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Author

Masel, R.I.

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CALCULATION OF ATOM SURFACE SCATTERING

R. I. Masel, R. P. Merrill, and W. H. Miller

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Semiclassical theories and quantum hardwall calculation of atom surface scattering*

R. I. Masel and R. P. Merrill

Department of Chemical Engineering, University of California, Berkeley, California 94720

W. H. Miller

Department of Chemistry and IMRD, University of California, Berkeley, California 94720

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A semiclassical formalism for atom and electron scattering from solid surfaces is presented and compared to exact quantum calculations for scattering from a sinusoidal hardwall and to experimental scattering distributions for thermal helium and neon beams scattered from W(112). The helium results are well represented by elastic calculations, but large inelastic effects are evident in the neon scattering. The semiclassical calculations for the hardwall are in agreement with the exact quantum results to within a few percent. Qualitatively, either a specularly dominated distribution or a rainbow pattern is predicted, depending on the k vector and the amplitude of the surface periodicity. A preliminary attempt to apply this formalism to low-energy electron scattering from Ni(100) is also presented. The results, while not in exact agreement with more conventional dynamic LEED calculations, do reproduce absolute peak positions to within 7 V.

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INTRODUCTION

In recent years there has been a great deal of experimental and theoretical interest in the scattering of well collimated beams of rare gases and simple molecules from single crystal faces.¹ In these experiments an atomic or molecular beam is directed onto the test surface at a preselected angle and one measures the angular distribution of scattered particles. Typical results for scattering of thermal beams from highly structured surfaces [in this case the (110) direction of W(112)], are shown in Fig. 1 for He (Ref. 2) and Ne (Ref. 3).

The He diffracts, exhibiting a strong specular peak and two less intense secondary peaks, which can be shown to correspond to first order diffraction beams. By contrast, neon scattering has a form referred to as "rainbow" scattering. It is much broader with less structure. The intensity maxima which are observed do not correspond to any particular diffraction condition. The angular positions of the most prominent maxima, one forward-scattered and one backscattered, are termed the "rainbow angles."

Potentially the elastic part of these scattering profiles will yield information about the structure (i.e., morphology) of the surface potential while the inelastic part of the scattering profiles can yield information about surface phonons, gas-solid collision dynamics, and adsorption mechanisms. Here, the focus will be on the elastic part. The results of a dynamic, semiclassical theory⁴ of the scattering processes will be

presented and compared to quantum hardwall calculations⁵ and some experimental data from W(112). The purpose of these dynamical calculations is to identify the nature of the structural information which can be recovered from the elastic scattering.

SEMICLASSICAL LIMIT

The semiclassical theories are best presented via the Feynmann path integral⁶:

$$\mathcal{K}(\mathbf{r}_2, t_2; \mathbf{r}_1, t_1) = \int_{\text{all possible paths from } \mathbf{r}_1 \text{ to } \mathbf{r}_2} \left[\begin{array}{l} \text{probability} \\ \text{amplitude for} \\ \text{the path } \mathbf{r}(t) \end{array} \right] \mathcal{D}[\mathbf{r}(t)], \quad (1)$$

FIG. 1. A comparison of helium and neon scattering patterns in the (110) direction of W(112). Data is from White.³

FIG. 2. Semiclassical corrections (—) to the classical intensity envelope (···).

where $\mathcal{K}$ is the propagator kernel. Equation (1) represents a system by examining all the possible ways it can evolve and then assigning a probability amplitude to each path. The integral simply sums these probability-weighted paths. Work in gas-phase scattering⁷ has shown that it is a reasonable approximation to consider only those paths that satisfy classical mechanics. If this approximation is made then it is easy to show⁴ that the scattering amplitude $S(\theta)$ is given by

$$S(\theta) = [(\text{classical part}) \\ \times (\text{structure factor for intracellular interference}) \\ + (\text{tunneling correlations})] \\ \times (\text{diffraction conditions}). \quad (2)$$

In Fig. 2 the classical part is plotted as a dotted line. It is rainbow-like, with two sharp infinities and a broad minimum. The infinities are caused by the many trajectories which contribute to scattering at these maximum allowed scattering angles (i.e., there is a maximum in the classical deflection function). This leads to infinities in a differential intensity at the rainbow angles. Semiclassical theory attenuates and broadens these infinities and produces supernumerary rainbows, i.e., periodic maxima within the rainbow angles. The interference which gives rise to these maxima occurs because two stationary phase trajectories add amplitudes for each scattering angle. It is

FIG. 3. Specular (solid lines) and rainbow (dashed lines) created when the Lawe condition is included.

analogous to the interference caused by scattering from different atoms within a unit cell in x-ray diffraction. The product of this "structure factor" and the classical part added to the tunneling corrections are also shown (solid line) in Fig. 2. When the diffraction conditions are imposed, the results are as shown in Fig. 3. If the wavelength of the incident particles is large (dark lines in Fig. 3), then most of the intensity will be in the specular peak, and only a small amount of intensity will be in the diffraction peaks. Lowering the wavelength (dashed lines) moves in the diffraction peaks and raises their relative intensity, producing a rainbow-like pattern. A similar effect can be seen if one changes the amplitude of the surface periodicity. Small amplitudes (smooth surfaces) result in rainbow angles close to the specular, which attenuate the diffracted beams strongly. Large amplitudes result in rainbow angles far from the specular, and the entire rainbow envelope modulates the intensities of the diffracted beams.

Qualitatively then, both types of scattering patterns normally observed (see Fig. 1) are recovered from the semiclassical calculations. A quantitative comparison is shown in Fig. 4. These are elastic semiclassical calculations of thermal (300 K) helium scattering from a modified Lennard-Jones 3-9 potential,⁸ and are compared to data of Stoll *et al.*² for helium scattering from W(112). The results have been averaged over the experimental beam aperture. Relative intensities and peak positions are predicted to within experimental accuracy. Absolute peak intensities and peak widths are not predicted accurately, but it is expected that much of the difference would be eliminated by including in the calculations a Debye-Waller analysis with peak broadening.^{2,8}

A comparison with an experimental neon scattering pattern is shown in Fig. 5. Both the semiclassical calculations and the data show rainbow-like patterns, but there is little quantitative agreement. Inelastic effects have been ignored in the model, and neon scattering from tungsten is believed to involve strong inelastic effects.⁹

FIG. 4. A comparison of semiclassical calculations (lines) of helium scattering to the data of Stoll² (squares and triangles).

FIG. 5. A comparison of calculated neon scattering pattern to the data of White.³

QUANTUM HARDWALL CALCULATIONS

Since the semiclassical methods are approximate, it would be helpful to determine the magnitude of the errors associated with the formalism and to clarify as much as possible the physics implied by these techniques. While the coupled channel calculations of Wolken¹⁰ and Tschuda¹¹ represent the exact quantum result for elastic scattering, the calculations are lengthy and make direct comparison with the semiclassical calculations over a broad range of system parameters impractical. It is worth noting, however, that Doll,¹² using semiclassical techniques, has achieved close agreement with the Wolken results.

The coupled-channel calculations have been carried out for realistic potentials (i.e., Morse¹⁰ and Lennard-Jones¹¹). Simpler potentials can be treated by methods requiring less calculational labor. One such potential is a sinusoidal hardwall.⁵ This is a particularly interesting case for comparison with the semiclassical calculations because the impulse potential of the hardwall represents a "worse case" for semiclassical theory, and more physically realistic potentials should be represented even more accurately than the hardwall.

The formalism for the solution to the hardwall is based on the Lippmann-Schwinger equation:

$$\psi(\mathbf{r}) = \phi_I(\mathbf{r}) + \int d\mathbf{r}_0 G_0^+(\mathbf{r}, \mathbf{r}_0) V\psi(\mathbf{r}_0), \quad (3)$$

where ψ = the wave function, ϕ_I = the incident wave, V = the potential, and G_0^+ = the outward-going free-particle Greens' function. For a hardwall, the potential goes to infinity when z , the distance coordinate perpendicular to the surface, is less than the surface contour, $D(\mathbf{x}_0)$. Equation (3) becomes

$$\psi(\mathbf{r}) = \phi_I(\mathbf{r}) + \int d\mathbf{r}_0 G_0^+(\mathbf{r}, \mathbf{r}_0) \delta[z_0 - D(\mathbf{x}_0)] f(\mathbf{x}_0), \quad (4)$$

where $f(\mathbf{x}_0)$ is yet to be determined.

For a sinusoidal surface it can be shown⁵ that the wave function above the surface is given by

$$\psi(\mathbf{r}) = \exp(-i\mathbf{k} \cdot \mathbf{r}) + \sum_{l=-\infty}^{\infty} S_l \exp(i\mathbf{k}_l \cdot \mathbf{r}), \quad (5)$$

where

$\exp(-i\mathbf{k} \cdot \mathbf{r})$ is the incident wave,

$\exp(+i\mathbf{k}_l \cdot \mathbf{r})$ are the diffraction beams,

with S_l given by

$$S_l = \sum_{n=-\infty}^{\infty} C_n J_{l-n}(hak \cos \theta_l), \quad (6)$$

where θ_l is the angle of the l th order diffraction, a is the lattice constant, h is the amplitude of the surface periodicity, and the coefficient C_n are determined by

$$\delta_{l,0} \cos \theta_l = \sum_{n=-\infty}^{\infty} C_n J_{n-l}(hak \cos \theta_l). \quad (7)$$

These calculations can be done essentially exactly. Some of the results are shown in Fig. 6. With increasing $\mathbf{k}$ vector, the scattering distribution changes from a specular to a rainbow pattern, in qualitative agreement with the semiclassical model previously discussed. Quantitatively, the calculations that have been done so far indicate excellent agreement (within $\sim 2\%$) between the exact calculations and the semiclassical ones.

In summary, the procedure at present is to assume a potential and calculate a scattering pattern, and then iterate on the potential until reasonable agreement with the experimental data is obtained. This procedure, while useful, suffers from the fact that it is not precise enough to define a completely unique morphology for the scattering potential. Scattering patterns at a single energy are not very sensitive to small changes in the interaction potential. By analogy to LEED and x-ray, more precision should be obtainable by examining the effect of energy of the incident beam on the scattering distributions. This has not yet been accomplished experimentally, but it can be done easily with the theory. Figure 7 is a calculated specular intensity as a function of increasing $\mathbf{k}$ vector for a relatively rough hardwell ($h=0.1$); but one where multiple scattering

FIG. 6. Quantum hardwall calculations of scattering at various energies, $h=0.02$, $\theta_I=0$.

FIG. 7. The intensity of the specular peak as a function of energy calculated by various methods:—exact quantum; $\times$ unnormalized semiclassical; $\times$ renormalized semiclassical, $\circ$ and $\diamond$ unnormalized semiclassical—given two symbols to emphasize the change in scale.

in the classical trajectories is negligible. The semiclassical ($\circ$, $\diamond$, and $\times$) and exact quantum results (solid line) are almost identical.

In the semiclassical formulation Bragg-like maxima from a sinusoidal hardwall are spaced according to the reciprocal of the amplitude of the surface periodicity h ,

$$k_B a = \frac{\pi}{2h} \left[n + \frac{1}{2} + \frac{(-1)^{l+1}}{4} \right], \quad (8)$$

where k_B is the k vector for a peak maximum. The surface is nearly kinematic, but the specular peaks ($l=0$) are shifted by an almost constant amount ($\pi/8ah$) in k space. An empirical "inner-potential" could be used to shift the high energy peaks to their kinematic positions, but this procedure fails at lower energies because the shift is constant in k space but not in E space. There is a slight additional shift evident at low energies which arises because the envelope of the Bragg maxima is decreasing very rapidly with energy. When this envelope is multiplied by the periodic portion of the scattering intensity, the peak maximum shifts downward in k space. For the case shown in Fig. 7 this shift is $\sim -0.5ka$ for the first of the Bragg maxima. This same effect is also responsible for a monotonic decrease in the peak intensities at high energies.

Equation (8) is derived from the semiclassical calculations and predicts the $\pi/8ha$ k shift for the specular beam. The shift arises from a factor, $\sqrt{i}$, which enters through the phase addition of two trajectories scattered from different regions of the potential.

ON DYNAMICAL LEED CALCULATIONS

The complex I - V spectrum for LEED results from the dynamical interference among scattered beams from an array of discrete scattering centers near the surface of a solid. The analogous spectrum for atom scattering from the hardwall (Fig. 7) is simple indeed by comparison, though similar spectra for more realistic potentials calculated via the semiclassical techniques are much more complex than Fig. 7.

From Fig. 7 it is clear that the semiclassical calculations do very well when $ka > 7$ or 8. For electrons this

corresponds to energies of 10–30 eV which is below the energies where reliable LEED data can normally be obtained experimentally and below the energies where most dynamical calculations have been attempted. It is also interesting to note that semiclassical calculations have been applied to electron scattering from gas-phase atoms. Above about 30 eV the experimental results are well represented.

These considerations suggest that dynamical LEED calculations may be possible using semiclassical techniques. The most lengthy portion of currently used calculations is determining the scattering within a single layer of atoms within the surface selvedge, and it is possible that semiclassical calculations can be applied to this portion of the problem. Of course the LEED scattering is far from elastic, yet most procedures represent the inelastic interactions by a constant optical potential. Such "potential scattering" can be handled within the semiclassical formalism.

One approach is to invert the phase shifts to a scattering pseudopotential, calculate deflection functions, and identify the pertinent stationary phase trajectories from the layer symmetry. These trajectories are then used to calculate the intralayer scattering. The sum over layers can be handled using current procedures.

Figure 8(a) shows an initial attempt at calculating a LEED I - V spectra using this procedure. The intensity of the specular beam is plotted, as a function of energy for scattering at normal incidence, from a stationary Ni(001) surface. This is a crude calculation in that only those trajectories that scatter once or start in the incident beam and scatter twice were included in the single-layer sum. The multilayer sum was done exactly using RFS perturbation theory.¹³ Five phase shifts were used.

In Fig. 8(b) are plotted the five phase-shift calculations of Kesmodal¹⁴ and in Fig. 8(c) are plotted the data of Anderson¹⁵ (at 300°K). Considering the limited multiple scattering which has been included in the semiclassical calculations, they have done remarkably well. All of the major peaks in the I - V spectrum appear in the calculations, although peak positions and relative peak intensities are not reproduced exactly. This is much better than one might have expected from such a simple calculation. At present the calculational procedures are being modified so that more of the intralayer multiple scattering can be included.

Considering the success of this relatively simple initial calculation, it would appear that semiclassical methods can be used to calculate LEED I - V spectra. Semiclassical methods have a twofold advantage over more conventional LEED calculations: first, they are computationally efficient; and second, they help to make the physics of the dominant features of the scattering more transparent. It may be the latter that will make the semiclassical methods the most useful. If, for example, key features of the I - V spectra can be

FIG. 8. The intensity of the specular beam as a function of energy for low-energy electron diffraction at normal incidence from Ni(100), normal incidence calculation, (a), (b) are for an optical potential of $14 + 3.6i$ V and 5 Wako phase shifts: (a) semiclassical calculations, stationary lattice; (b) quantum calculations of Kesmodal,¹⁴ stationary lattice; (c) data of Anderson,¹⁵ $T = 300$ K.

identified with relatively simple scattering trajectories such as singly or doubly scattered paths, then it may be possible to use such features to deduce structural parameters without reproducing the complete experi-

mental I - V spectra. Likewise, it seems probable that delineation of the dominant physics in the diffraction experiment may lead to more efficient averaging procedures and more useful transform methods than those which have been suggested so far.

CONCLUSION

The semiclassical theories can be used successfully for atom surface scattering calculations. They are in nearly quantitative agreement with exact calculations from a sinusoidal hardwall potential and represent experimental flux distributions very well indeed for thermal beams. The possibility of using the methods for dynamical LEED calculations is being investigated and a preliminary calculation for Ni(100) suggests the approach is promising.

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