AN ITERATIVE SOLUTION TO THE SURFACE SCATTERING PROBLEM: APPLICATION TO He DIFFRACTION BY Cu

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ABSTRACT

We present a method for calculating the diffraction intensities in low energy atom-surface scattering which is based on Neuman iteration of the scattering equations. Comparisons of calculations using a corrugated Morse potential to new experimental data for He scattered by several Cu crystal faces gives good agreement and shows that the softness of the repulsive part of the potential is very important in He-metal interactions.

Since the early days of quantum mechanics it has been recognized that low energy atoms and molecules would be excellent projectiles for studying surface structure[1]. The wavelengths of light thermal energy atoms are approximately of the same dimension as the interatomic crystal spacing and because of the strong repulsive barrier there is little or no distortion of the crystal structure, hence only the outer surface layer is sampled. Before 1970, progress in this field was relatively slow due to the experimental difficulties, particularly with obtaining clean surfaces. However, with the advent of large and efficient vacuum systems together with molecular jet beams substantial experimental progress was begun[2] and appropriate theoretical methods were developed[3]. In recent years this type of experiment has become a well established tool for determining surfaces structure, and even more recently, surface phonon distributions[1].

In the interpretation of experimental data a very useful, even if somewhat oversimplified theoretical model has been to consider the interaction potential to consist of a hard corrugated

wall with an attractive potential in front corresponding to the adsorption well. This corrugated hard wall model can be represented by:

$$V(\underline{r}) = \begin{cases} \infty \; ; \; z < \phi(\underline{R}) \\ V(\underline{R},z) \; ; \; z > \phi(\underline{R}) \end{cases} \tag{1}$$

where z is the direction perpendicular to the surface and $\underline{R}$ is a vector lying in the surface. The function $\phi(\underline{R})$ gives the corrugation of the hard wall and $V(\underline{R},z)$ (which is usually taken to be independent of $\underline{R}$) is chosen to have the correct asymptotic behavior and to have bound state energies which agree with observed resonance behavior.

In this paper we wish to demonstrate an efficient and useful way of treating realistic potentials (particularly those potentials with soft repulsive parts) in the surface scattering problem. We also present new experimental data for the scattering of He by stepped Cu surfaces and the comparison with the present theory gives a far better agreement than can be obtained using the simple hard corrugated wall.

Potentials more realistic than (1) have been treated exactly by direct integration of the Schrödinger equation (coupled channel calculations)[1] but this method has definite limitations due to the computer time involved. The theoretical method described here is an iterative approach which is, in essence, exact and adapted to virtually all realistic potentials. Good convergence is obtained even under conditions of resonance with a bound state by using projection techniques. The calculations presented for the He-Cu systems are carried out using a corrugated Morse potential and they reproduce very well the data for scattering of He by a stepped Cu surface over a large range of incident beam angles[4].

The theory is based on the two potential formalism of scattering theory in which the potential is divided into two parts $V(\underline{r}) = U + v$. Then the scattered intensities are readily obtained from the distorted wave transition matrix t_{fi} which obeys the equation

$$t_{fi} = v_{fi} + \sum_{\ell} v_{f\ell}(E_i - E_\ell + i\varepsilon)^{-1} t_{\ell i} \tag{2}$$

where the v_{pq} are matrix elements of v taken with respect to eigenstates of U. Normally, in obtaining eq. (2) one has to be careful in defining the difference between outgoing and incoming wave solutions to $V(\underline{r})$ and U. However, in the surface scattering problem such questions are trivial, the difference between an outgoing and incoming solution of U is simply a phase factor equivalent to the

S-matrix for specular scattering. If $\underline{G}$ is a reciprocal lattice vector of the surface, then the perpendicular component of the wave vector associated with the Gth diffracted beam is $k_{Gz} = [k_o^2 - (\underline{K}_o + \underline{G})^2]^{1/2}$ where $\underline{k}_o = (\underline{K}_o, k_{oz})$ is the incident wave vector with components $\underline{K}_o$ and k_{oz} parallel and perpendicular to the surface, respectively. The diffracted intensities are given by

$$I_G = \left|\delta_{\underline{G}o} - i\, m\, t_{\underline{G}k_{Gz};i}/\hbar^2\sqrt{k_{Gz}\, k_{oz}}\right|^2 \tag{3}$$

where m is the particle mass.

We solve for t_{fi} by repeated Neumann iteration of eq. (2), a process that is completely equivalent to distorted wave perturbation theory carried out to high order. The usual choice for the distorted potential U in eq. (2) is the surface average of $V(\underline{r})$ but there are many other possibilities. For example, substantial improvements in convergence can be obtained by taking a U which is displaced with respect to the surface average or has a different well depth[5].

For incident angles and energies near conditions of resonance with a surface bound state the convergence of the iterative process is limited by singularities arising from the bound state denominators in the discrete part of the sum in eq. (2). These difficulties can be circumvented by simple projection techniques. Formally, eq. (2) is the operator relation $t = v + vGt$. We can write $G = G_1 + G_2$ and then it is simple to show that the transition operator is given by the pair of equations $t = h + hG_1t$ and $h = v + vG_2h$, or in matrix element form

$$t_{fi} = h_{fi} + \sum_b{}' \, h_{fb}(E_i - E_b)^{-1} t_{bi} \tag{4}$$

$$h_{fi} = v_{fi} + \sum_\ell{}' \, v_{f\ell}(E_i - E_\ell + i\varepsilon)^{-1} h_{\ell i} \tag{5}$$

If we place all resonant terms in G_1 then the singular denominators do not appear in the sum in eq. (5) for h_{fi}, thus the h-matrix is still amenable to an iterative solution. The t-matrix is subsequently obtained from eq. (4) by inversion of a small matrix involving only the resonant bound states.

As a specific example, for a simple resonance involving only a single bound state b, the transition matrix is of the form

$$t_{fi} = h_{fi} + h_{fb}\, h_{bi}/(E_i - E_b - h_{bb}) \tag{6}$$

It is clear from the presence of the term h_{bb} in the denominator, that the resonance associated with the kinematical condition

$E_i = E_b$ no longer gives rise to a divergence, but is shifted in energy by Re h_{bb} and has a linewidth determined by Im h_{bb}. If (6) is inserted in the diffracted beam intensity (3), we obtain the standard form

$$I_G = |A|^2 \, |1 - i\, b/(x - i)|^2 \tag{7}$$

where the explicit values of A, b and x are obvious. By examination of this form, the signatures of the resonances can be characterized as a function of incident energy E_i or incident angle θ_i[6]. In general if b is complex the resonance as a function of E_i or θ_i will have two extrema, a minimum and a maximum. If b is real, or nearly so, one of the extrema disappears and the resonance is of Lorentzian form, a minimum if $-2 \leq b \leq 0$ and a maximum otherwise. An important advantage of this projection method is that generally in eq. (7) A and b are slowly varying and only the variation in the normalized energy difference x is important. Then, to a very good approximation, the whole resonance can be mapped out by calculating A and b at a single point near the resonance and then considering I_G to be a function of x alone. (Even in the case of multiple or simultaneous resonances the entire resonance region can be mapped out in a very similar manner.)

We have carried out a series of numerical calculations using the corrugated Morse potential defined by

$$V(\underline{r}) = D\{\exp[2\kappa(\phi(\underline{R}) - z)]/v_o - 2\exp[-\kappa z]\} \tag{8}$$

where v_o is the surface average of $\exp[2\kappa\,\phi(\underline{R})]$. The surface average of (8) is then a Morse potential and the perturbing potential v can be expressed as a Fourier series

$$v(\underline{R},z) = \sum_{\underline{G} \neq 0} v_{\underline{G}}\, e^{i\,\underline{G}\cdot\underline{R}}\, e^{-2\kappa z} \tag{9}$$

with

$$v_G = \frac{1}{S}\int_{u.c.} d\underline{R}\; e^{-i\,\underline{G}\cdot\underline{R}}\, e^{2\kappa\,\phi(\underline{R})} \tag{10}$$

Since the matrix elements of $\exp(-2\kappa z)$ with respect to Morse potential eigenstates are well known the matrix elements v_{fi} of (9) which appear on eqs. (2) and (5) can be calculated analytically.

Figure 1 gives the results of a typical calculation and is for the case of a 63 meV He beam scattered by the (110) surface of Cu. The Morse potential parameters are $\kappa = 1.05\ A^{-1}$ and D = 6.35 meV and the corrugation function is a one dimensional sinusoid $\phi(x) = ha\cos(2\pi x/a)$ with a = 3.6 Å and h = 0.012. The experimental

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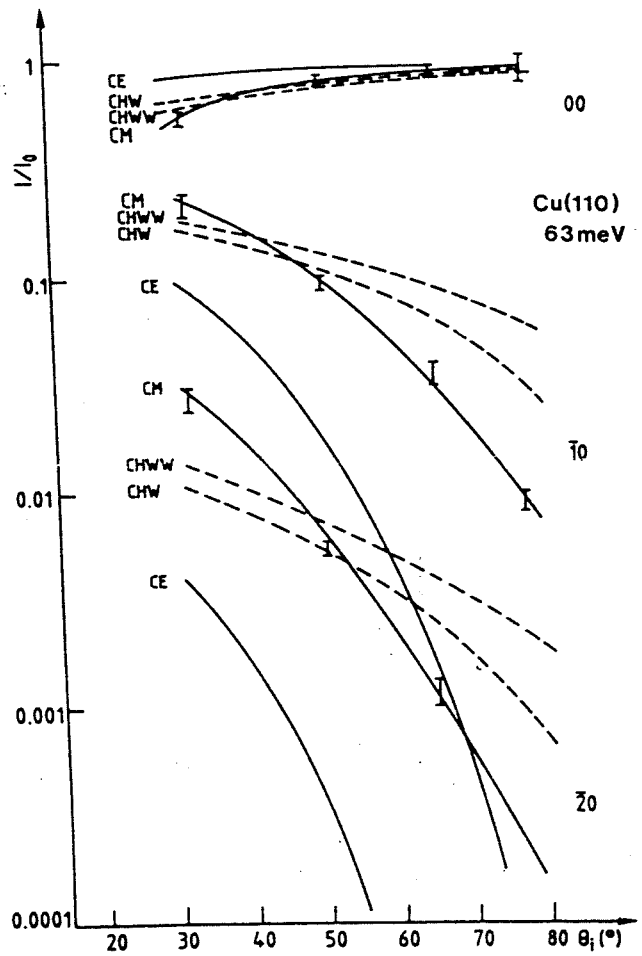

Fig. 1. Comparison between the experimental data and four theoretical models for the scattering of 63 meV He by a Cu(110) surface: CHW, corrugated hardwall with corrugation parameter h = 0.013; CHWW, corrugated hard wall with well, h = 0.013 and well depth 6.35 meV; CE, corrugated exponential, h = 0.012, κ = 1.05 $Å^{-1}$; CM, corrugated Morse potential, h = 0.012, κ = 1.05 $Å^{-1}$ and D = 6.35 meV. The incident plane contains the 100 direction.

data shown with error bars are obtained by extrapolation to zero temperature[4] and renormalizing the sum of the inplane diffraction intensities to unity. The renormalization is carried out in order to eliminate the effects of out-of-plane diffraction in the comparison with the one-dimensional calculations. The data are compared with four different models, the corrugated hard wall, the corrugated hard wall with an attractive well, a repulsive corrugated

exponential potential, and the corrugated Morse potential of eq. (8). It is seen from this and numerous other calculations that the corrugated Morse potential agrees with the data over a large range of incident beam energies, while the other potentials (and in particular the hard wall models) cannot give adequate agreement for the diffracted peak intensities even if they are reasonably good for the specular peak.

Equally good agreement is found for the same experiment as in Fig. 1 but with an incident energy of 21 meV. The only adjustment that must be made is to decrease the corrugation parameter h to a value of 0.008 for the Morse potential calculation. This decrease in corrugation is in agreement with recent theoretical predictions indicating that the corrugation is given directly by the electron density[7]. More recent calculations using a modification of the corrugated Morse potential which incorporates the increase in corrugation amplitude with energy are in excellent agreement with experiment at energies from 21 meV to 240 meV[8].

No resonances were observed experimentally for the He/Cu(110) system and this is consistent with the calculations which showed that the resonances would have widths of only a few hundredths of a degree in θ_i, i.e., they are far too narrow to be seen with the current experimental precision. Clear resonance behavior was seen on the (113), (115) and (117) faces[9] and all three are consistent with bound states of energies -4.5 meV, -2.2 meV, -0.95 meV, and -0.35 meV. Since the same bound states were observed for all three of the different strongly stepped surfaces, it appears evident that the adsorption well is essentially the same for all faces of Cu.

Figure 2B shows for He/Cu(113) the behavior of the specular beam in the neighborhood of the resonance of the (10) reciprocal lattice vector with the lowest (n = 0) bound state at an energy of 21 meV. Calculations with a one dimensional corrugation give a narrow maximum instead of the broad experimentally observed minimum. Because the resonance couples strongly only with the specular this corresponds to eq. (7) with $-b \gtrsim 2$. The value of Re b can be reduced by adding more diffraction channels out of plane that couple with the resonance. Hence Fig. 2A is calculated with the following corrugation function corresponding to the two dimensional unit cell in the form of a parallogram:

$$\phi(x,y) = a\{h_{10} \cos(2\pi x/a) + h_{01} \cos(\pi x/a) \cos(2\pi y/a) + h_{11} \cos(3\pi x/a) \cos(2\pi y/a) - C_{01} \sin(\pi x/a) \cos(2\pi y/b)\} \quad (11)$$

with x and y rectangular coordinates, a = 4.227 Å is the distance between steps, and b = -2.55 Å is the nearest neighbor distance. The corrugation coefficients are $h_{10} = 0.017$, $h_{01} = -h_{11} = 0.006$, and $C_{01} = -0.002$. The presence of diffracted peaks out of the

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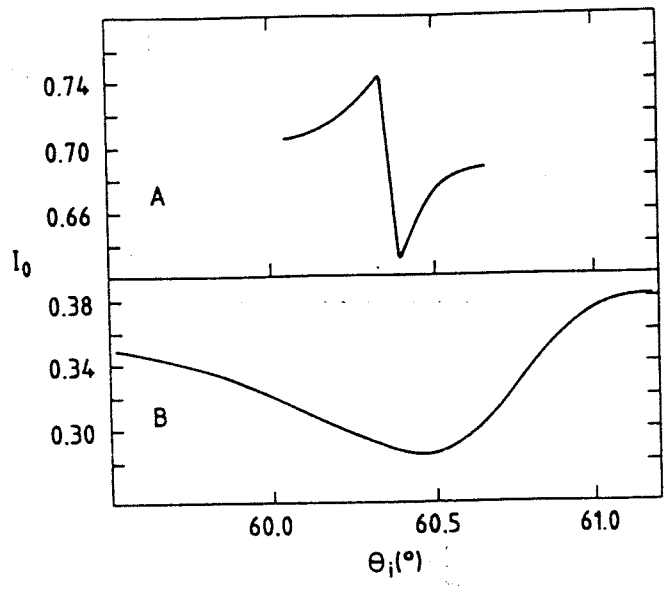

Fig. 2. Behavior of the specular peak as a function of incidence angle in the region of the resonance of the (10) reciprocal lattice vector with the n = 0 bound state for He/Cu(113) at an energy of 21 meV. B. experimental curve; A. calculation using the Morse potential with $\kappa = 1.05$ Å^{-1}, D = 6.35 meV, and the corrugation function of eq. (11).

plane of incidence could not be measured in the experiment, hence their effect is not known. To test the importance of out-of-plane diffraction extensive calculations have been carried out with the corrugation of eq. (11) particularly at the low incidence energy of 21 meV. When compared with the non-renormalized experimental data, the agreement is quite good and not appreciably different from that such as shown in Fig. 1. The effect of the out-of-plane channels is to reduce Re b and enhance Im b producing the double structure of Fig. 2A with a slightly predominent minimum. If inelastic events were included in the calculation, more channels would be coupled to the resonance and it is virtually certain that the structure would become a pronounced minimum in better agreement with experiment as has been demonstrated with hard wall models for the scattering of He by graphite[10]. Thus it is clear that the behavior of the diffracted peaks can be quite well described by a one dimensional corrugation except near a resonance where a small amount of out-of-plane diffraction can have a large effect on the form of a resonance curve.

In conclusion, we have demonstrated how a theory can be developed for the elastic surface scattering of atoms by a soft potential

model. The theory is based on an iteration of the t-matrix equation for scattering with appropriate projection techniques for handling the bound state resonances. Calculations have been performed with the corrugated Morse potential and compared with new experimental results for the diffraction of He by several Cu surfaces. The detailed comparison with experiment seems to indicate that inelastic effects are important near resonance conditions, since inclusion of extra elastic diffraction channels caused by a weak corrugation in close packed directions on the stepped surface does not completely adequately describe the resonance signature. However, the overall trend of the calculations for the diffracted intensities as a function of incidence angle is very well described by the corrugated Morse potential. In fact, a comparison with hard wall calculations demonstrates clearly that the softness of the repulsive part of the atom-surface potential is very important in the scattering of He at metal surfaces.

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