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AN EXACT ITERATIVE SOLUTION OF THE ATOM–SURFACE SCATTERING PROBLEM FOR REALISTIC POTENTIALS

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A general method, based on high order distorted wave perturbation theory, is developed to obtain exact reflection intensities for low energy atoms scattered by solid surfaces. Resonance shapes are calculated using projection techniques to obtain uniform convergence. Important differences with the hard corrugated wall model arise when the calculations for a corrugated Morse potential are compared with experiment for helium scattered by a Cu(110) surface.

In recent years large advances have been made in interpreting the elastic surface scattering of low energy atoms and molecules using the hard corrugated wall model (HCW) [1]. In particular, a great deal of information has been obtained from studying the bound state resonances or selective adsorption which occurs when a particle in the incident beam can diffract into one of the adsorption levels while still conserving energy. The HCW can be expressed as a potential of the form

$$\begin{aligned} &V(\boldsymbol{r}) = \infty, \quad z < \phi(\boldsymbol{R}), \\ &V(z, \boldsymbol{R}), \quad z > \phi(\boldsymbol{R}), \end{aligned} \tag{1}$$

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

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The adjustment of the bound state levels appears to be rather insensitive to the stiffness or slope of the repulsive potential. On the other hand, the diffracted intensities can be strongly affected by this parameter [2–4]. The repulsive potential is, to a good approximation, proportional to the surface electronic density [5] which is known to be very nearly exponential in form [6].

In order to investigate the effects of softness in the potential, the authors have developed a perturbation method of solving exactly for the diffraction intensities. This has been applied to the corrugated exponential potential [2,3] where it has been shown to be convergent for all corrugation amplitudes of current practical interest [4]. In this paper we show how the iterative method can be extended in a general manner to include an attractive part near the surface for studying the effects of the potential well and particularly the bound states. Detailed numerical calculations have been carried out in an accompanying paper showing excellent theoretical agreement with the diffracted intensities of He scattered from the (110) face of Cu [7]. In particular, it is shown that the HCW model is completely inadequate to describe the data. In this letter we present a short description of the general method and some calculations indicating the resonance behavior for the He/Cu(110) and similar systems.

As a model of the atom–surface interaction we adopt the corrugated Morse potential defined by

$$V(\boldsymbol{r}) = D\{\exp[2\chi(\phi(\boldsymbol{R}) - z)]/v_0 - 2\exp(-\chi z)\}, \tag{2}$$

with v_0 the surface average of $\exp(2\chi\phi)$. The leading term of (2) has the correct behavior for the repulsive potential since it is essentially the corrugated exponential potential. The second term of (2) is not corrugated since the attractive part of the potential is expected to be smooth. A Morse potential, modified so as to have the correct $1/z^3$ asymptotic behavior, has been shown to agree quite well with the experimentally observed bound states for graphite and LiF [8]. However, the exact form of the attractive tail will not strongly affect the diffracted intensities except for very low incoming particle energies.

The basic theoretical approach is to divide the potential into two parts $V(\boldsymbol{r}) = U + v$, then the scattered intensities are readily obtained from the transition matrix t_{fi} given by

$$t_{fi} = v_{fi} + \sum_l v_{fl} \frac{1}{E_i + E_l + i\varepsilon} t_{li}, \tag{3}$$

where the v_{pq} are matrix elements of v taken with respect to eigenstates of U. The usual choice for U is the surface average of $V(\boldsymbol{r})$, but there are may other possibilities; for example substantial improvements in convergence can be obtained by taking a U which is displaced with respected to the surface average [4].

For the Morse potential it is convenient to define a dimensionless transition

matrix satisfying the following set of coupled equations:

$$F_J(r) = v_J f(r,p_0) + \tfrac{1}{4}\sum_N \int_0^\infty \mathrm{d}q\, v_{J-N} \frac{f(r,q)\, F_N(q)}{p_N^2 + q^2 + \mathrm{i}\varepsilon} + \frac{1}{4\pi^2}\sum_N \sum_n v_{J-N} \frac{\mathfrak{L}(r,n)\, F_N(n)}{p_N^2 + (d-n-1/2)^2}, \tag{4}$$

$$F_J(n) = r_J\, \mathfrak{L}(p_0,n) + \tfrac{1}{4}\sum_N \int_0^\infty \mathrm{d}q\, v_{J-N} \frac{\mathfrak{L}(q,n)\, F_N(q)}{p_N^2 - q^2 - \mathrm{i}\varepsilon} + \tfrac{1}{4}\sum_N \sum_m v_{J-N} \frac{\mathfrak{M}(n,m)\, F_N(m)}{p_N^2 + (d-m-1/2)^2}, \tag{5}$$

where J is a surface reciprocal lattice vector, $d^2 = 2MD/\hbar^2\chi^2$, $\chi^2 p_N^2 = k_i^2 - (K_i - N)^2$ with k_i the incident wavevector, K_i its surface parallel component and M the particle mass. The functions $f(p,q)$, $\mathfrak{L}(q,n)$ and $\mathfrak{M}(m,n)$ are the matrix elements of $\exp(-2\chi z)$ for continuum states (p,q) or bound states (m,n) [9], and

$$v_J = \frac{1}{S}\int_{\mathrm{uc}} \mathrm{d}R\, \mathrm{e}^{\mathrm{i}J\cdot R}\, \mathrm{e}^{2\chi\phi(R)}\,(1-\delta_{J,0}), \tag{6}$$

with S the area of the unit cell. The diffracted beam intensities are given by

$$I_G = |\delta_{G,0} - \mathrm{i}\pi F_G(p_G)/4\sqrt{p_G p_0}\,|^2. \tag{7}$$

The system of eqs. (4) and (5) is solved to convergence by the Neumann iterative technique, a process completely equivalent to distorted wave perturbation theory carried out to high order.

Near conditions for resonance convergence is limited by the singularities arising from the bound state denominators in eqs. (4) and (5). These problems can be avoided by some straightforward manipulations on the transition matrix equation (3). In operator notation, eq. (3) is $t = v + vGt$. If G can be expressed as the sum of two parts, $G = G_1 + G_2$, then the transition operator can be written as $t = h + hG_1 t$, where $h = v + vG_2 h$. This implies that in the present case, eq. (3) can be replaced by the equivalent pair of coupled integral equations

$$t_{fi} = h_{fi} + {\sum_g}' h_{fg} \frac{1}{E_i - E_g + \mathrm{i}\varepsilon} t_{gi}, \tag{8}$$

$$h_{fi} = v_{fi} + {\sum_l}' v_{fl} \frac{1}{E_i - E_l + \mathrm{i}\varepsilon} h_{li}, \tag{9}$$

where the Σ' implies that the quantum numbers summed in eq. (8) are not summed over in (9) and vice-versa.

There are two immediate and convenient choices for this type of separation.

The first is to let eq. (9) include a sum over only those states which are participating in the resonance. This prescription is identical to reducing eq. (3) by direct elimination of a selected set of (resonant) states. It is clear that this method cannot resolve all the fundamental convergence problems at resonance, because the small denominators still appear in the renormalized matrix elements h_{pq} of eq. (8). However, in practice we find that this approach can lead to substantially quicker convergence of the iterative procedure in the vicinity of resonances, and when combined with a displacement of the potential U with respect to the surface average of $V(r)$, can even lead to convergence when the kinematical denominator $p_N^2 + (d - m - 1/2)^2 \approx 0$.

A second and perhaps more logical choice is to include in the sum of eq. (8) for t_{fi} only those terms involving a resonant denominator, leaving eq. (9) well behaved and appearing exactly like eq. (3), except with a restricted sum. Eq. (9) is solved by iteration and the transition matrix is subsequently obtained from (8) by a simple resolution of a finite number of coupled equations. This prescription is a projection of the resonant terms out of eq. (3) and has been used by Weare et al. in a lowest order approximation to predict resonance signatures [10]. They have also used an equivalent approach to apply the Rayleigh scattering method to the HCW [11]. This procedure has the distinct advantage that all convergence difficulties associated with resonance have been lifted out of eq. (9), the price paid is that one must solve an additional iterative equation for the h_{fn}.

The accompanying paper [7] gives several examples of calculations based on eqs. (4) and (5). It suffices to repeat here that the comparison with experiment for He scattered by the (110) face of Cu clearly demonstrates the effects of the attractive well, the softness (or a finite slope) in the repulsive part of the potential, and points out the problems associated with the HCW model. Furthermore, the corrugation depends on incoming energy in precisely the manner expected [6].

We would like to present several examples of bound state resonances calculated using the projection operation on eqs. (8) and (9). As a model of the system He/Cu(110), we take in eq. (2) $D = 6.5$ meV corresponding to three bound states, $\chi = 1.05$ Å^{-1} and a one-dimensional sinusoidal corrugation of the form

$$\phi(X) = ha\cos(2\pi X/a), \tag{10}$$

with $a = 3.6$ Å. The incoming energy is the lower experimental value $E_i = 21$ meV corresponding to $k_i = 6.4$ Å^{-1}. Fig. 1a shows a plot of the specular beam versus incident angle for the case $\binom{10}{0}$ (the (10) state is in resonance with the $n = 0$ or ground state) for the observed corrugation amplitude $h = 0.008$. Convergence to a unitarity of 0.9999 is obtained after four iterations. The resonance is a strong peak but extremely narrow and this is interpreted as being in agreement with observation; i.e. the experimental search revealed no resonance features at all, but these calculations indicate that the resonances are

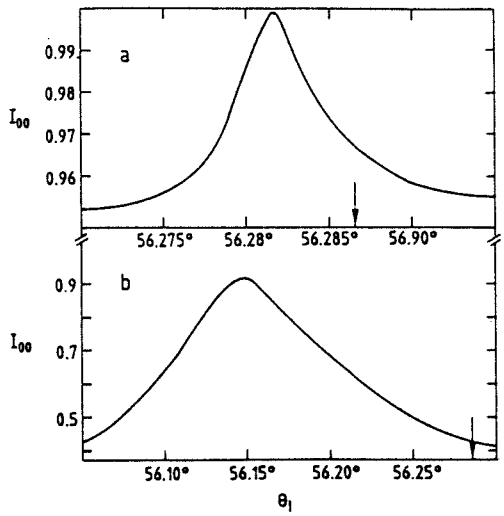

Fig. 1. (a) Specular intensity as a function of incidence angle near the $\binom{10}{0}$ resonance for the system He/Cu(110); $k_i = 6.4$ Å^{-1}, $\chi = 1.05$ Å^{-1}, $D = 6.4$ meV and $h = 0.008$. The arrow marks the position given by the kinematical resonance condition $E_i - E_b = 0$. (b) Same as (a) except for a stronger corrugation, $h = 0.04$.

so sharp that they would not be detected in most of the experimental situation. Fig. 1b shows the same resonance but with a corrugation amplitude five times as large ($h = 0.04$), a unitarity of 0.9999 being achieved after 15 iterations. It is seen that an increase in corrugation amplitude broadens considerably the resonance peaks, futhermore it is noted that for all corrugation amplitudes the shift of the peak towards the normal can be comparable to the peak width. This shift is a manifestation of the band structure effects introduced by the corrugation.

Fig. 2 shows the $\binom{20}{0}$ resonance for a corrugation amplitude $h = 0.02$ with the standard unitarity obtained after 8 iterations. All of the specular resonances shown in figs. 1 and 2 are local maxima and no minima occur among all the important $\binom{10}{n}$ and $\binom{20}{n}$ resonance peaks. This behavior is in agreement with the rules developed by Wolfe and Weare [12] and with the further discussions of Celli et al. [13]. For example, with the $\binom{20}{0}$ resonance the rules of Celli et al. hold as the resonance yields a maximum on the 00 and 10 beams and a minimum on the 10 beam. But for the $\binom{10}{0}$ resonance the prediction of the Celli rules is in contradiction with our results.

Near an isolated resonance, the t matrix element is given by:

$$t_{fi} = h_{fi} + h_{fR} h_{Ri} / (E_i - E_R - h_{RR}),$$

where R labels the resonant state. The intensity can be put into the standard

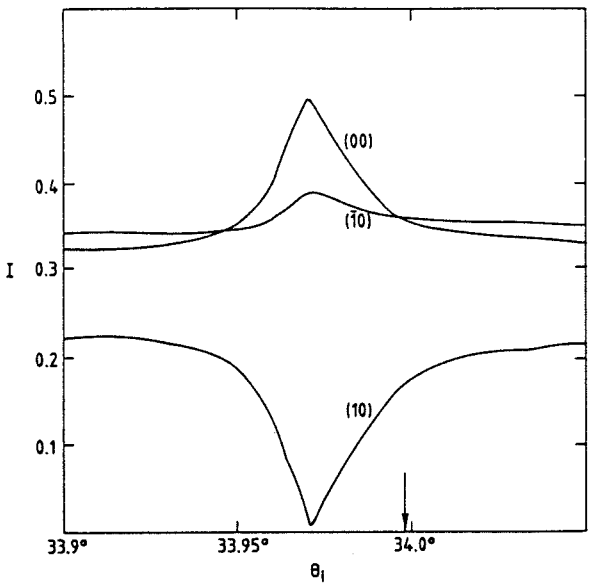

Fig. 2. The specular, (10) and ($\bar{1}$0) diffraction intensities for the $\binom{20}{0}$ resonance of the same system as fig. 1, except with $h = 0.02$.

form [13]:

$$I = |C|^2 |1 - \mathrm{i}b/(x - \mathrm{i})|^2$$

where $x = [E_\mathrm{i} - E_R - \mathrm{Re}(h_{RR}/4)]2/\Gamma$, with $\Gamma = \mathrm{Im}(h_{RR}/4)$ the line width, and where $|C|^2$ is the diffracted intensity if the resonance is suppressed. The cancellation of x gives the band structure point which is shifted with respect to the resonance kinematic condition. Putting b_R and b_I respectively the real and imaginary part of b it is easy to show that the line displays a maximum and a minimum for x_1 and x_2 values with the relation $x_1 x_2 = -1$. These extrema are therefore located on each side of the band structure point. The corresponding intensities are given by

$$I_\mathrm{extrema} = |C|^2 \times \tfrac{1}{2}\left[1 + X^2 + Y^2 \pm \left((X^2 + Y^2 - 1)^2 + 4Y^2\right)^{1/2}\right],$$

with

$$X = 1 + b_\mathrm{R}, \quad Y = b_\mathrm{I}.$$

Now the difference $|C|^2 - I_\mathrm{min}$ will be larger than $I_\mathrm{max} - |C|^2$, i.e. the line shape will have the structure of a minimum if

$$(1 + b_\mathrm{R})^2 < 1 - b_\mathrm{I}^2. \tag{11}$$

In the case discussed by Celli et al. [13] with repulsive hard corrugated wall,

Kirchhoff approximation and corrugation (10), b_I is always equal to zero. Then one of the x values, x_1 for instance, is equal to zero and the other is rejected to minus infinity. The resonance line has a symmetric lorentzian shape and is a minimum if

$$-2 < b_R < 0.$$

For the results presented in figs. 1 and 2, the b_I values are in each case very small; x_1 is then proportional to b_I and the other solution has a great absolute value giving a non-realistic angle for the appearance of the corresponding extremum. But this produces the asymmetric shape which is apparent on each resonance line. However, condition (11) gives the resonance signature.

To second order in the iteration process, the line width is given by

$$\Gamma = \frac{\pi}{4} \sum_{G \text{ open}} M_{R-G} M_{G-R} \frac{2m}{\hbar \chi k_G^z},$$

where M_{R-G} is the matrix element of the $R - G$ potential Fourier component taken between resonant and G states. With corrugation (10) and small ha values, M_{R-G} is respectively proportional to χha and $(\chi ha)^2$ for the $\binom{10}{0}$ and $\binom{20}{0}$ resonance. The line width is then respectively proportional to $(\chi ha)^2$ and $(\chi ha)^4$, in agreement with results of Celli et al. [13].

We have demonstrated in this letter a general method of treating elastic atom–surface scattering using high order perturbation theory. It was convenient to apply the method to the corrugated Morse potential because the matrix elements can be obtained analytically. However, we emphasize that the method is quite general as it depends only on a knowledge of the matrix elements v_{pq}. Once these matrix elements have been numerically calculated for any general potential the diffraction intensities for all incident beam conditions can be readily obtained.

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