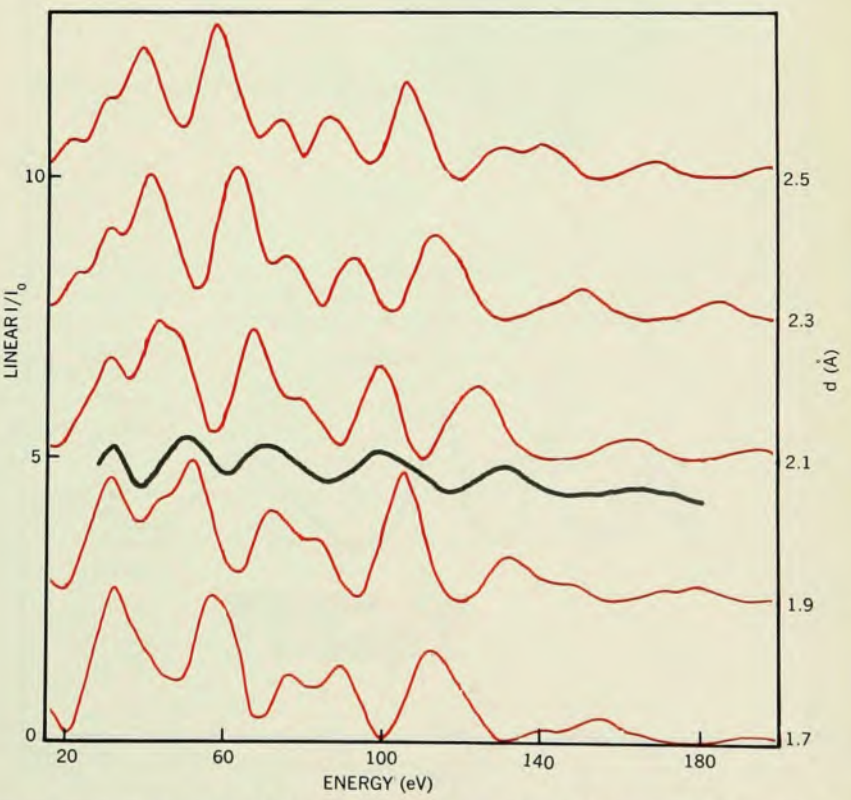
For most materials, including heavy transition metals, the perturbation iteration converges for $n \lesssim 5$, with an accuracy practically as good as that of an exact calculation. A perturbation method works so much faster to reach similar numerical accuracy because it calculates scattering terms in a well ordered sequence. The computation is stopped as soon as the required accuracy is reached. An exact calculation, on the other hand, evaluates large and small scattering terms in a mixed manner, wasting relatively large amounts of computational effort in the process.

One such scheme starts from the planar-scattering factor of a single layer and iterates multiple scattering events by following the incident electron as it scatters in and out of the crystal layers. The number of layers included in the iterations depends on the depth of penetration of the incident electron. This layer-by-layer interation is carried out until the reflectivity converges. Pendry[14] first introduced this layer-iteration method with calculations on Cu(001). Tong[15] showed that, for Ni(001), the layer-iteration method saved a factor of more than 36 in computation time and a factor of 10 in the core-storage requirement over Beeby's matrix-inversion method.

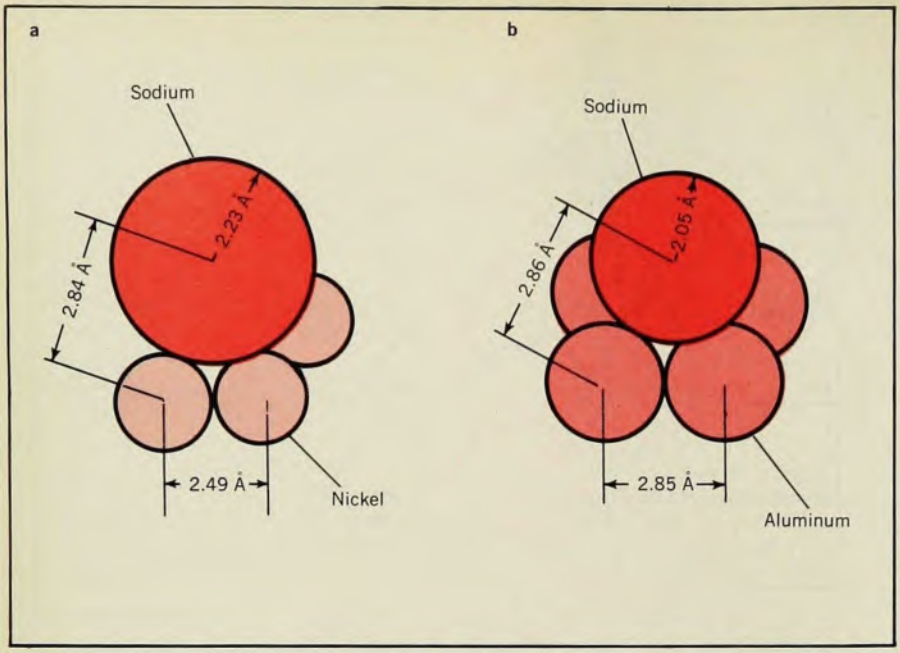
The layer-iteration method converges well for nickel, copper and many other materials but it is not applicable when two layers in a strongly scattering material are closely spaced to one another. In such cases a second iterative perturbation method can be used, which does not have this limitation. In the second method, intraplanar and interplanar multiple scattering events are solved exactly for a pair of layers; the resulting transmission and reflection matrices are then used to solve for those of four



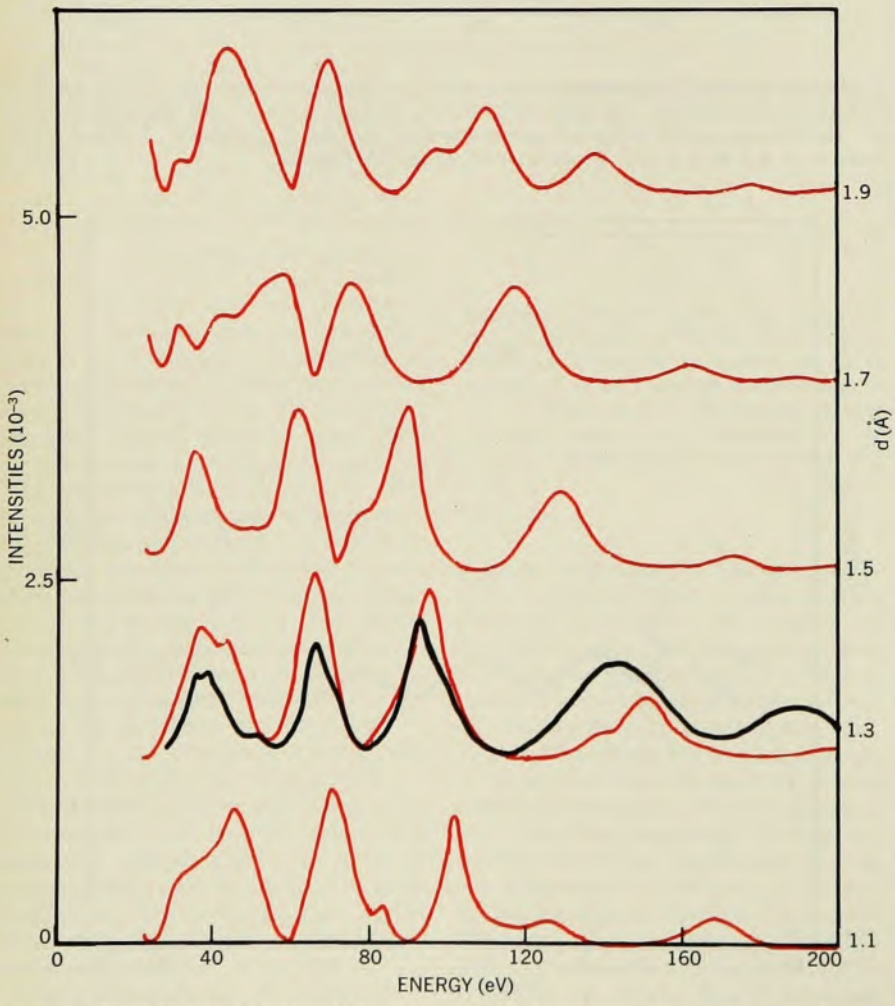

**A structure calculation is compared** with experimental data (grey curve) for c(2 × 2) sodium on Al(100) at a fourfold site. The data are for the (½ ½) beam at $\theta = 0°$; the temperature is 110 K. The numbers shown on the left are the interlayer spacings in angstroms. The best fit was found to be at 1.96 ± 0.1 Å. (From Hutchins, Rhodin and Demuth.) Figure 3




**Another structure analysis on the same system** as that of figure 3, performed independently by another group at the same time. With the same site, beam and temperature the best fit between theory (colored curves) and experiment (grey curve) was determined to be 1.98 ± 0.12 Å, in agreement with the above results. (From Van Hove, Tong and Stoner.) Figure 4




**Hard-sphere models showing the local geometry** and dimensions for sodium atoms on a nickel (100) surface **(a)** and on an aluminum (100) surface **(b)**. The measurements and calculations in **a** are from reference 9 and those in **b** are from Hutchins, Rhodin and Demuth. Figure 5




**The layer-iteration method was used** in this structure determination of a primitive 2 × 2 sulfur overlayer on a fourfold site of the (001) surface of a nickel crystal. The experimental curve (black line) is for a (½ 0) beam at $\theta = 0°$. The interlayer spacing of best fit was determined to be 1.3 ± 0.1 Å. (From reference 6.) Figure 6

layers. This process is repeated until the reflected intensities converge. This second method is about 30% slower than the layer-iteration method but it has converged for every material that has been tested.

Van Hove and Tong applied the iterative perturbation schemes extensively to structure analysis of clean surfaces and of overlayer systems including surface structures of W(001), W(110), oxygen on W(110), and carbon on Ni(001). Recently, Bernard Mrstik, Tong, Ray Kaplan and Achinta Ganguly used the layer-iteration method to study the surface structure of two-dimensional layered compounds. As an example of the successful use of perturbation method for structure analysis, we show in figure 6 the calculated curves[6] for a p(2 × 2) sulfur overlayer on Ni(001) compared to the experiment[5] of Demuth and Rhodin.

### Data-reduction techniques

The dynamical approach of LEED is based on an exact description of the incident electron as it undergoes a series of complicated interactions and multiple scattering events in the surface region of a solid. It is therefore important to include accurately all major scattering events of the electron. Two data-reduction methods, carried out by Maurice Webb and Max Lagally[16] at University of Wisconsin (Madison) and by David Adams and Uzi Landman[17] at Xerox, attempt to select out from the complex intensity–energy data those features that originated primarily from kinematic-scattering conditions of the surface layers. Once such "Bragg-like" features are extracted, structures can be determined directly with methods similar to those in x-ray crystallography. The data-reduction method proposed by Webb and Lagally, called the "Constant Momentum Transfer Averaging" scheme, "washes away" multiple-scattering peaks by averaging the measured data taken at a mesh of incident angles. Lagally, Jeffrey Buchholz and Gwo-Ching Wang[18] used this scheme to study clean tungsten and found that the top layer of W(110) is not contracted or expanded from the bulk spacing. A recent study by Van Hove, Tong and Stoner,[19] who use the dynamical approach, agrees with this finding. Lagally and his colleagues[18] also applied this data-reduction scheme to a p(2 × 1) oxygen overlayer on W(110). They found that it is difficult to determine the positions of the oxygen atoms from the averaged data. The reason is that multiple-scattering contributions are hard to average out at low energies, so that one must work at relatively high energies—above 150 eV. At such high energies there is a loss of surface sensitivity due to the deeper penetration of the incident electrons. As a result it is

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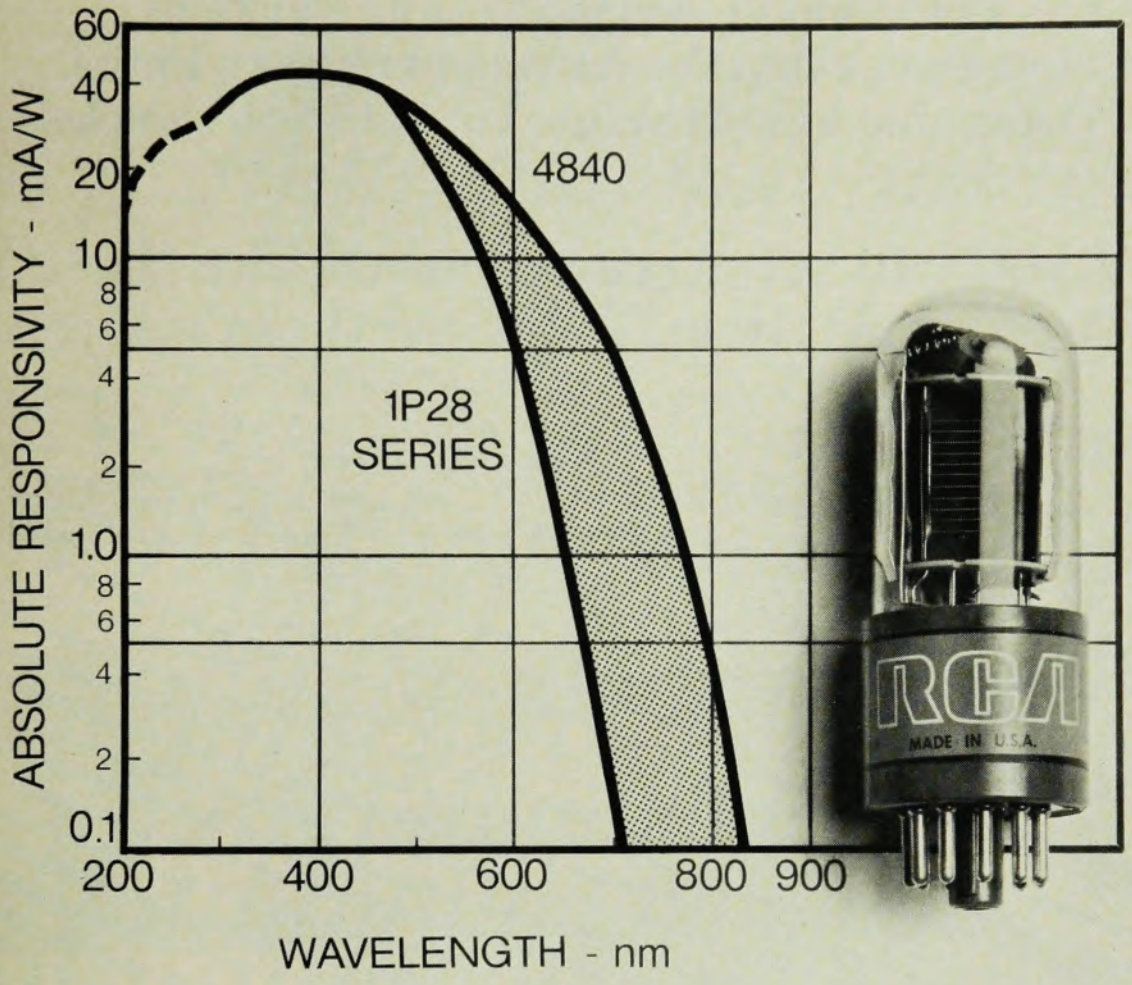


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- Program Levels (3). A main program can call up to two levels of subroutines.
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harder to distinguish the scattering effects of oxygen and determine its position.

A second data-reduction scheme is the "Fourier Transform-Deconvolution" method used recently by Landman and Adams.[17] This has the merit of being a direct scheme of determining surface structures from the reduction of experimental data. They Fourier integrated the intensity–energy data in a given energy range and deconvoluted the result. Applying this method to the surface structure of clean Al(001), they found that there is no contraction or expansion of the top layer, a result consistent with earlier findings by dynamical calculations. They also tested their method on kinematical model calculations of the sodium-on-Al(001) system. The resolution of this method and its ability to extract surface bond lengths and binding locations from real overlayer–substrate systems, and from clean surfaces where there is layer contraction or expansion, still need to be established.

### Fruitful directions

We have seen that when accurate and well-defined dynamical calculations of LEED are carried out, they can extract useful structure information for simple overlayer systems on a number of substrate materials. The use of convergent-perturbation methods made possible the economical application of this approach to a great many systems. Quantitative results of chemisorption bond lengths and bonding sites provide new chemical information not available otherwise. It would be worthwhile to verify the LEED structure results by other surface techniques or by direct binding-energy calculations.

Although present structure results are still confined to simple overlayer systems, the quantitative knowledge gained with this technique is important because it can lead to an understanding of the basic physics and chemistry of surface interactions on many substrate materials. Because of the unique sensitivity of dynamical calculations to the positions of surface atoms, their continued development should be pursued. It is likely that new formulations and adaptations will be made to enable this approach to study complex overlayer structures. These include large organic molecules (for example, the recent data of Gabor Somorjai and his co-workers) and the structures of semiconductor surfaces such as the Si(111) surface with the (7 × 7) structure. As a first step towards such development, structure studies are already underway on the (2 × 1) reconstructed surface of Si(100).

The continued investigation of data-reduction schemes should also produce fruitful results. Their underlying logic is simple and the computation straightforward, enabling experimentalists to analyze their own data. Because data-reduction methods rely more heavily on the accuracy of measured intensities, their use is more sensitive (compared to the dynamic approach) to the quality of the experimental data and to the exact knowledge of surface inputs such as surface-vibration amplitudes and surface inelastic damping. However, studies along these lines could lead to better experimental techniques and a better understanding of such dynamical quantities as inelastic loss mechanisms and layer vibration amplitudes in the surface region.

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