Scattering by a hard corrugated wall: An exact solution

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We present an exact solution to Schrödinger's equation for the scattering of particles by a hard corrugated wall with a triangular corrugation profile. The solution is applied to the problem of scattering of low-energy atoms by a solid surface, and comparisons are made with the recent experimental data for scattering of helium by stepped copper surfaces. We also give a discussion of the convergence properties of the solution and a detailed comparison with the numerical method of Garcia and Cabrera.

I. INTRODUCTION

A theoretical model which has been extremely successful in interpreting the results of recent experiments on low-energy atom-surface scattering is the potential known as the corrugated hard wall. The interaction potential is taken to be zero in front of the surface and infinite behind, the surface itself being described by a periodic function, or "corrugation."

This problem was first considered by Rayleigh[1] in the context of acoustic waves using a method that is now known to converge only under special conditions. However, the Rayleigh method remains an extremely important technique in the case of scattering of electromagnetic waves.[2] More recently the corrugated-hard-wall potential has been used for solving the problem of scattering of low-energy neutral atoms by a solid surfaces.[3-6] Notably, the numerical calculations of Garcia and Cabrera have given remarkably good results in interpreting experimental data for widely differing surface conditions.[7-9] However, all of the above treatments are open to a certain number of criticisms either because they introduce "approximate" boundary conditions[3-7] or because the numerical procedure used does not necessarily assure that the boundary condition is satisfied on all points of the boundary zone.[8]

We present here a solution to this problem which is exact and free of objection, that is to say a solution which introduces in an analytical way the correct boundary condition. This method is applied to the case of a triangular profile corrugation and the numerical results are compared with the experimental data of Lapujoulade and Lejay[10] for a vicinal surface. We also make a comparison with the numerical method proposed recently by Garcia and Cabrera,[8,9] and the comparison allows us to answer the objections which have been raised against this procedure, at least for the case of this particular corrugation shape.

II. GENERAL SOLUTION OF THE SCATTERING BY A CORRUGATED-HARD-WALL POTENTIAL

The corrugated-hard-wall potential can be written

$$V(\vec{r}) = \begin{cases} 0, & z > \varphi(\vec{R}); \ \text{region I} \\ \infty, & z < \varphi(\vec{R}); \ \text{region II} \end{cases} \tag{1}$$

where we have written the position vector $\vec{r}$ as a component z perpendicular to the surface and a component $\vec{R}$ parallel, and $\varphi(\vec{R})$ is a periodic function describing the surface corrugation. The problem is to find the solution to Schrödinger's equation

$$[H_0 + V(\vec{r})]\psi_i(\vec{r}) = E\psi_i(\vec{r}) \tag{2}$$

which obeys the appropriate boundary conditions.

The general solution of Eq. (2) can be obtained by a variety of different approaches. In terms of the Green's function G_0 of H_0 (the Green's function of the Helmholtz equation) the wave function is given by[11]

$$\int_D \delta(\vec{r} - \vec{r}')\psi(\vec{r}')\, d\vec{r}' = \frac{1}{4\pi}\int_D G_0(\vec{r}, \vec{r}')\, V(\vec{r}')\psi(\vec{r}')\, d\vec{r}' - \frac{1}{4\pi}\int_S d\vec{S}\cdot[\psi(\vec{r}')\vec{\nabla}G_0(\vec{r}, \vec{r}') - G_0(\vec{r}, \vec{r}')\vec{\nabla}\psi(\vec{r}')], \tag{3}$$

where D is the volume enclosed by the surface S. If the volume of integration is considered to be the region I in front of the surface $[z > \varphi(R)]$ then $V = 0$ and the volume integral does not contribute, and the wave function is determined by the surface integral. One gets

$$\psi(\vec{r}) = \phi_i + \frac{1}{4\pi}\int_{S'} d\vec{S}\cdot[\psi(\vec{r}_s)\vec{\nabla}G_0(\vec{r}, \vec{r}_s) - G_0(\vec{r}, \vec{r}_s)\vec{\nabla}\psi(\vec{r}_s)], \quad \vec{r} \in \text{region I} \tag{4a}$$

and

$$0=\phi_i+\frac{1}{4\pi}\int_{S'} d\vec{S}\cdot[\psi(\vec{r}_s)\vec{\nabla}G_0(\vec{r},\vec{r}_s) - G_0(\vec{r},\vec{r}_s)\vec{\nabla}\psi(\vec{r}_s)]$$

$\vec{r}\in$ region II (4b)

with ϕ_i an eigenfunction of H_0, S' coincides with the surface corrugation, and $\vec{r}_s$ refers to a point on the surface.

On the other hand one may choose the volume in Eq. (3) to be all of space, in which case the surface integral equals ϕ_i and after writing the explicit form of the G_0 operator we are left with the usual integral equation for quantum scattering (sometimes referred to as the Lippmann-Schwinger equation)

$$\psi_i^{(+)}=\phi_i+\frac{1}{E_i-H_0+i\epsilon}V\psi_i^{(+)} . \quad (5)$$

Either approach leads directly to the same final form but for the results presented here we find it more convenient to use Eq. (5), which in terms of the eigenfunctions of H_0 becomes

$$\psi_i=\phi_i+\sum_l \phi_l\frac{1}{E_i-E_l+i\epsilon}T_{li} , \quad (6)$$

where T_{li} is the transition matrix

$$T_{li}=\int d\vec{r}\,\phi_l(\vec{r})V(\vec{r})\psi_i^{(+)}(\vec{r}) . \quad (7)$$

The convenience of this approach lies in the fact that the integral over z in Eq. (7) becomes trivially simple due to the fact that for this particular potential the product $V\psi$ is given by[5]

$$V\psi=e^{i\vec{K}_0\cdot\vec{R}}f(\vec{R})\delta(z-\varphi(\vec{R})) , \quad (8)$$

where the "source" function $f(\vec{R})$ is to be determined by application of the boundary condition on ψ at the surface. [We note that Eq. (8) says nothing about the value of the wave function on the surface.]

Putting (8) into (7) and (6) one gets after some calculation

$$\psi_i(\vec{r})=\exp(i\vec{K}_0\cdot\vec{R})\exp(-ik_{0z}z)-\sum_{\vec{G}}\frac{\exp[i(\vec{K}_0+\vec{G})\cdot\vec{R}]}{k_{Gz}}\int_{\text{u.c.}} d\vec{R}'\,F(\vec{R}')\exp(-i\vec{G}\cdot\vec{R}')\exp[ik_{Gz}|z-\varphi(\vec{R}')|] \quad (9)$$

a result which is valid whatever the $\vec{r}$ value may be. $\vec{K}_0$ and k_{0z} are, respectively, the parallel and perpendicular components of the particle incident wave vector, $\vec{G}$ is a surface reciprocal-lattic vector, and k_{Gz} is given by the energy conservation relation

$$k_{Gz}^2=K_0^2+k_{0z}^2-(\vec{K}_0+\vec{G})^2 .$$

One can see immediately that $\psi_i(\vec{r})$ has the correct asymptotic form in the region $z>\varphi_{\max}$, an incoming plane wave plus outgoing diffracted waves. The coefficients of the diffracted beams are given by

$$C_{\vec{G}}=\frac{1}{k_{Gz}}\int_{\text{u.c.}} d\vec{R}\,F(\vec{R})\exp(-i\vec{G}\cdot\vec{R})\exp[-ik_{Gz}\varphi(\vec{R})] . \quad (10)$$

The experimentally measured intensity is given by

$$I_G=(k_{Gz}/k_{0z})|C_{\vec{G}}|^2 . \quad (11)$$

The remaining problem is to apply the appropriate boundary conditions to ψ_i in order to determine the source function $F(\vec{R})$. In principle it appears that one should be able to determine $F(\vec{R})$ if the value of ψ_i is known for all $\vec{R}$ on any hypersurface given by $z=\zeta(\vec{R})$, but this choice is not indifferent with respect to the physical problem to be solved. In fact the ψ_i function given by Eq. (9) was obtained by introducing into the general scattering equation the condition (8) imposed by the physics of the particular problem at hand, that is to say the potential. This condition implies that the product $V\psi$ equals zero for z greater than or less than $\varphi(\vec{R})$. On the surface $[z=\varphi(\vec{R})]$ the product $V\psi$ is indefinite and consequently ψ is not specified there. Therefore it is necessary to use a boundary condition which states that the ψ function takes the value at the surface which is specified by the hard-wall potential, that is to say

$$\psi(\vec{R},z=\varphi(\vec{R}))=0 . \quad (12)$$

Now in order to be sure that this condition is sufficient it is necessary to prove that it imposes the correct behavior on ψ in regions I and II. We put condition (12) into Eqs. (4a) and (4b) and obtain

$$\psi(\vec{r})=\phi_i-\frac{1}{4\pi}\int_{S'} d\vec{S}\cdot G_0(\vec{r},\vec{r}_s)\vec{\nabla}\psi(\vec{r}_s) ,$$

$\vec{r}\in$ region I (13a)

$$0=\phi_i-\frac{1}{4\pi}\int_{S'} d\vec{S}\cdot G_0(\vec{r},\vec{r}_s)\vec{\nabla}\psi(\vec{r}_s) ,$$

$\vec{r}\in$ region II . (13b)

The two surface integrals in these equations will be of the same analytical form since G_0 depends on position only through the magnitude $|\vec{r}-\vec{r}_s|$. The calculation is carried out in Ref. 6 and the

result for these integrals is exactly the sum over reciprocal-lattice vectors of Eq. (9). Thus comparing (9) and (13) shows that the two give identical forms for the wave function, and furthermore it shows explicitly that the wave function of (9) vanishes if $\vec{r}$ lies in region II. This shows that the condition $\psi(\vec{R}, z = \varphi(\vec{R})) = 0$ is a sufficient as well as necessary condition on the wave function, and consequently this boundary condition will always give an exact solution to the problem of scattering by a hard-wall potential.

Applying condition (12) to the wave function of Eq. (9) gives an integral equation for the determination of $F(\vec{R})$

$$0 = \exp[-ik_{0z}\varphi(\vec{R})] - \sum_{\vec{G}} \frac{e^{i\vec{G}\cdot\vec{R}}}{k_{Gz}} \int_{\text{u.c.}} d\vec{R}'\, F(\vec{R}') e^{-i\vec{G}\cdot\vec{R}'} \exp[ik_{Gz}|\varphi(\vec{R}) - \varphi(\vec{R}')|] \,. \tag{14}$$

Other boundary conditions have been used leading to a much simpler integral equation than (14). In the so called Rayleigh method the expression of ψ_i in free space, that is to say for z greater than $\varphi_{\max}$, is assumed to be valid in the selvedge region ($\varphi_{\min} < z < \varphi_{\max}$) and set equal to zero on the surface. The solution obtained is known to converge only for a sinusoidal corrugation of small amplitude.[2] Another boundary condition is to force the wave function to be zero on an arbitrary plane lying inside the surface ($z < \varphi_{\min}$).[5] This is, of course, a necessary condition, but it is open to the possibility that it is not a sufficient condition to produce a convergent solution. In fact numerical difficulties have been encountered using this boundary condition for certain corrugation shapes and particularly for large corrugation amplitudes.[9,12] In any case these two boundary conditions may give a convergent solution in which case this must be the exact solution by the uniqueness theorem,[13] the only other alternative being that the solution does not converge at all. A contribution to the discussion of this problem will be given in another paper.[12]

III. EXACT CALCULATION: APPLICATION TO A TRIANGULAR PROFILE

For simplicity we choose to work with a one-dimensional surface corrugation $\varphi(\vec{R}) = \varphi(x)$ having a period of length a, however, the extension to a full two-dimensional corrugation is obvious. Rather than obtaining the source function directly it is more convenient to consider the Fourier transform.

$$F(x) = \sum_N F_N e^{iNx} \,, \tag{15}$$

where N is again a one-dimensional reciprocal-lattice vector ($N = 2\pi n/a$, $n = 0, \pm 1, \pm 2, \cdots$). In this case the boundary condition (14) and coefficient of the diffracted beam (10) become, respectively,

$$0 = \exp[-ik_{0z}\varphi(x)] - \sum_G \frac{e^{iGx}}{k_{Gz}} \sum_N F_N \int_{\text{u.c.}} dx'\, e^{i(N-G)x'} \exp[ik_{Gz}|\varphi(x) - \varphi(x')|] \tag{16}$$

with $G = 2\pi g/a$, $g = 0, \pm 1, \pm 2, \cdots$ and

$$C_G = \sum_N \frac{F_N}{k_{Gz}} \int_{\text{u.c.}} dx\, e^{i(N-G)x} \exp[-ik_{Gz}\varphi(x)] \,. \tag{17}$$

Taking the Fourier transform of Eq. (16) gives a system of linear equations, or otherwise stated, a matrix equation for the unknown column matrix F_N.

$$A_M(k_{0z}) = \sum_N F_N C_{NM} \,, \tag{18}$$

where $M = 2\pi m/a$ is a surface reciprocal-lattice vector,

$$A_M(q) = \int_{\text{u.c.}} dx \exp[-iMx - iq\varphi(x)] \tag{19}$$

and

$$C_{NM} = \sum_G \frac{1}{k_{Gz}} \int_{\text{u.c.}} dx\, e^{i(G-M)x} \times \int_{\text{u.c.}} dx'\, e^{i(N-G)x'} \times \exp[ik_{Gz}|\varphi(x) - \varphi(x')|] \,. \tag{20}$$

The coefficient $C_{\vec{G}}$ of the diffracted beam intensity is given by

$$C_G = \sum_N \frac{F_N}{k_{Gz}} A_{G-N}(k_{Gz}) \,, \tag{21}$$

where $A_P(k)$ is given by Eq. (19). For the case of an arbitrary corrugation function $\varphi(x)$, it is the double integral of Eq. (20) which is difficult to handle. However, for a corrugation profile consisting only of straight lines all of the integrals are relatively straightforward. In particular for the triangular profile of Fig. 1, defined by

$$\varphi(x)=\begin{cases}2hax/b; & 0<x<b\\ 2ha(a-x)/(a-b); & b<x<a\end{cases} \tag{22}$$

(where $2ha$ is the corrugation height and $x=b$ is the position of the triangle vertex) the integration is straightforward.

Before discussing the results of the calculations it is important to consider the convergence properties of the formalism, because at first glance the matrices involved have some rather interesting properties. Formally, we can write the solution to Eq. (18) for the coefficients F_N as

$$F_N=\sum_M C^{-1}_{NM}A_M(k_{0z})\ . \tag{23}$$

However, one can show readily that the inverse matrix C^{-1}_{NM} is not defined, in the sense that for M large the elements are proportional to M. Nevertheless, the Fourier coefficients F_N and the experimentally important quantities C_G always remain well defined.

To explain this behavior we have to look first at the matrix element C_{NM} given by

$$C_{NM}=\frac{-2ha^3\alpha}{(2\pi)^3(\alpha^2+4h^2)}\left(\frac{[n(\varphi-\beta)+\gamma-\beta\varphi]\sinh 2\pi\omega-\omega(n-\varphi)\sin 2\pi\beta}{\omega(\varphi^2-2\beta\varphi+\gamma)(\cosh 2\pi\omega-\cos 2\pi\beta)(n-m)}\right)+\text{same term replacing } \alpha \text{ by } (1-\alpha)$$
$$+4h^2a^4\sum_{G=-\infty}^{+\infty}k_{Gz}[F(b)(e^{i(N-M)b}-\exp\{i[(N+G)b+2k_{Gz}ha]\})-F(a-b)(\exp\{-i[(M+G)b-2k_{Gz}ha]\}-1)] \tag{24}$$

with

$$\alpha=\frac{b}{a},\quad \beta=\frac{n\alpha^2+4h^2K_i\sin\theta_i}{\alpha^2+4h^2},$$
$$\gamma=\frac{n^2\alpha^2-4h^2K_i^2\cos^2\theta_i}{\alpha^2+4h^2},$$

$K_i=(a/2\pi)(K_0^2+k_{0z}^2)^{1/2}$, and θ_i is the incident angle. In addition

$$\varphi=m(1-\alpha)+n\alpha,\quad \omega=(\gamma-\beta^2)^{1/2},$$

and

$$F(b)=\{[(N+G)(a-b)-2k_{Gz}ha][(N+G)b+2k_{Gz}ha]$$
$$\times[(M+G)(a-b)-2k_{Gz}ha][(M+G)b+2k_{Gz}ha]\}^{-1}\ .$$

For large values of $|N|$ or $|M|$ with $N\neq M$ one can see that the two first terms go to zero as $[N(N-M)]^{-1}$ or $[M(N-M)]^{-1}$. One can show that the remaining sum over G behaves in the same way. However, for the diagonal term C_{NN}, the leading part of which being equal to

$$\frac{2a^2\alpha^2}{(2\pi)^2(\alpha^2+4h^2)}\frac{\pi\sinh 2\pi\omega}{\omega(\cosh 2\pi\omega-\cos 2\pi\beta)}$$
$$+\text{same term replacing } \alpha \text{ by } (1-\alpha)$$

clearly goes to zero as N^{-1} for large $|N|$.

Thus in the limit $|N|$ or $|M|$ large the only important matrix elements are the diagonal terms C_{NN} which become smaller as $1/N$. Consequently in the same limit the only important elements of the inverse C^{-1}_{NM} are the diagonal terms which are proportional to N. In other words the matrix C_{NM} can be thought of as composed of submatrices, where the submatrices of elements with large index values approach either null matrices or diagonal form, with diagonal elements falling off as $1/N$. The inverse C^{-1}_{NM} is then of the same form where for large index values the submatrices are either null or diagonal, with the diagonal elements proportional to N. Thus for $|N|$ very large Eq. (23) becomes

$$F_N=C^{-1}_{NN}A_N(k_{0z})\ .$$

On the other hand Eq. (19) gives

$$A_N(q)=\frac{2iha^2q\{\exp[-i(Nb+2qha)]-1\}}{(Nb+2qha)[N(a-b)-2qha]} \tag{25}$$

showing that $A_N(k_{0z})$ varies as N^{-2} for large $|N|$. Consequently, in spite of the fact that C^{-1}_{NN} grows as $|N|\to\infty$, the coefficients F_N decrease as N^{-1} and are well defined. Furthermore Eq. (25) indicates that $A_{G-N}(k_{Gz})$ varies also as N^{-2} in the same limit. Thus the summand in Eq. (21) giving

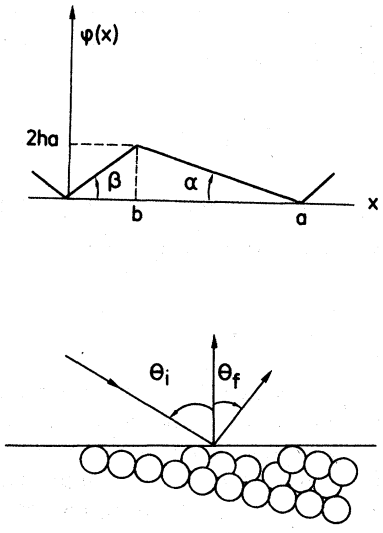

FIG. 1. Triangular corrugation profile as defined by Eq. (22).

the C_G coefficients varies as N^{-3} and the convergence of this summation is very rapid.

Finally we note one other apparent difficulty with C_G that appears as $|G|$ becomes large. In this limit k_{Gz} is imaginary (corresponding to an evanescent wave) and approaches iG, thus from the form of $A_{G-N}(k_{Gz})$ of Eq. (25) we see that the coefficients C_G grow as e^{+2Gha}. However, this is not a difficulty at all, because in the asymptotic wave function [see Eq. (9)] this term is always multiplied by the corresponding evanescent plane wave, i.e.,

$$e^{ik_{Gz}z}C_G \to e^{-Gz}e^{+2Gha}; \quad z \geq 2ha \ .$$

This is the expected behavior for an evanescent wave, it is of finite amplitude near the surface but is rapidly damped.

IV. NUMERICAL RESULTS OF EXACT CALCULATIONS

We have carried out calcluations using the results of Sec. III for a number of different systems to check the various aspects of the method, and we have made a comparison with the experimental results of Lapujoulade and Lejay[10] on stepped copper surfaces. A comparison with the numerical method of Garcia is discussed in Sec. V.

The approach is to convert the infinite system of Eq. (18) into a finite matrix equation by truncation at a dimension large enough to insure good convergence. The internal summation over G in (20) is carried over a sufficient number of terms to obtain the desired accuracy for the elements C_{NM}. The matrix is inverted to find the F_N according to (23) and the diffraction coefficients are then calculated from (21).

In general we find that the method converges for all values of the parameters a, h, and b $(b \neq 0, a)$. By "convergence" we mean that the individual diffracted intensities are stable and the sum of all intensities (commonly referred to as the "unitarity") equals 1. It is always found that the individual intensities are quite stable under conditions of good unitarity. For values of $h \gtrsim 1$ we find that the result converges quickly when the total number of source function Fourier components considered [i.e., the dimension of the truncated matrix of Eq. (18)] is only slightly larger than the number of diffracted beams. We find that the internal sum in the matrix C_{NM} [the sum over G in Eq. (20)] is important in obtaining good unitarity and this is handled either by taking a number of terms in the summation which is approximately twice the dimension of the matrix, or by cutting off the summation when the terms become very small. In all cases the results give the correct specular scattering behavior in the limit of small corrugation amplitudes.

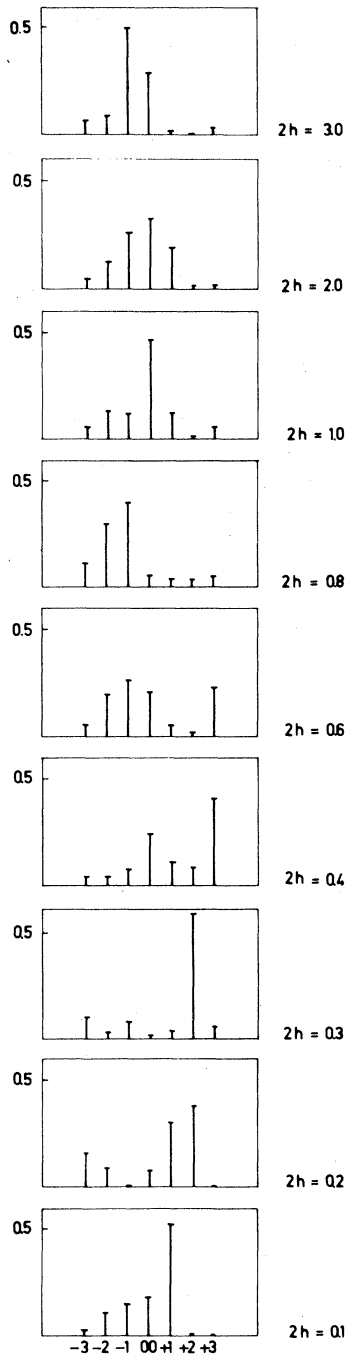

FIG. 2. Diffracted intensities from a triangular corrugation profile for various values of h, $\theta_i = 0$ (perpendicular incidence), $k_0 a = 21.18$, and $b = 0.75a$. In all cases the unitarity is better than 0.999.

Shown in Fig. 2 are a number of calculations for different values of the corrugation height h carried out for helium perpendicularly incident

on a surface under conditions which produce seven diffracted beams. For this system k_0a, the product of the corrugation period and the incident wave vector is 21.18, and b, the position of the triangle vertex, is $0.75a$. In all of the cases the unitarity sum is better than 0.999.

It is seen that for small values of h (height of the corrugation small compared to the period) the diffraction intensities follow the typical quantum mechanical rainbow pattern.[4] (The classical rainbow angles are the angles of specular scattering from the flat portions of the surface, thus this model exhibits two distinctly different classical rainbow angles, even with perpendicular incidence.) It is interesting to note that for very strong corrugations $2h \gtrsim 1.0$, where the classical rainbow picture becomes much more complicated, there is still a large variation in the relative peak intensities but the scattering seems to be strongly in the forward, or specular direction. This is the region where clearly multiple scattering is extremely important and is a very good test of the convergence properties of the method.

A more definitive test is the comparison with the experimental results of Lapujoulade and Lejay for the scattering of helium at stepped copper surfaces.[10] The experiments were carried out using the (117) face of the copper which consists of (100) terraces separated by linear steps parallel to the [110] direction. Figure 1 shows the triangular corrugation which we have used to approximate the experimental situation. The period is 9.13 Å and the angle α is 11.25° [α is the angle between the plane of the (117) surface and the (100) terraces]. The angle β, which is the angle of the steps, is not determined *a priori* and thus we regard it as a parameter. Figures 3 and 4 show the comparison with the data at an incidence angle of 60° for $\beta = 20°$ and $\beta = 22°$. There is surprisingly good agreement with the data especially for $\beta = 20°$. The strong rainbow at $\theta_f \simeq 82°$ [corresponding to classical specular scattering from the (100) terraces], the rainbow centered at $\theta_f \simeq 20°$ (due to scattering from the step face), and the secondary rainbow due to multiple scattering centered around $\theta_f \simeq 50°$ are all in agreement with the calculations. With the exception of diffraction orders −10 and −6 the calculated intensities are about twice the experimental values which is consistent with the fact that the calculations always exhibit unitarity but the sum of the experimental intensities is only 0.568 after correction for the Debye-Waller effect.[10] This agreement is more striking when one realizes that the behavior of approximately ten experimental peak intensities has been matched with a theory having only one adjustable parameter, namely, the angle β.

The calculation shown in Fig. 4 for $\beta = 22°$ is also very interesting. The general pattern is quite

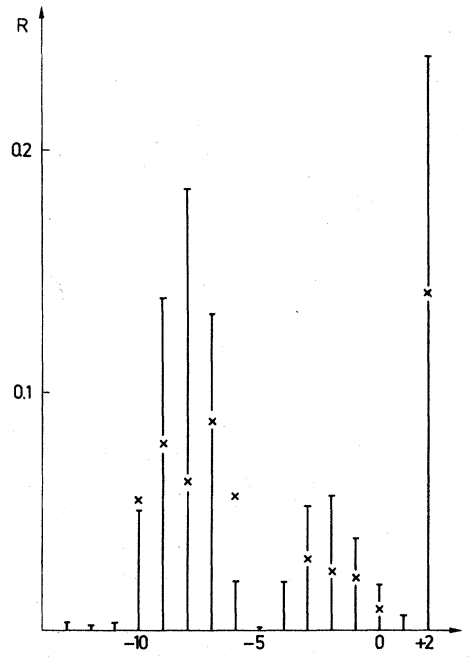

FIG. 3. Comparison with the experimental results of Lapujoulade and Lejay using the triangular corrugation profile with $a = 9.13$ Å, $\alpha = 11.25°$, $\beta = 20°$, $k_0 = 1.1 \times 10^9\ \mathrm{cm}^{-1}$, and $\theta_i = 60°$. The unitarity is 0.998. The experimental points are denoted by ×.

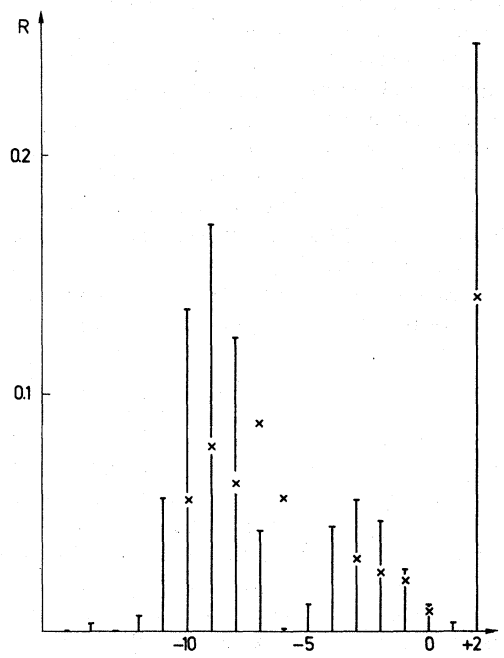

FIG. 4. Same as Fig. 3 except $\beta = 22°$. The unitarity is 1.000.

similar to the case for $\beta = 20°$ except that the rainbow pattern associated with the step face and the secondary rainbow are shifted by about 4° (approximately by one reciprocal-lattice vector) towards the normal direction. This is consistent with the fact that a change $\delta\beta$ in the angle of the surface will cause a change $\delta\theta_f = 2\delta\beta$ in the classical rainbow angle. This ability to detect subtle differences in surface structure is an example of the sensitivity of the experimental technique of atom surface scattering, and indicates how powerful this tool should become as a method for determining surface information.

Lapujoulade and Garcia have recently used the corrugated-hard-wall model to explain the scattering of the same He-Cu system for all angles of incidence[14] using the numerical method that is not limited to triangular corrugations.[8] They find that the best agreement with all the data is obtained for a corrugation which is basically triangular having $\beta = 22°$ and with the addition of rounding at the sharp points ($x = 0, b$ in Fig. 1) and a slight shoulder at the peak of the step ($x = b$ in Fig. 1). (The shoulder possibly corresponds to a combination of a slight outward relaxation of the edge atoms with the Friedel oscillations of the electrons.) However, it should be mentioned that their agreement for large angles of incidence ($\theta_i \geq 60°$) is no better than that discussed above in Figs. 3 and 4. Even if the Lapujoulade and Garcia model seems to be the more probable from a physical viewpoint, more precise experimental data are needed in order to define without ambiguity the surface potential shape.

V. COMPARISON WITH THE METHOD OF GARCIA AND CABRERA

The Garcia and Cabrera method,[8] which is a completely numerical way of solving for the source function in Eq. (14), has up to now been used only for the case of one-dimensional corrugations. It consists in dividing the unit cell of length a into $2N$ intervals of equal length and then replacing the integral over x of Eq. (14) by a finite summation over the $2N$ intervals of this grid. Equation (14) is then converted into a system of linear algebraic equations by evaluating it at each point on a second identical grid of elements denoted by $2N'$. That is to say the ψ function is forced to zero at a set of $2N'$ points $x = x_{n'}$, $z = \varphi(x_{n'})$ as follows:

$$0 = \exp[-ik_{0z}\varphi(x_{n'})] - \frac{a}{2N}\sum_{G}\frac{\exp(iGx_{n'})}{k_{Gz}}\sum_{n=-N}^{N} F(x_n)e^{-iGx_n}\exp[ik_{Gz}|\varphi(x_{n'}) - \varphi(x_n)|]\,. \tag{26}$$

This system is inverted to obtain the $F(x_n)$ values and then the reflection coefficients are calculated by numerical integration of the one-dimensional form of Eq. (10). The number $N = N'$ is taken sufficiently large to satisfy the condition of unitarity.

In spite of its success in explaining experimental data the Garcia-Cabrera method [called the NN' method because of the form of Eq. (26)] has been criticized on a number of points. One of the most important objections is that it is a rather complex numerical procedure and is open to the possibility of a variety of systematic errors. Secondly, since the wave function is forced to zero at only a finite number of points on the surface there is possibly some penetration of the wave function into the solid. An effect of this sort could lead to results which still obey the condition of unitarity but do not give the correct diffracted intensities.

Both of these objections, at least in the case of a triangular corrugation, seem to be clearly answered by the work presented here. We have made numerous comparisons of the present method with the calculations of NN' and in every case the values of the diffracted intensities are identical within the limits of the unitarity defect.

A comparison of the two methods for the seven diffracted beam system of Fig. 2 is given in Table I. The first two columns show that the results of the two methods are almost exactly the same with the slight differences being explained by the unitarity defect. A distinct advantage of the exact method is that it can produce results which converge to very good unitarity with a substantially smaller matrix than the NN' approach. (However, it should be remembered that the two matrix dimensions are not exactly equivalent. In the exact case the dimension N is the number of Fourier components of the source function retained, while in the NN' formalism the dimension $2N$ is the number of intervals into which the unit cell is divided.) From Table I, we see that results equivalent to the NN' method with dimension $2N = 100$ are obtained using the present approach with only 15 Fourier components of the source function, while substantially better results are obtained with 25 components.

For comparison the NN' calculation of dimension $2N = 16$ gives unitarity of only 0.998, while the exact method gives a comparable unitarity of 0.999 with only 9 Fourier components. It is interesting to note that the present method still gives good results for small h even if only a small number of Fourier components are calculated (that is to say, the dimension of the matrix to be

TABLE I. Exact solution and comparison with the Garcia–Cabrera (NN') method for the triangular profile with $k_0a = 21.18$, $h = 0.1$, and $b = 0.75a$. For the exact calculation N is the dimension of the matrix and $2G$ is the number of terms kept in the intermediate sum over G in Eq. (24). For the NN' method $2N$ is the dimension of the matrix.

Order	$N=25$ $G=500$	$N=25$ $G=200$	$N=15$	$N=9$	$N=7$	NN' method $2N=100$	NN' method $2N=16$
−3	0.00377	0.00377	0.00367	0.00424	0.00505	0.00377	0.00657
−2	0.37950	0.37935	0.37913	0.38844	0.39481	0.37936	0.40842
−1	0.29592	0.29614	0.29635	0.28820	0.28105	0.29599	0.27302
0	0.07416	0.07418	0.07467	0.07221	0.06744	0.07409	0.07004
1	0.00443	0.00444	0.00443	0.00436	0.00376	0.00441	0.00737
2	0.08604	0.08597	0.08584	0.07797	0.06273	0.08616	0.07449
3	0.15619	0.15614	0.15586	0.16354	0.17034	0.15620	0.15836
Total (unitarity)	0.99999	0.99998	0.99996	0.99896	0.98427	0.99998	0.99828

inverted is small). For the model of Table I the unitarity with 7 Fourier components (the same as the number of diffracted beams) is 0.98. This may be an advantage if one wishes to calculate the diffracted peak intensities from a two-dimensional corrugated surface.

Another objection to the NN' method is that the infinite sum over reciprocal-lattice vectors G in Eq. (26) is restricted to roughly not greater than $2N$ terms. The reason for this is clear, for larger values of G the exponential e^{iGx} oscillates rapidly and cannot be considered a slowly varying function over the interval $a/2N = \Delta x$. In practice if one arbitrarily extends the summation over G to larger values of G the convergence of the solution becomes progressively worse. On the other hand, with the calculations presented here the integration is carried out exactly and the corresponding intermediate sum over G in Eq. (20) can be extended indefinitely and the unitarity continues to become better and better.

Considering further the question of the intermediate summation over G in Eq. (26) there is an apparent divergence which arises in the Garcia-Cabrera method when $x_n = x_{n'}$. In this situation the sum becomes $\sum_G 1/k_{Gz}$ which is undefined if the sum is carried out over the infinite set of reciprocal-lattice vectors, and special care must be taken to avoid the problem.[9] Again we note that this problem does not exist in the present calculation.

The final comparison we would like to make concerns the interesting question of what happens to the solution when there is a discontinuity in the corrugation profile. Such a situation arises with the triangular profile in the limit $b/a \to 0$ or $b/a \to 1$, which gives a profile in the form of a sawtooth wave. Clearly the Garcia-Cabrera method fails in this limit because it depends on the assumption that the surface profile varies slowly over the interval $\Delta x = a/2N$, thus the wave function is not forced to equal zero on the vertical part of the profile. A similar problem arises with the exact method presented here. One can not arbitrarily set $b/a = 1$ in Eq. (24) to obtain the sawtooth limit, in fact a simple form for the limit does not exist. The explanation comes from regarding the sums over N and G appearing in (18) and (20). Since the sums range over all reciprocal-lattice vectors from $-\infty$ to $+\infty$ one can never regard terms such as $G(a-b)$ or $N(a-b)$ (in the limit $b \to a$) as small. Thus for values of b/a near unity the dimensions of the matrix C_{NM} as well as the sum over G must be increased to values that go well beyond the minima which always appear in the denominator of F of Eq. (24). This result is borne out by the calculations; for the simple system as in Fig. 2, but with $h = 0.01$ and $b/a = 0.99$ the unitarity is only 0.94 if the matrix dimension is 25, but the unitarity is 0.99 if the dimension is increased to 95.

We should mention here that the problem of vertical components ($b = a$) in the surface profile has recently been solved using a method which replaces the integrals over x in (16) and (17) by integrals over z, the direction perpendicular to the surface. With this method the vanishing of the wave function on the vertical portion of the profile is assured and well defined equations for the diffracted intensities are obtained.[15]

VI. CONCLUSIONS

We have given here an exact analytical solution (in the sense that all integrals have been evaluated exactly) to the problem of the scattering of a plane wave from a hard corrugated surface with a triangular profile. The diffracted intensities are found in terms of solutions to an infinite matrix

equation. In practice the matrix is truncated at a finite dimension and inverted to obtain the final results. The solution converges very rapidly as the dimension of the matrix is increased (that is to say the intensities of the diffracted beams become stable and the sum approaches unity) and the convergence becomes better and better even if the matrix is made very large. We have made a comparison with the experimental data for the scattering of helium atoms at a stepped copper surface and the agreement is surprisingly good. The rainbow patterns are in the correct positions and the intensities are in quite reasonable agreement if one takes into consideration the unitarity deficit of the experimental data.

We have made a number of comparison between the Garcia and Cabrera[8] method (called *NN'*) and the exact calculation and in every case the results agree to within the unitarity deficit. This seems to indicate that the objections raised against the *NN'* method (which involve questions of systematic numerical errors and cancellation of the wave function at the surface boundary) are not important, at least in the case of the triangular corrugation. However, this should be a rather good test of the method because the triangular profile has two sharp points (the peaks of the triangle) and it is well known that solutions to Schrödinger's equation converge slowly near such structures.

This is an important result because the *NN'* method is a much more flexible approach as it can be easily applied to a wide range of surface profiles, while the present work is a limited to profiles for which the relevant integral can be carried out (and, in fact, calculations have only been presented for the triangular profile).

Finally we note that the analysis presented here together with the comparison with the experimental data show that the corrugated-hard-wall model and the experimental technique of atom-solid scattering have the potential of becoming very powerful tools for the examination of surface properties.

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