# Structure determination of disordered organic molecules on surfaces from the Bragg spots of low-energy electron diffraction and total energy calculations

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We show that an analysis of the intensity versus energy variation of Bragg spots due to low-energy electron diffraction from a disordered overlayer of molecules on a crystal surface allows a much more convenient method of determining the local adsorption geometries of such molecules than previously analyzed weak diffuse diffraction patterns. For the case of methanol on Pd(111), we show that the geometry determined by this means from experimental diffraction data is in excellent agreement with the predictions of density functional total energy calculations.

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## I. INTRODUCTION

The adsorption of organic molecules on surfaces is a phenomenon at the core of many processes of far-reaching technological importance in fields ranging from the lubrication of automobile engines to processes of heterogeneous catalysis that underpin much of our industrial civilization. The key to a fundamental understanding of these processes is the nature of the bonding of such molecules to surfaces, which in turn requires the determination of the geometrical relation of the molecules to the surfaces.

A standard method of determining the adsorption geometry of molecules that form *ordered* overlayers on surfaces is the analysis of intensity versus beam energy ($I/E$) variations of (mainly) superstructure Bragg diffraction spots from low-energy electron diffraction (LEED). Unfortunately, many adsorbates do not form ordered layers on crystal surfaces. Rather, they tend to take up arrangements of locally identical geometries relative to the substrate, but with limited (or nonexistent) long-range order. The signature of such surfaces is background (diffuse) LEED scattering from the disordered overlayer, rather than superstructure Bragg reflections. In such cases, alternative methods such as photoelectron diffraction[1] or x-ray standing wave measurements[2] have been able to determine aspects of the adsorption geometries. However, such techniques require access to synchrotron radiation sources, thus limiting their applicability. Scanning tunneling microscopy (STM) is also capable of probing the structure of disordered layers but cannot accurately measure bond lengths and angles. It has been shown that diffuse LEED intensities contain enough information to determine the structures of disordered surfaces.[3,4] Although this has proven effective in several cases,[5] experimental difficulties in measuring the low background intensities have prevented the widespread use of the technique. We point out in this paper that a much more easily accessible signal for accurately determining the structures of such disordered adsorbates is the monitoring of their much stronger effect on the Bragg reflections of the ordered substrate. We demonstrate this idea by determining the adsorption geometry of methanol on Pd(111). The tilted C-O bond found is confirmed by indepen-

dent density functional total energy calculations that also determine the positions of the H atoms.

## II. THEORY

The complex dynamical scattering amplitude from a surface of $N$ unit cells forming a two-dimensional (2D) lattice parallel to the surface may be written

$$B_{\mathbf{q}} = \frac{c}{N\sqrt{V}} \sum_{j=1}^{N} h(\mathbf{q})\exp[i\mathbf{q}\cdot\mathbf{r}_j] = \delta_{\mathbf{q},\mathbf{g}}\frac{c}{\sqrt{V}}h(\mathbf{q}), \quad (1)$$

where $V$ is a normalization volume for the incident electron, $c = 2\pi i/A|k_z|$ the usual LEED prefactor,[6] $A$ the area of the unit cell, $\mathbf{q} = \mathbf{k}_0 - \mathbf{k}$ the difference between the incident, $\mathbf{k}_0$, and scattered, $\mathbf{k}$, electron wave vectors, $k_z$ the component of the latter wave vector perpendicular to the surface, $\mathbf{r}_j$ a lattice vector, and $h(\mathbf{q})$ a dynamical (multiple-scattering) structure factor of the entire unit cell (including all subsurface atomic layers). The right-hand equality follows from the fact that the summation over $j$ would be expected to be zero unless $\mathbf{q} = \mathbf{g}$, where $\mathbf{g}$ represents a reciprocal lattice vector of the substrate. The corresponding structure factor of $M$ adsorbates on $N$ substrate lattice sites ($M < N$) is

$$S_{\mathbf{q}} = \frac{c}{N\sqrt{V}} \sum_{j=1}^{M} f(\mathbf{q})\exp[i\mathbf{q}\cdot\boldsymbol{\rho}_j], \quad (2)$$

where $\boldsymbol{\rho}_j$ represents a set of $M$ lattice vectors, and $f(\mathbf{q})$ is an effective (dynamical) scattering factor of the molecule that includes multiple scattering with the substrate.

The total scattered intensity from the surface is

$$I_{\mathbf{q}} = |B_{\mathbf{q}} + S_{\mathbf{q}}|^2 = |B_{\mathbf{q}}|^2 + [B_{\mathbf{q}}^* S_{\mathbf{q}} + \text{c.c.}] + |S_{\mathbf{q}}|^2. \quad (3)$$

From Eq. (2) we see that the last term on the right-hand side (RHS) above may be written

$$|S_{\mathbf{q}}|^2 = \frac{|c|^2}{N^2 V}|f(\mathbf{q})|^2\{M + \delta_{\mathbf{q},\mathbf{g}}M(M-1)\}, \quad (4)$$

where the first term in the braces on the RHS of Eq. (4) arises from the diagonal terms in the double summation from the square modulus of Eq. (2), and the off-diagonal terms are zero unless $\mathbf{q} = \mathbf{g}$. Substituting Eqs. (1) and (4) into Eq. (3), collecting together terms contributing to the scattering in the direction $\mathbf{q} = \mathbf{g}$, and substituting for $c$, the flux of electrons contributing to a Bragg spot is

$$F_{\mathbf{g}} = \frac{4\pi^2}{A^2 V |k_z|} \{ |h(\mathbf{g})|^2 + \Theta[h(\mathbf{g})^* f(\mathbf{g}) + \text{c.c.}] + \Theta^2 |f(\mathbf{g})|^2 \} \tag{5}$$

where the coverage $\Theta = M/N$. The diffuse flux [from the first term in Eq. (4), which has no contributions from the pure substrate structure factor $B_{\mathbf{g}}$] is

$$F_{\mathbf{q}} = \frac{k^2 \cos\theta}{A V |k_z|} \Theta |f(\mathbf{q})|^2 d\Omega, \tag{6}$$

where $d\Omega$ is the solid angle subtended by the detector area at the sample and $\theta$ is the angle of the detected beam to the surface normal. Inserting typical numbers into Eq. (6) and the terms in Eq. (5) containing $f(\mathbf{g})$ suggests that *the contributions to the Bragg spots due to adsorbate scattering are two orders of magnitude larger than typical measured diffuse fluxes* (see the Appendix). This is due to the fact that, despite the disorder, the scattered complex amplitudes from the collection of adsorbates add up coherently in the directions of the Bragg spots, while they sum incoherently to form the diffuse background. For the same reason, the electron flux contributing to the integer-order Bragg spots from an ordered overlayer of the same coverage $\Theta$ is identical to Eq. (5) (neglecting the usually small multiple scattering between adsorbates[7]). The computational convenience is further enhanced by the fact that the $I/E$ curves for an adsorbed layer may be simulated from a standard LEED computer program by a calculation for an ordered overlayer of the smallest possible $(1 \times 1)$ periodicity with fractional occupancy of the same magnitude as $\Theta$. The notion that a calculation involving only integer-order beams may be sufficiently accurate for practical calculations of the integer-order Bragg spots for large unit-cell overlayers may be regarded as a special case of the *beam set neglect* method.[8,9] The extra simplification introduced in the present paper is that the *quasidynamical*[7] treatment of the adlayer allows it to be treated as literally a $(1 \times 1)$ overlayer with an adsorbate scattering factor reduced by a factor of $\Theta$. Thus one is able to overcome the difficulties of calculating large unit-cell structures typically expected of organic adsorbates due to the typical $n^3$ scaling of the computer time of the multiple-scattering calculations (where $n$ is the number of atoms of the unit cell of a layer parallel to the surface). We note that, in principle, this method may be applied also to ordered overlayers of adsorbates. However, since these give rise to additional diffraction spots, greater accuracy may be obtained by including these also in a conventional LEED analysis.

In the following, we seek to determine the local geometry and coverage of molecular methanol adsorbed on a Pd(111) surface at[10] 80 K by an analysis of the effect of the adlayer on the $I/E$ curves of the Bragg spots. Molecular methanol

does not form an ordered structure on Pd(111) and its structure has not yet been determined. The usual method of determining the structure of disordered adlayers by LEED involves the analysis of the elastic diffuse intensities.[5] Following the indication of our theoretical analysis above, we attempted instead to determine this structure by varying geometrical and coverage parameters for optimal agreement of a calculation for an ordered $(1 \times 1)$ adsorbate layer, of varying (fractional) occupancy $\Theta$ with experimental data from the methanol-covered Pd(111) surface. We chose to study this system as methanol is likely to bond to this surface via the lone pair electrons on the oxygen atoms, leading to a C-O bond that is tilted with respect to the surface normal, thus providing a reasonably stringent test of the idea. Previous work on methanol on Pd(111) has suggested that methanol adsorbs molecularly at low temperatures, and dissociates into both methyl and methoxy species on heating.[10]

## III. EXPERIMENT

LEED measurements were carried out in a doubly $\mu$-metal shielded ultrahigh vacuum chamber operating at a base pressure of $5 \times 10^{-11}$ Torr, and containing a Pd(111) single crystal, which could be cooled to 80 K and resistively heated to 1200 K. The sample was cleaned using standard procedures.[11] LEED patterns of the clean surface were photographed as a function of incident energy using a Nikon Coolpix digital camera (5.0 Mbytes resolution) and the images stored on an IBM Smartcard memory (1 Gbyte). The images were then downloaded to a personal computer for subsequent analysis. Images were initially collected for the clean surface every 5 eV between 80 and 325 eV, a procedure that took approximately 15 min. The sample was then heated briefly to 740 K to remove any background contaminants that may have adsorbed during this process, allowed to cool to 80 K, and exposed to 1.4 L of methanol (Aldrich, 99.8%) leading to a methanol coverage of 0.33 monolayers.[10] Diffraction patterns of the adsorbate-covered surface were then collected at identical energies and again transferred to a microcomputer.

## IV. RESULTS AND DISCUSSION

The intensities of the substrate $(1 \times 1)$ spots for both the clean and adsorbate-covered surfaces were measured using NIH IMAGE[12] and are displayed as dashed lines in Fig. 1. Notice the large differences between the experimental $I/E$ curves of the clean and adsorbate-covered surfaces shown in the left- and right-hand columns of Fig. 1, respectively. We measured also the reflection absorption infrared spectrum (RAIRS) and the resulting infrared spectrum (not shown), as well as previously collected x-ray photoemission spectroscopy (XPS) data,[10] indicate the presence of a single type of species on the surface. In addition, the relative intensities of the infrared features indicate that the C-O bond is oriented within 30° of the surface normal.

The angles of incidence of the electron beam onto both the clean and adsorbate-covered surfaces were first determined using a standard LEED package[13] to find the best fit
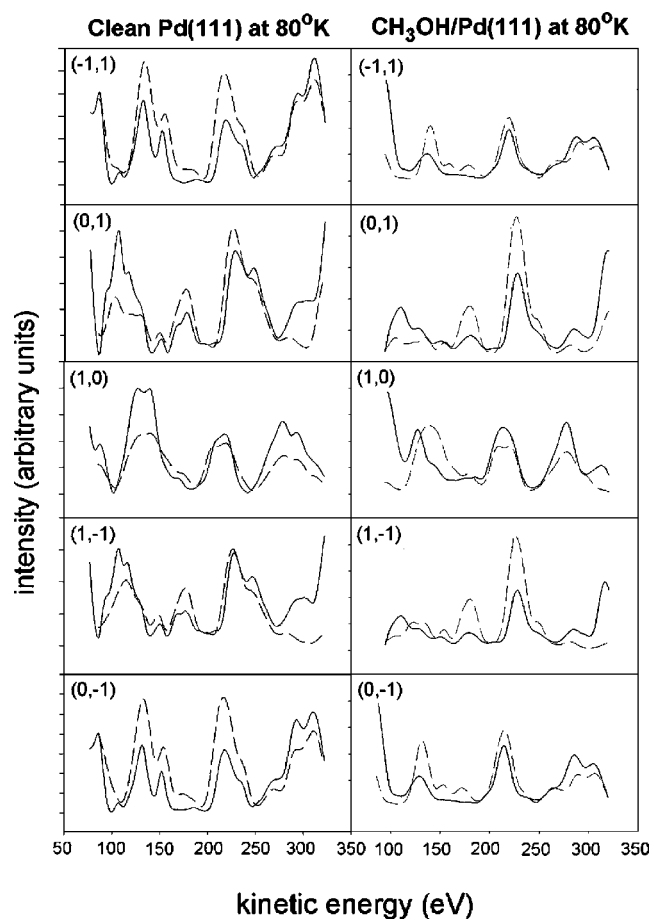
FIG. 1. Comparison of calculated LEED $I/E$ curves (solid lines) and corresponding experimental ones (dashed lines) of integer-order diffraction spots measured at a sample temperature of 80 K for clean Pd(111) and Pd(111) exposed to 1.4 L of methanol. The direction of electron incidence for both surfaces was first determined from the clean Pd(111) data to be a polar angle of 4° to the surface normal and an azimuthal angle of 2° from a plane through first and second layer Pd atoms. The adsorbate structural parameters were determined by optimizing the fit of calculated $I/E$ curves (shown) to the experimental data for the methanol-covered surface.

of calculated $I/E$ curves (shown as solid lines in the left-hand column of Fig. 1) to the clean Pd(111) data. The polar angle of incidence was found to be 4° to the surface normal, and the azimuthal angle 2° from a plane normal to the surface passing through atoms in the first and second layers of the substrate. A global search was also conducted with the C-O bond length fixed at the gas-phase value of 1.427 Å for different adsorption sites that include the face centered cubic (fcc) hollow, the hexagonal close packed (hcp) hollow, the bridge, and the top sites (see Fig. 2). The fcc hollow site is favored over all the other sites. The C-O axis was found to have a considerable tilt from the normal. The distance of O from the substrate is about 1.5 Å. However, the $R$ factor was found to be insensitive to the azimuth of the tilted C-O axis. Nonstructural parameters like the coverage and average thermal vibration amplitudes were also optimized during this global search. The Pendry $R$ factor as functions of average thermal vibration amplitude and coverage are shown in Fig.
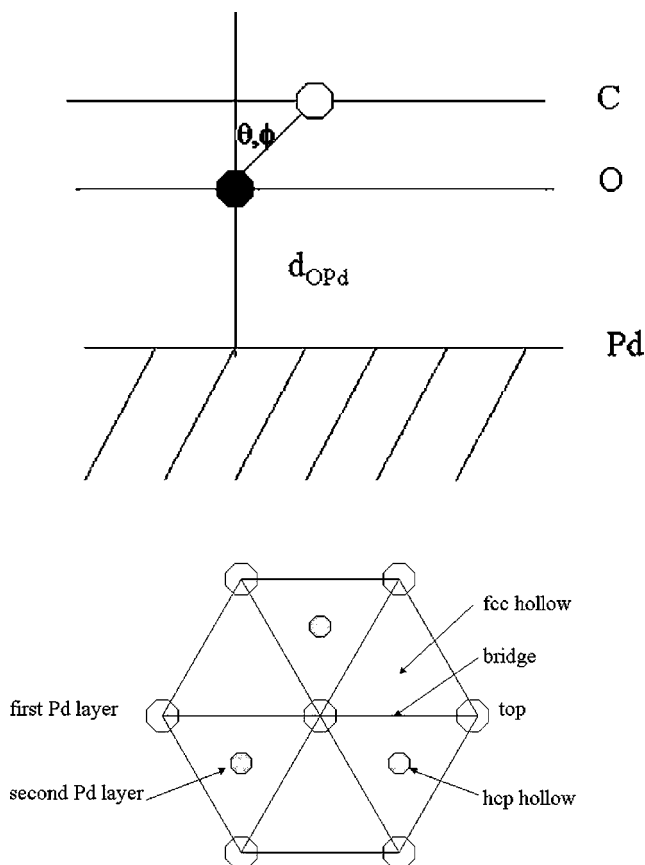


FIG. 2. Schematic diagram for the surface structure of methanol on Pd(111) and the different adsorption sites considered in this work (hydrogen atoms not shown as they are invisible in LEED).

3 and Fig. 4, respectively. It was found that the coverage of methanol is about 0.3, which agrees quite well with that expected from the methanol dose. The structural results of the global search are summarized in Table I.

Structural parameters of the adsorbate at the fcc hollow site were then refined by an *automated tensor LEED* program[14] for the same angles of electron incidence. The right-hand panel of Fig. 1 shows the calculated $I/E$ curves that fit best the experimental data from the adsorbate-covered
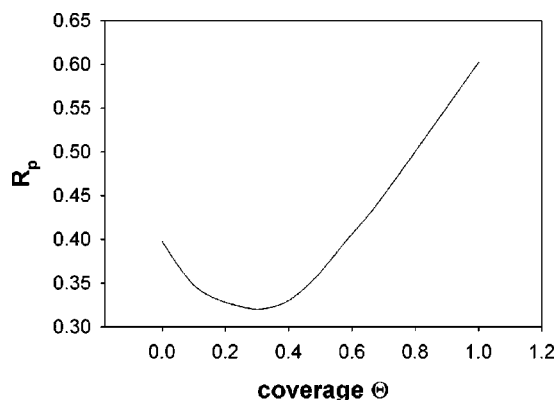


FIG. 3. Pendry's $R$ factor versus the average atomic thermal vibration amplitude with all other parameters fixed at their optimal values for methanol on Pd(111).
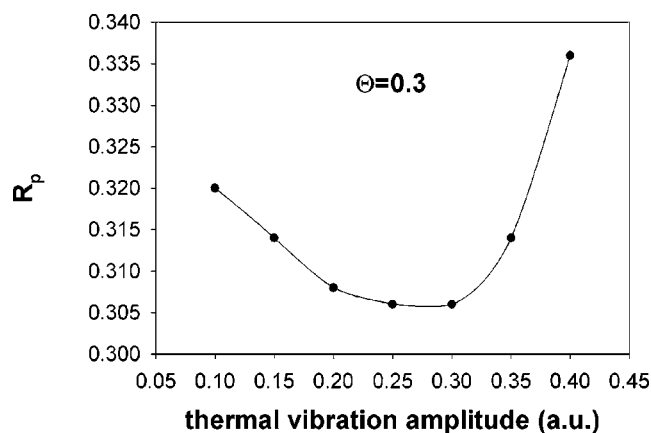
FIG. 4. Pendry's *R* factor versus the coverage with all other parameters fixed at their optimal values for methanol on Pd(111).



FIG. 5. Depiction of the geometry of methanol on a 22-atom Pd(111) cluster predicted by density functional total energy calculations.

surface (solid lines). The search was initialized with the C-O axis vertical and the oxygen atom bonded to the fcc hollow site. Hydrogen atoms were ignored since they make very little contribution to the LEED intensities. The carbon and oxygen atoms as well as the first two palladium layers were allowed to move in the first iteration. The Pd atoms were fixed in subsequent iterations. Since the algorithm is based on expansion up to the first order of intensity about the reference structure, it contains some error unless the atomic displacements are very small. The carbon and oxygen atoms were moved to the minimum found by the algorithm and both the structure tensors and intensities were recalculated with the new reference structure. The atoms were found to move by less than 0.03 Å after two iterations. For this particular system, the *R* factor was found to be sensitive only to the sum of O-Pd and C-O distances. Molecular methanol is known to have a C-O bond length of 1.425 Å in the gas phase,[15] and the dissociated methoxy species CH$_3$O has a C-O bond length of 1.43 Å on Cu(111) and Ni(111).[16,17] Therefore, the search was repeated with the C-O bond length constrained to be 1.45 Å, while the other structural parameters of C and O atoms were allowed to relax freely. These calculated *I/E* curves on the right-hand column of Fig. 1 yielded a Pendry *R* factor[18] of 0.23, indicating a good fit to experiment. The corresponding structural model assumed molecular adsorption at each substrate lattice site with occupancy (equivalent to the coverage) of 1/3, with a C-O bond length of 1.45 Å, an O-Pd distance of 1.50 Å, and a C-O bond oriented at 15° to the surface normal, where the oxygen atom of the methanol was centered over each of the fcc threefold hollow sites.

TABLE I. Optimal structures and Pendry *R* factors for different adsorption sites obtained by a global search. Parameters used here are explained in Fig. 2.

| Site | $R_p$ | $\theta$ | $\phi$ | $d_{OPd}$ (Å) |
|---|---|---|---|---|
| Bridge | 0.41 | 50° | 240° | 1.3 |
| fcc hollow | 0.30 | 20° | 30° | 1.5 |
| hcp hollow | 0.35 | 60° | 60° | 1.5 |
| Top | 0.50 | 40° | 90° | 1.7 |
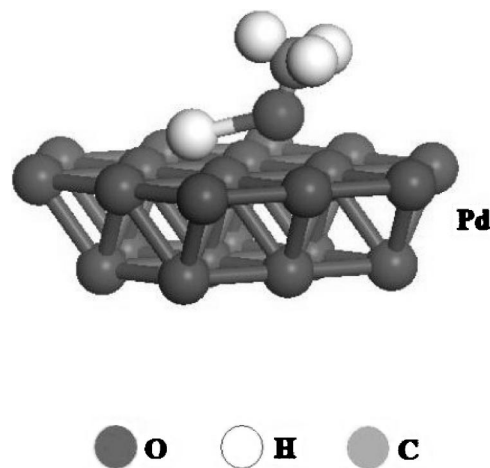
The density functional predictions of the structure of methanol on a cluster of atoms representing a Pd(111) surface were computed using the DMOL program.[19] The calculations were initially carried out for a 14-atom cluster comprising a hexagonal array of palladium atoms with a Pd-Pd spacing of 2.75 Å to represent the Pd(111) surface. The structure of methanol on this surface was optimized including all electrons and allowing the atoms of the molecule to move freely until an energy minimum was reached. A second layer of palladium atoms was then included to yield a 22-atom Pd(111) cluster with the oxygen on the methanol adsorbed over a face-centered cubic site. The inclusion of the extra electrons in the larger cluster necessitated the use of an effective core potential. The geometry of the methanol, holding the Pd atoms fixed, was then optimized. The resulting metastable structure is shown in Fig. 5 and is in essential agreement with the results from the smaller cluster. (A lower energy solution corresponding to dissociated H and methoxy species was also found.) The calculated parameters of this structure and the geometry determined using LEED are given in Table II. Clearly the agreement between the two geometries is extremely good. It is also evident that the O-H bond has been considerably lengthened on adsorption onto the surface, changing from 0.956±0.015 Å for gas-phase methanol[14] to ~2.3 Å when adsorbed onto the cluster. This observation is in general accord with the chemistry of methanol on Pd(111) where dissociation into methoxy species and adsorbed atomic hydrogen occurs when the surface is heated to ~120 K.[10]

## V. CONCLUSION

To summarize, a method is described in which the structure of a disordered overlayer of organic molecules determined by an analysis of its effect on the LEED *I/E* curves of the substrate Bragg spots. We show theoretically and experimentally that such signals are significantly larger than those of the diffuse background. Since the analysis of the data requires only standard LEED analysis packages for relatively

TABLE II. Comparison of the structural parameters for methanol on Pd(111) at 80 K from LEED measurements of the disordered overlayer with the results of density functional calculations.

| Parameter | LEED calculation | Density functional calculation |
|---|---|---|
| C-O distance (Å) | 1.45 | 1.40 |
| O-Pd distance (Å) | 1.50 | 1.51 |
| CO tilt angle (deg) | 15 | 15 |
| Adsorption site | fcc threefold hollow | fcc threefold hollow |

small surface unit-cell structures, it may be performed easily in a moderately equipped home laboratory for even relatively large molecular systems. This approach is thus substantially more convenient than alternative synchrotron-based techniques such as photoelectron diffraction or x-ray standing wave measurements.

In the particular system analyzed, methanol is found to adsorb molecularly on Pd(111) at 80 K with the C-O bond oriented at 15° to the surface normal in accord with density functional calculations of the geometry. The accuracy of the method is confirmed by the good agreement with the structure predictions of total energy calculations based on density functional theory. Since the method does not rely on the ability to prepare ordered structures, it can easily be applied to a wide range of molecular adsorbates on surfaces, and thus opens up the possibility of accurately and conveniently determining a wide range of practically important structures, e.g., those of organic adsorbates, that are not currently easily accessible. In addition, since structures can be measured at any coverage, this strategy also allows differences in surface structure to be measured as a function of coverage, for either ordered or disordered adsorbates, to probe effects that are likely to be important in understanding catalytic processes.

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### APPENDIX: DIFFUSE FLUX DUE TO DISORDERED ADSORBATES ON A SURFACE

The diffuse electron flux measured by a detector of solid angle $d\Omega$ is

$$F_{\mathbf{q}} = \frac{NA}{4\pi^2}\int_{d\Omega}d^2 k_{\parallel}k_z |S_{\mathbf{q}}|^2 = \int_{d\Omega}d^2 k_{\parallel}\frac{\Theta}{Ak_z V}|f(\mathbf{q})|^2, \tag{A1}$$

where $NA/4\pi^2$ is the density of $k_{\parallel}$ states, and the second equality follows from Eq. (4). From the relation $d^2 k_{\parallel} = k^2 \cos\theta d\Omega$, we get Eq. (6). The number of electrons entering the detector per unit time is

$$dw = NAF_{\mathbf{q}} = \frac{Nk}{V}\Theta|f(\mathbf{q})|^2 d\Omega. \tag{A2}$$

Assuming the scattering factors $f(\mathbf{q})$ and $h(\mathbf{q})$ in Eqs. (5) and (6) to be of the same order of magnitude, the ratio of the diffuse flux into $d\Omega$ to the corresponding flux into a Bragg spot is equal to

$$\frac{k^2 A \cos\theta\, d\Omega}{4\pi^2}. \tag{A3}$$

Taking $A = 25$ a.u., $E = 2k^2 = 8$ hartrees, and $d\Omega \approx 10^{-3}$, the ratio is approximately equal to $10^{-2}$.

An alternate way of deriving Eq. (6) is to expand the wave function in spherical waves instead of plane waves. The asymptotic form the wave function is

$$\psi(\mathbf{r}) \underset{r\to\infty}{\to} \frac{f(\mathbf{q})e^{ikr}}{r}\sum_i e^{i\mathbf{q}\cdot\mathbf{r}_i}. \tag{A4}$$

The differential cross section is

$$\frac{d\sigma}{d\Omega} = \left|f(\mathbf{q})\sum_i e^{i\mathbf{q}\cdot\mathbf{r}_i}\right|^2. \tag{A5}$$

The number of electrons going into the detector per unit time is

$$\frac{dw}{d\Omega} = \frac{d\sigma}{d\Omega}F_{\text{inc}}, \tag{A6}$$

where $F_{\text{inc}} = k/V$ is the incident electron flux. For non-Bragg directions,

$$\left|\sum_i e^{i\mathbf{q}\cdot\mathbf{r}_i}\right|^2 = M + \sum_{i\neq j} e^{i\mathbf{q}\cdot(\mathbf{r}_i - \mathbf{r}_j)} = M. \tag{A7}$$

Therefore,

$$\frac{dw}{d\Omega} = \frac{Mk}{V}|f(\mathbf{q})|^2 = \frac{Nk}{V}\Theta|f(\mathbf{q})|^2, \tag{A8}$$

which is the same as Eq. (A2).

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