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Linear approximation to dynamical low-energy electron diffraction

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A linear approximation to dynamical low-energy electron diffraction (LEED) is proposed, called linear LEED (LLEED). It may hold the key to the solution of complex surface structures with large atomic displacements, in a way complementary to tensor LEED. More ambitious possibilities also present themselves, based on direct inversion schemes and related in spirit to holographic ideas. Linear LEED relies on the approximate linear independence of diffracted amplitudes from subunits such as atoms or molecules, and reduces enormously the number of full dynamical LEED calculations needed in a structural search.

Without doubt the most successful surface science tool for structure determination is low-energy electron diffraction (LEED), currently accounting for 40% of new structures. Until recently LEED structure determination has relied on large-scale calculations which can become quite expensive in terms of computer CPU time for complex structures. The inability to invert LEED data directly has necessitated a full dynamical (i.e., multiple scattering) calculation to be performed for each candidate geometry which is then compared with the experimental data. The process is repeated until as much of structural parameter space as possible has been explored. This trial-and-error approach has limited the method's applicability to relatively simple systems.[1]

Recently, new approaches to LEED have been developed which have greatly increased the power of the technique. A particularly successful set of methods is known by the generic term tensor LEED (TLEED).[2-7] The basic idea is to expand diffraction amplitudes linearly in terms of small atomic displacements away from a reference structure, for which a full dynamical LEED calculation is made: this yields a computationally efficient way to explore many nearby trial structures. Using tensor LEED, Pendry and Heinz[8] have also developed powerful direct inversion methods capable of extracting vibrational data from LEED measurements. Schemes based on spherical wave expansions and an automated search have been utilized to solve relatively complex clean and adsorbate-induced reconstructions.[9] However, while these methods have greatly increased the applicability of LEED, they suffer from a uniform failing—a radius of convergence of the spatial expansion of typically only a few tenths of an angstrom. While it is often possible to guess structures for simple systems to this degree of accuracy via hard-sphere models, more complex structures may prove less amenable. Consequently, one is reduced to the old trial-and-error method in order to locate candidate structures close enough to the true solution from which to start the tensor LEED analysis.

Two assumptions go into the construction of a tensor LEED scheme: (i) the trial structure is close enough to the true structure for the difference to be accounted for to first order in multiple scattering; (ii) the correction term to first order in multiple scattering can itself be expanded in a series: either a power series in the position coordinates of the atoms, or a spherical-wave expansion. These are two distinct assumptions, and the failure of the tensor LEED scheme at large displacements is mainly due to the breakdown of assumption (ii) rather than (i). In fact the integrity of (i) carries with it a profound implication: the scattered amplitudes are linear in the displacement of the individual atoms or molecules. As an example, consider a system of many atoms (such as an entire surface), in which two atoms are displaced from locations $\mathbf{r}_1$ and $\mathbf{r}_2$ to locations $\mathbf{r}_1+\delta\mathbf{r}_1$ and $\mathbf{r}_2+\delta\mathbf{r}_2$, respectively. If $A(\mathbf{r}_1,\mathbf{r}_2)$ represents a scattered LEED amplitude, then the linear LEED expression is

$$\begin{aligned}A(\mathbf{r}_1+\delta\mathbf{r}_1,\mathbf{r}_2+\delta\mathbf{r}_2)\\ &=A(\mathbf{r}_1,\mathbf{r}_2)+[A(\mathbf{r}_1+\delta\mathbf{r}_1,\mathbf{r}_2)-A(\mathbf{r}_1,\mathbf{r}_2)]\\ &\quad+[A(\mathbf{r}_1,\mathbf{r}_2+\delta\mathbf{r}_2)-A(\mathbf{r}_1,\mathbf{r}_2)]\ . \qquad (1)\end{aligned}$$

Here, the terms on the right-hand side (RHS) are calculated by conventional LEED theory, for relatively few structures, in which only one atom is displaced at a time. The LHS produces amplitudes for any desired combination of one-atom displacements. Equation (1) holds exactly in the kinematic limit, and its validity is therefore limited only by multiple scattering. The problem is said to be linear because Eq. (1) contains no higher-order products of the changes in amplitudes. Linearity opens to us a huge range of mathematical tools developed for linear analysis. At the simplest level it speeds the calculation of amplitudes for trial structures: once we know how each atom contributes individually to the amplitude, the effect of several atoms simultaneously displaced can be found as a linear combination of the individual terms.

As an instance of the flexibility imparted by linearity we cite holography: the diffraction pattern from a structure can be "solved" by Fourier transformation because the diffraction pattern is a linear combination of independent Fourier components.[10] In LEED the contribution of each atom is usually more complex than a single Fourier component, hence the complexity of current theories of LEED. Nevertheless the signature of each atom is contained in the diffraction data and can be extracted directly by a transformation, rather than by trial and error. A simple instance of this process was implemented in Ref. 8 for the case of tensor LEED.

Establishing the validity of linear superposition in LEED opens horizons for the interpretation of LEED spectra. This approximation can also be thought of as an extension of the kinematic sublayer addition method,[11] which shares many similarities with the linear LEED approach, but is only applied at the composite-layer level rather than at the full-surface level.

In order to test the accuracy of the linear LEED approach in the dynamical limit we performed test calculations on two systems. We began by considering the Pt(111)-(2×2)-C_2H_3 system which is almost identical to the already studied[9] Rh(111)-(2×2)-C_2H_3 structure. This structure is shown in Fig. 1. We considered structures in which the ethylidyne was displaced upward from its optimum position by 0.5 Å while the Pt surface atom not coordinated to carbon was simultaneously moved upward by 0.2 or 0.6 Å. The latter structure was outside the radius of convergence of conventional tensor LEED. Full dynamical calculations were performed for these structures which were then compared with the approximation of Eq. (1). In Table I we present the results of this comparison by means of the Pendry R factor for each beam, together with the overall R factor. The overall R factor is extremely good, being of the same order as typical errors in experimental measurements (e.g., between symmetrically equivalent beams). In Fig. 2 we display I-V curves for these structures for visual comparison.

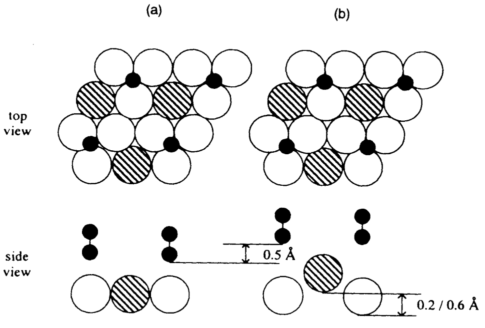

FIG. 1. The Pt(111)-(2×2)-C_2H_3 structure. (a) represents the undistorted structure, while (b) illustrates the displacements used in this study.

TABLE I. Pendry R factors for distorted Pt(111)-(2×2)-C_2H_3, comparing linear and exact LEED I-V curves for displacements of Pt atoms by 0.2 and 0.6 Å (see text for more details).

Beam	R (0.2 Å)	R (0.6 Å)
(0,0)	0.076	0.057
(1,0)	0.029	0.052
(0,1)	0.040	0.059
(0.5,0)	0.054	0.133
(0,0.5)	0.047	0.067
(0.5,0.5)	0.121	0.155
Weighted average	0.061	0.087

We then performed similar calculations for the clean Pt(100) surface, modeling a rigid expansion of the top layer of the crystal as a combination of two separate $c(2\times2)$ structures, i.e., as a combination of two checkerboard structures, with first one half of the atoms raised and then the other half. Again, these calculations produced extremely good R factors, displayed in Table II. There is one slight complication for these calculations: the approximation cannot move the location of the surface barrier where damping cuts in. It is therefore important to include this effect independently by means of a straightforward exponential damping factor.

Linear LEED is a good approximation to the full dynamical LEED calculation, but how does this help us with the initial problem of rapidly searching through complex structural parameter spaces when performing LEED structure determinations? This is best demonstrated by a simple example. Consider a structure in which we need to move 10 coordinates through 10 independent values each to explore parameter space. Using conventional methods this would require 10^{10} full calcu-

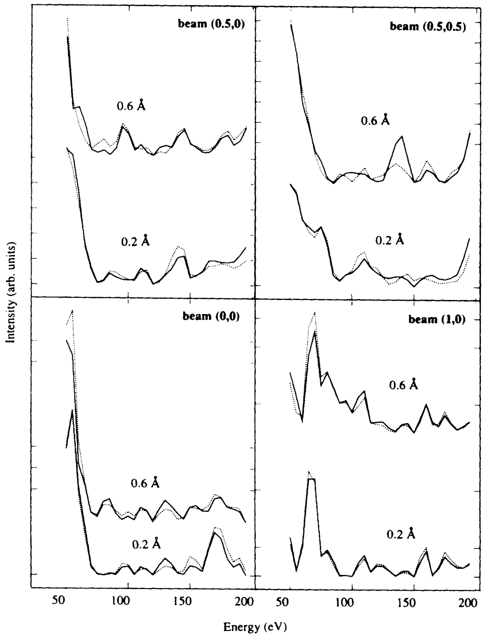

FIG. 2. I-V curves produced by an exact LEED calculation (full lines) and the approximate linear LEED calculation (dashed lines) for the Pt(111)-(2×2)-C_2H_3 structure, in which the molecule is moved up by 0.5 Å, while a Pt atom is moved up by either 0.2 or 0.6 Å.

TABLE II. Pendry R factors for the expansion of clean Pt(100), comparing linear and exact LEED I-V curves for displacements of Pt atoms by 0.2 and 0.6 Å (see text for more details).

Beam	R (0.2 Å)	R (0.6 Å)
(0,0)	0.098	0.087
(1,0)	0.033	0.064
(0.5,0.5)	≈0.000	≈0.000
(1.5,0.5)	≈0.000	≈0.000
Weighted average	0.066	0.076

lations: an impractical computational requirement. Using the linear approximation we require only 10^2 calculations, plus appropriate simple summations of amplitudes, in order to conduct a full exploration of parameter space: a far more tractable computational proposition. The situation can be likened to a locksmith trying to open a tumbler lock. The trial-and-error approach of conventional LEED would correspond to the brute force method of trying every key in existence until one fits. By contrast, the linear LEED method tries to pick the lock with a set of skeleton keys, matching one tumbler at a time: a far more elegant solution to the problem.

The importance of the linear LEED approximation is its validity for large displacements. In systems of this sort, the damping of the electron wave field via the mean free path will effectively remove the multiple-scattering correlations. Consequently, the method can be thought of as the complement of tensor LEED: it improves with larger displacements.

To conclude, we have proposed a new and efficient approximation, of value in all areas of LEED and other electron scattering techniques, which we tested on two systems and found to be extremely accurate. It is hoped that this method will circumvent the problem of locating candidate structures for examination by tensor LEED, and allow the efficient examination of highly complex structures, including coadsorption, multilayer relaxations, and systems which have so far been beyond the reach of conventional LEED calculations. In addition, the existence of a linear superposition theorem opens the way for analytic analysis of multiple-scattering data previously thought to be intractable.

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