

Efficient Scheme for Calculation of Low-Energy Electron-Diffraction Intensities in the Presence of Large Superlattices, with Application to the Structural Analysis of Benzene Adsorbed on Rh(111)

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A powerful calculational low-energy electron-diffraction scheme is introduced for superlattices with unit cells of any size: beam-set neglect. It is applied in the first structural analysis from low-energy electron-diffraction intensities of a large molecule, benzene, adsorbed on a single-crystal metal surface, Rh(111). In a $\left(\frac{1}{3}\frac{1}{3}\right)$ lattice, benzene is found to lie flat on the surface, centered over hcp-type hollow sites. A planar, possibly distorted C_6 ring is found with Rh-C bond lengths of 2.35 ± 0.05 Å.

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The determination of surface structures by low-energy electron diffraction (LEED) has been very successful for not too complex structures.¹ A limitation has been the unit cell size of superlattices, because of computational costs. But many important surfaces exhibit large unit cells, whether due to reconstruction [e.g., Si(111)(7×7)²] or adsorption [e.g., Pt(111)-(6×3)- $2C_{10}H_8$ (naphthalene)³]. We present an approximation to the dynamical theory of LEED that is accurate and very effective for surfaces which have large unit-cell superlattices.

The approximation we propose is based on the familiar concept of beam sets¹ and consists of disregarding certain beam sets. In the beam (i.e., plane-wave) representation of LEED between atomic layers, a (1×1) structure and a superlattice generate beams that we label by the reciprocal-lattice vectors \vec{g}^b and \vec{g}^s , respectively. If the unit cell area of the superlattice is M times that of the (1×1) unit cell area, there are M times as many \vec{g}^s beams as \vec{g}^b beams. We shall only consider commensurate superlattices, so that M is an integer.

The beams \vec{g}^s can be grouped into M beam sets, such that within each set all beams are interrelated by (1×1)-type reciprocal-lattice vectors \vec{g}^b (called integral-order or IO beams). An important property of these beam sets is that the substrate layers, with their (1×1) periodicity, cannot diffract a beam from one beam set into any beam of another beam set.¹

We now ask which beams within the surface ultimately contribute significantly to a given emergent beam. We shall use two definitions based on the layer representation of LEED. First, the surface atoms which repeat with the superlattice

periodicity rather than the (1×1) periodicity shall belong to a single atomic layer of appropriate thickness. Second, the term "deviation" shall describe any event in which an electron beam is scattered through a nonzero angle by an atomic layer (intralayer multiple scattering may occur within such a deviation). If we restrict ourselves to scattering paths which include only one or two such deviations, we find that (1) an emergent IO beam is not affected by any fractional-order beams (FO beams, defined as non-integral-order beams); (2) an emergent FO beam is affected only by beams which belong either to its own beam set or to the IO beam set. Thus, with only one or two deviations, the intensity of a given emergent beam is influenced solely by other beams in its own beam set and by IO beams. Since scattering paths with three or more deviations (i.e., with third- or higher-order multiple scattering) are known to yield weak contributions,⁴ one may therefore expect that neglecting all but these two beam sets is a good approximation: This is the justification for our "beam-set-neglect" (BSN) method, in which all but one or two beam sets are ignored. (One may nevertheless choose to include more than one or two beam sets, for symmetry and for higher accuracy.)

Computation times are affected as follows by beam-set neglect. The conventional generation of layer diffraction matrices by reverse scattering perturbation (RSP)¹ and the stacking of layers by renormalized forward scattering both scale¹ as M^2 for large M (in RSP, the most time-consuming part is the conversion from the spherical-wave to the plane-wave representation, which scales asymptotically as M^2). In computing the intensities of all beams by beam-set neglect, a

time proportional to $4M$ is obtained (if we assume M pairs of beam sets for simplicity), which yields a time reduction by a factor of $4/M$. A further reduction results by using only a fraction of the beams in a structural analysis; the time may even become independent of M .

The validity of the BSN method, which will be exhibited below, has important consequences, already predicted by Yang, Jona, and Marcus.⁵ It implies that the dependence of LEED intensities on energy (and angle) is primarily determined by the short-range order in the surface structure. One way to see this is by recognizing that the BSN approximation, by neglecting a majority of beam sets, removes most of the information which is needed to define the original superlattice; therefore, if BSN is valid, the superlattice and the long-range order are irrelevant, leaving only the short-range order.

Another point of view uses the connection noted above between the validity of BSN and the weakness of third- or higher-order multiple scattering. This weakness can occur only in the weak-scattering kinematic limit (whatever the mean free path length) or with a short mean free path (whatever the scattering strength), or both. In our case, the multiple scattering between substrate and overlayer is not very strong; but, in addition and more importantly, a short mean free path applies, which is the key to insensitivity to long-range order in I - V curves. Namely, the distorted spherical wave which leaves a particular surface atom towards the detector cannot have previously sampled other surface atoms distant by more than a few mean free path lengths. The diffraction can now be viewed as approximately the product of an energy-independent structure factor, due to the long-range order, and a form factor, representing the three-dimensional short-range order as sampled by multiple scattering within about a mean-free-path distance from any scatterer (multiple scattering can be viewed to yield an effective atomic scattering factor that multiplies into the structure factor).

By extension, one could apply these concepts to surfaces that have short-range order but *no* long-range order: Only the structure factor is affected by the absence of long-range order, producing diffuse scattering without sharp FO LEED beams. The diffuse intensity should have an energy dependence equivalent to that of a sharp spot in the same location of two-dimensional reciprocal space (e.g., at a half-order position at all energies). Our BSN method is a generalization of a

recent "unit-cell reduction" method⁶ which was itself a development beyond similar work by Yang, Jona, and Marcus.⁵

We have tested and applied the BSN method in the case of the determination of the surface structure of benzene (C_6H_6) adsorbed on Rh(111). The BSN method was used within the framework of the combined space method, with reverse scattering perturbation inside atomic layers and renormalized forward scattering between layers.¹ In addition, the efficient approximation of partial multiple scattering⁷ has been applied in early stages of the structure analysis, within the model benzene overlayer (which consists of carbon atoms, but no hydrogen atoms, since these are largely undetected by LEED). In addition, beam R factors were contrasted for easy detection of unpromising structures.⁸ Nonstructural parameters were the same as in previous hydrocarbon structure analyses on Rh(111).⁹

In our experiments with benzene on Rh(111),¹⁰ an ordered LEED pattern with matrix notation $\begin{pmatrix} 31 \\ 13 \end{pmatrix}$ was observed [the matrix notation defines the two basis vectors of a superlattice in terms of those of the (1×1) substrate]. LEED I - V curves were measured and a cumulative nondegenerate energy range of 1224 eV in thirteen beams at normal incidence was used in our structural work. From thermal desorption spectroscopy it is concluded that most of the benzene molecules are intact in this structure¹⁰ which is confirmed by high-resolution electron-energy-loss spectroscopy studies.¹¹ The latter data in addition strongly favor an orientation of the molecules parallel to the surface, while suggesting a $C_{3v}(\sigma_d)$ adsorption symmetry (i.e., a threefold rotation axis and mirror planes bisecting C-C bonds).

Tests of the BSN method were performed on this system. Figure 1 clearly illustrates the validity of BSN. Intensities calculated with all $\begin{pmatrix} 31 \\ 13 \end{pmatrix}$ beams (eight beam sets), which include all multiple scattering (labeled "exact" in the figure), compare very well with intensities obtained with fewer beam sets, especially at higher energies.

A search through a list of about 960 trial structures both with and without the BSN approximation yielded a clear structural determination, already with an undistorted C_6 ring, as illustrated in Fig. 2. With accurate calculations, structural refinements were investigated. The C_6 ring, which has sixfold symmetry in the free benzene, was buckled with no success; but a considerable planar distortion from the free-benzene shape,

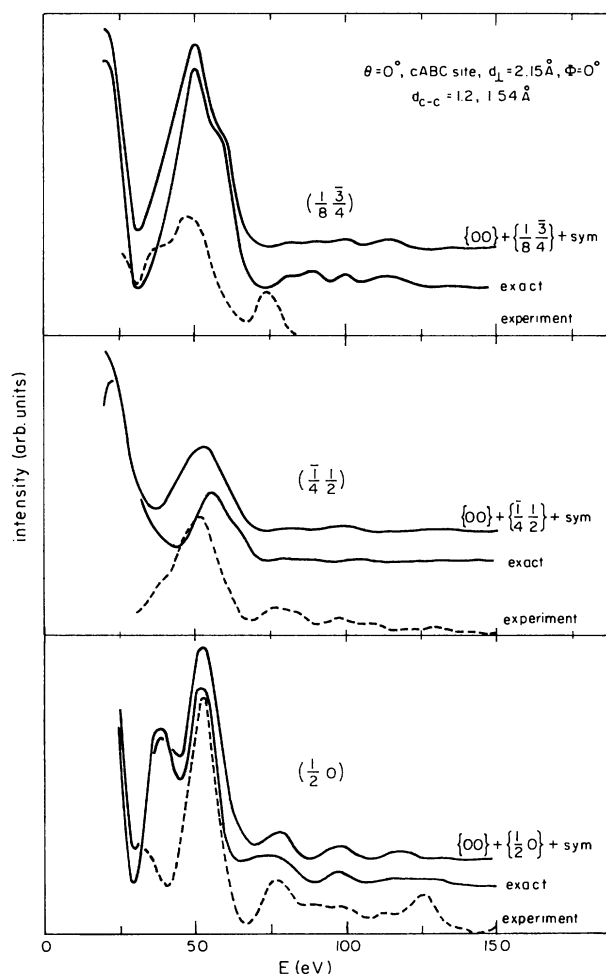


FIG. 1. Selected calculated LEED I - V curves for $\text{Rh}(111)-\left(\frac{31}{13}\right)\text{C}_6\text{H}_6$ (H ignored) at normal incidence ($T = 240$ K). The benzene molecules have the near-optimal distortion shown in Fig. 2 and are located over hcp-type hollow sites with a Rh-C layer spacing of 2.15 \AA .

as shown at the right in Fig. 2, improved the agreement between theory and experiment (decrease of Zanazzi-Jona R factor, Pendry R factor, and five- R -factor average⁸ from 0.35 to 0.29, 0.62 to 0.55, and 0.26 to 0.25, respectively). In this model, the optimum Rh-C bond length is $2.35 \pm 0.05 \text{ \AA}$, while the C-C bonds alternate between $1.25 \pm 0.1 \text{ \AA}$ and $1.6 \pm 0.1 \text{ \AA}$. The ring distortion may be connected to the molecular decomposition that occurs around 413 K on $\text{Rh}(111)$,¹⁰ and may be relevant to the mechanism of catalytic reactions involving aromatic (i.e., ringlike) molecules.

For structural comparison, organometallic clusters containing benzene and other aromatic molecules¹² have metal-C bond lengths of 2.09

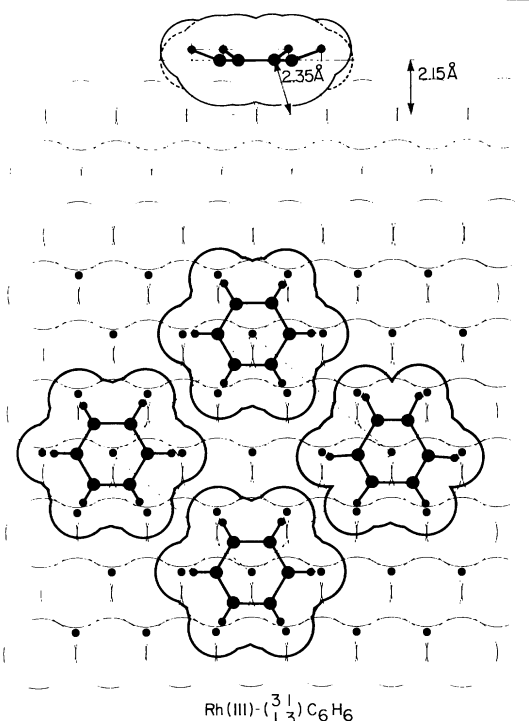


FIG. 2. Optimal structure found for $\text{Rh}(111)-\left(\frac{31}{13}\right)\text{C}_6\text{H}_6$ (H positions are assumed), including van der Waals radii of 1.8 and 1.2 \AA for C and H, respectively. A unit cell is outlined in the bottom panel. The right-hand benzene molecule shows the preferred in-plane distortion (C-C bond lengths of 1.25 and 1.6 \AA). The side view in the top panel includes possible CH bending away from the surface.

to 2.45 \AA (for metals with atomic radii within 0.02 \AA of that of Rh). C-C bond lengths in the benzene-containing clusters vary from 1.36 to 1.49 \AA and in the other clusters from 1.31 to 1.61 \AA .

In conclusion, we have demonstrated the quality and great computational effectiveness of a new approximation (beam-set neglect) in LEED calculations. It applies to any superlattice and is particularly valuable with large unit cells. The method was used in a structural determination of benzene on $\text{Rh}(111)$: In a $\left(\frac{31}{13}\right)$ arrangement, we find flat-lying molecules centered on hcp-type hollow sites, with possible planar C_6 ring distortions (cf. Fig. 2).

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