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THRESHOLD RESONANCES IN THE DIFFRACTION OF ATOMS AND MOLECULES BY SURFACES

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We examine the problem of threshold resonances in the diffraction of atomic and molecular beams by solid surfaces. We show that the divergence in the slope of the intensity as a function of incident polar angle appears generally in all diffraction peaks. However, for interactions with realistically soft repulsive parts we find that the resonances are weakened to the point where they will be difficult to observe experimentally.

In the elastic scattering of atomic or molecular beams by periodic surfaces the diffraction intensities should exhibit resonance behavior whenever the initial conditions are such that a new diffraction beam just becomes visible. These threshold resonances, or emerging beam resonances, are a general feature of diffractive systems and in fact have been discussed for many years in connection with low energy electron diffraction [1–3]. In atomic and molecular surface scattering, threshold resonances have been a subject to continued theoretical interest because of the information they would provide on the nature of the interaction potential [4–6]. However, unambiguous identification of these resonances with present day experiments appears difficult [7].

The typical experimental configuration is to measure the diffracted beam intensities as a function of incident polar angle with the incident energy held constant. When a newly allowed diffracted beam emerges from the surface its intensity increases rapidly from zero with a very steep slope. Conservation of flux would require that this rapid change would appear in the other diffracted beams as a rearrangement of intensities. Several calculations based on the hard corrugated wall model for the atom–surface interaction have indicated that threshold resonances should be readily observable for systems in which diffracted beam intensities are not too small [4,6]. In this paper we reexamine the problem in the context of a more realistic soft potential for the scattering interaction. We find that the resonance is manifest in every diffracted peak, but that the inclusion of softness in the interaction drastically weakens the effect so that it is noticeable only over an extremely small angular range. Thus, only for the most strongly corrugated and most rigidly interacting systems will threshold resonances be experimentally observable in diffraction intensities.

The name threshold resonance is somewhat misleading since it is not a true resonance in the sense of a coupling with a degenerate bound state, but since this appears to be the standard terminology in diffraction physics we will continue to use it. It usually is described as a divergence in the slope of the diffracted beam intensity as a function of incident polar angle under conditions of constant energy. The explanation of the resonance is relatively straightforward. We denote by I_G the intensity of a diffracted beam with $\boldsymbol{G}$ the associated two-dimensional reciprocal lattice vector parallel to the surface. This intensity I_G can be regarded as a function of incident particle wavevector $\boldsymbol{k}_\mathrm{i} = (\boldsymbol{K}_\mathrm{i}, k_{\mathrm{i}z})$ and final diffracted beam wave vector $\boldsymbol{k}_G = (\boldsymbol{K}_\mathrm{i} + \boldsymbol{G}, k_{Gz})$, with $k_{\mathrm{i}z}$ and k_{Gz} being the respective components perpendicular to the surface. The kinematical constraints of conservation of energy and parallel momentum give

$$k_{Gz}^2 = k_\mathrm{i}^2 - (\boldsymbol{K}_\mathrm{i} + \boldsymbol{G})^2, \tag{1}$$

and for convenience we write $\boldsymbol{K}_\mathrm{i} = \hat{e}k_\mathrm{i}\sin\theta_\mathrm{i}$. If we denote by $\boldsymbol{N}$ the reciprocal lattice vector associated with an emerging beam, the slope of its corresponding intensity is

$$\frac{\partial I_N}{\partial \theta_\mathrm{i}} = \left(\frac{\partial I_N}{\partial k_{Nz}}\right)\left(\frac{\partial k_{Nz}}{\partial \theta_\mathrm{i}}\right) + \ldots, \tag{2}$$

where other partial derivatives appearing in (2) are ignored because they are of no serious consequence to the discussion. We obtain immediately from (1)

$$\partial k_{Nz}/\partial\theta_\mathrm{i} = -\hat{e}\cdot(\boldsymbol{K}_\mathrm{i} + \boldsymbol{N})k_{\mathrm{i}z}/k_{Nz}, \tag{3}$$

the important point being that at emergence when $k_{Nz} \to 0$ the derivative diverges as $1/k_{Nz}$, and consequently so does the slope in eq. (2) unless I_N goes to zero at least as fast as k_{Nz}^2 for small k_{Nz}. We show below that in general I_N varies no faster than the first power of k_{Nz} and thus the origin of the divergence of the slope is in the Jacobian derivative in eq. (2). We mention in passing that the arguments above also show that the threshold resonance should appear in a variety of possible experimental configurations, including regarding I_N as a function of parallel momentum exchange at constant energy, or as a function of incident total energy with fixed incident angle.

To examine the question more closely we note that the intensity of a diffracted beam is given by [8]

$$I_G = |\delta_{G,0} - \mathrm{i}mt_{G\mathrm{i}}/\hbar^2\sqrt{k_{\mathrm{i}z}k_{Gz}}|^2, \tag{4}$$

where the transition matrix t_{Gi} obeys the integral equation

$$t_{Gi} = v_{Gi} + \sum_{l} v_{Gl}(E_i - E_l + i)^{-1} t_{li}. \tag{5}$$

We have assumed here a distorted wave formalism in which the total interaction potential $V(\boldsymbol{R}, z)$ between particle and surface is divided according to

$$V(\boldsymbol{R}, z) = U(z) + v(\boldsymbol{R}, z), \tag{6}$$

with $U(z)$ the average of V over the surface. The matrix element v_{fl} are then matrix elements of the potential v taken with respect to eigenstates of $U(z)$. Regarding now the intensity of an emerging beam

$$I_N = |m t_{Ni}/\hbar^2|^2/k_{iz}k_{Nz}, \tag{7}$$

conservation of total flux (i.e. the unitarity condition) requires that $0 \leq I_N \leq 1$ and the transition matrix t_{Ni} must go to zero at least as fast as k_{Nz} for small k_{Nz}. However, in general we can argue that

$$t_{Ni} \to k_{Nz} \quad \text{as} \quad k_{Nz} \to 0. \tag{8}$$

This is because, from the t-matrix equation (5), t_{Ni} will have the same limiting behavior as the matrix element v_{Ni} except in highly unusual circumstances, and for all potentials to date which admit to analytical calculation one finds linear behavior in v_{Ni} as $k_{Nz} \to 0$. This includes the corrugated Morse and exponential repulsive potentials as well as the corrugated hard wall or a simple step potential. This behavior is clear for the latter two potentials, where the perpendicular momentum dependence is given by [9]

$$v_{k_{Gz}, k_{iz}} = 4\hbar^2 k_{Gz} k_{iz}/2m, \tag{9}$$

and the two former potentials reduce to this same form for small k_z. This argument would fail if the matrix element varied as k_{Nz}^{α} with $\alpha \geqq 3/2$ for small k_{Nz} but this appears highly unlikely. Inclusion of the correct I/z^3 Van der Waals attractive part of the potential would not critically affect the situation since this would tend to enhance rather than reduce the matrix elements for small k_z [10]. An example of an effect which might produce a smaller matrix element is potential with an activation barrier in front of the repulsive part. It is very straightforward to show that an activation barrier has the effect of reducing the particle flux in the region of repulsive potential but the same linear dependence in k_{Nz} is obtained.

The above arguments serve to justify the statement that the emerging beam appears with an infinite slope for example in the plot of intensity versus θ_i. We now consider what occurs simultaneously in the other beams. Although our discussion up to this point has been limited to the emerging beam itself (which we continue to denote by the reciprocal lattice vector $\boldsymbol{N}$) a quick review will reveal that any diffracted intensity of eq. (4) will exhibit a similar divergence in slope $dI_G/d\theta_i$ if I_G contains terms proportional to k_{Nz}^{α} with $\alpha < 2$. Such terms do appear since the transition matrix couples all channels. We expand the Green function of eq. (5) into real and imaginary contributions

$$t_{fi} = v_{fi} - i\pi \sum_e v_{fe}\delta(E_i - E_e) t_{ei} + \sum_e v_{fe} \frac{P}{E_i - E_e} t_{ei}, \tag{10}$$

where P denotes the principal part integral. Then the transition matrix for a typical non-emerging diffraction channel G will contain, among others, the following terms

$$t_{Gi} = v_{Gi} - i\pi m v_{GN} t_{Ni}/\hbar^2 k_{Nz} - i\pi m \sum_{G' \neq N} v_{GG'} t_{G'i}/\hbar^2 k_{G'z} + \ldots, \tag{11}$$

the second term on the right being the coupling to the emerging beam coming from the energy shell contribution of eq. (10). We have argued above that both v_{GN} and t_{Ni} will be linear in k_{Nz} for small k_{Nz}, thus the coupling term in (11) will be linear in k_{Nz}. It is now clear that when t_{Gi} is inserted in the intensity of eq. (4) there will be cross terms which remain linear in k_{Nz} and these linear terms will all contribute a divergence to $\partial I_G/\partial\theta_i$, except under highly unusual circumstances in which all such linear terms cancel each other. Thus we find that not only does the resonance appear in the emerging beam, but a similar divergence in general appears simultaneously in each and every diffracted beam.

It now remains to consider the effect of a soft potential on these resonances. We illustrate this with a model calculation, choosing as the distorting potential an exponential repulsion

$$U(z) = D\,e^{-\kappa z}, \tag{12}$$

with the perturbing potential expanded in a Fourier series and each term having a similar exponential behavior

$$v = D \sum_{G \neq 0} \lambda_G e^{-\kappa z} e^{iGR}. \tag{13}$$

The matrix elements for such a potential are well known

$$v_{GQ} = \lambda_{G-Q} \frac{\hbar^2 \kappa \pi}{2m} \sqrt{p \sinh(p\pi)\, q \sinh(q\pi)}\, \frac{p^2 - q^2}{\cosh(p\pi) - \cosh(q\pi)}, \tag{14}$$

with $p = 2k_{Gz}/\kappa$ and $q = 2k_{Qz}/\kappa$. Since the intensity of an emerging beam is weak we are justified in using the distorted wave Born approximation $t_{Ni} = v_{Ni}$ and the relevant matrix element takes the form

$$v_{Ni} \underset{k_{Ni} \to 0}{\to} \lambda_N \frac{\hbar^2 \pi^{3/2}}{m} \left(\frac{2}{\kappa}\right)^{5/2} k_{Nz} k_{iz}^2 \frac{\sqrt{k_{iz} \sinh(2\pi k_{iz}/\kappa)}}{\cosh(2\pi k_{iz}/\kappa) - 1}. \tag{15}$$

For a light atom or molecule scattering from a surface typical parameter values are $k_i \approx 5$–10 Å^{-1} and $\kappa \approx 2$ Å^{-1}. Thus for all except grazing angles of incidence we are justified in replacing the hyperbolic functions in (15) by exponentials. Then the expression for the slope of the emerging beam intensity is

$$\frac{\partial I_N}{\partial \theta_i} = |\lambda_N|^2 \pi^3 \left(\frac{2k_{iz}}{\kappa}\right)^5 \hat{e} \cdot (\boldsymbol{K}_i + \boldsymbol{N})\, e^{-2\pi k_{iz}/\kappa}/k_{Nz}. \tag{16}$$

The strength of the resonance is dominated by the factor $(k_{iz}/\kappa)^5 \times \exp(-2\pi k_{iz}/\kappa)$ which is small. For comparison, the same slope calculated from the hard corrugated wall matrix elements of eq. (9) is

$$\frac{\partial I_N}{\partial \theta_i} = 4k_{iz}^2 \hat{e} \cdot (\boldsymbol{K}_i + \boldsymbol{N})\, d^2/k_{Nz}, \tag{17}$$

where d is the characteristic height of the corrugation. For all except very grazing angles of incidence, where the approximations leading to (16) break down, the hard wall result (17) is substantially larger. This analysis implies that for a physically realistic soft potential the $1/k_{Nz}$ divergence will be very weak and will appear over a much smaller angular spread than that predicted by the hard wall model.

We have carried out a series of detailed calculations to investigate threshold resonances for a variety of experimentally interesting systems. Shown in fig. 1 is an example for the case of H_2 scattered at a Cu(100) face. This is an exact calculation by iteration of the transition matrix equation (5) using the corrugated Morse potential [11]:

$$V(\boldsymbol{R}, z) = D\left\{e^{-2\beta[z-\phi(\boldsymbol{R})]}/v_0 - e^{-\beta z}\right\}. \tag{18}$$

The beam is incident in the $\langle 110 \rangle$ direction ($\phi_i = 45°$) with a wave vector $k_i = 8.6$ Å^{-1}. The potential parameters are $D = 21.6$ meV, $2\beta = 1.94$ Å^{-1} and the lattice spacing is a 2.55 Å. The corrugation function is

$$\phi(x, y) = (ba/2)[\cos(2\pi x/a) + \cos(2\pi y/a)], \tag{19}$$

with $b = 0.036$, and v_0 is the surface average of $\exp[2\beta\phi(\boldsymbol{R})]$. The (10) diffracted beam is emergent at an incident polar angle of slightly less than 50.96°. The step slope of its intensity and the singularities it causes in the slope of the $(\bar{1}0)$ and (00) beam intensities are evident. However, what is most important is the scale. The range of angles over which the resonance occurs is so small that it could not be observed within current experimental precision.

In order to make a direct comparison with the hard corrugated wall model the same resonance is examined in figs. 2 and 3 using the corrugated exponential potential [12], i.e. the repulsive part of eq. (18). Calculations are carried out for three values of the range parameters, $2\beta = 3$ Å^{-1}, $2\beta = 6$ Å^{-1} and $\beta \to \infty$ which corresponds to the hard wall limit; all other parameters are the same as for fig. 1. Fig. 2 shows the (00) and $(1\bar{1})$ peak intensities and the $(0\bar{1})$ and $(\bar{1}\bar{1})$

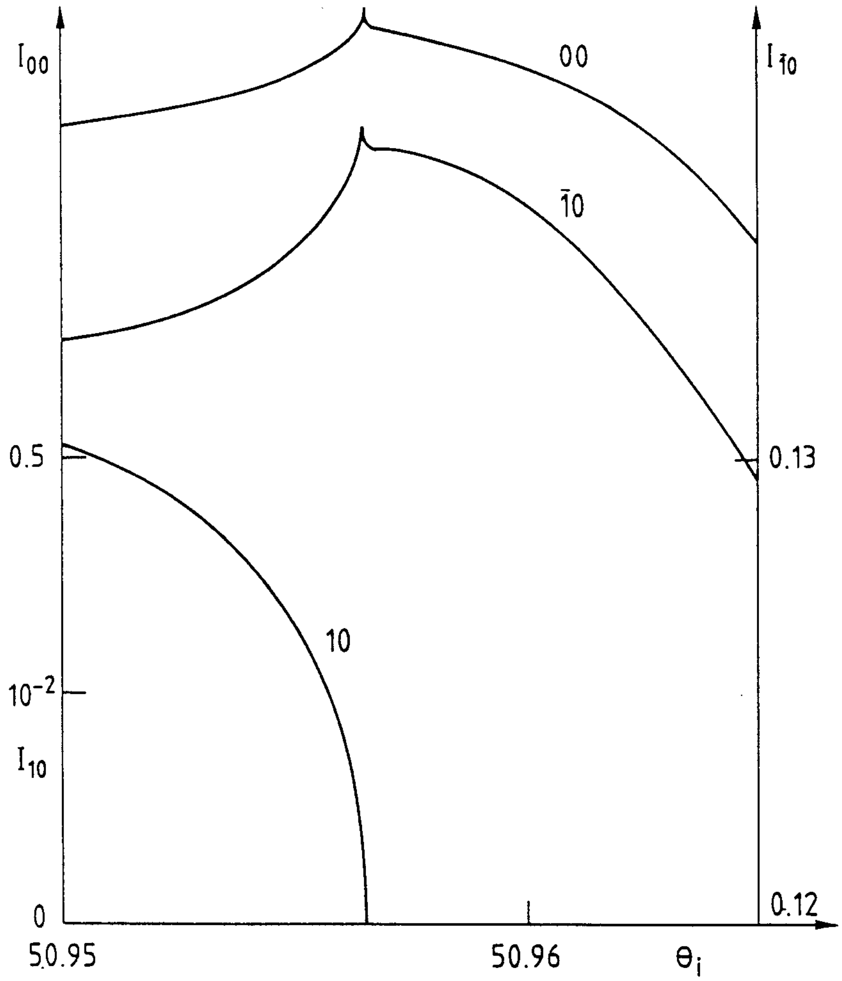

Fig. 1. Calculations using the corrugated Morse potential for H_2 scattered by a Cu(100) surface. Shown are the intensities of the (0.0) or specular beam, the ($\bar{1}$,0) and the (1,0) in the vicinity of the emergence of the (1,0) peak.

intensities are in fig. 3. For $2\beta = 3$ Å^{-1}, which would be a typical value for the surface of an insulator, the resonance occurs over such a narrow angular range as to be invisible on the scale plotted. Only when the surface is made unrealistically hard does the resonance become evident. Numerous other calculations tend to confirm the observation that if the repulsive part of the interaction potential is soft the threshold resonances will be too weak for easy observation [5,12].

In this paper we have reconsidered the problem of threshold resonances in atom–surface diffraction in the light of realistic potential models with soft repulsive parts. This type of resonance is characterized by a divergence in the slope of the intensity of an emerging beam as a function of incident polar angle or other convenient parameters. We show that in general a similar divergence in the slope appears simultaneously in all diffracted beams. Calcu-

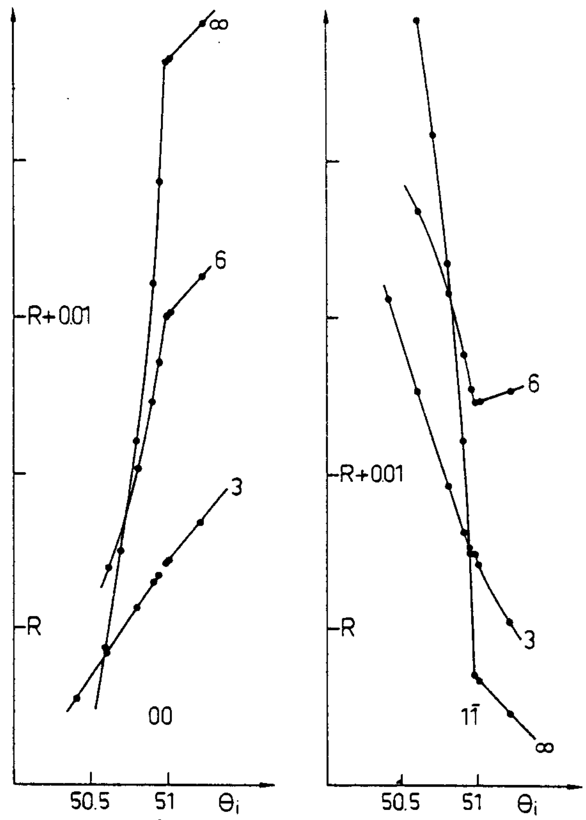

Fig. 2. Calculations using the corrugated exponential potential for the same system as fig. 1, showing the approach to the hardwall limit. The curve marked 3 is for $2\beta = 3$ Å^{-1}, that marked 6 is for $2\beta = 6$ Å^{-1} and the curved marked ∞ is the hardwall limit $\beta \to \infty$. Shown are the intensities for the (0,0) and $(1,\bar{1})$ peaks as marked.

lations based on hard corrugated wall models indicate that these resonances would be detectable experimentally. However, we find here that once the repulsive part of the potential is made realistically soft such resonances becomes very weak and occur over an angular range so small as to make them unobservable within the constraints of current experiments, the only possible exception being large surface corrugations coupled with grazing incident angles or very low incident energy. These conclusions are supported by both analytical and numerical calculations.

As a final note we should emphasize that the calculations presented in this paper are for the elastic diffraction of atoms and molecules, and we have demonstrated why the associated threshold resonances are difficult to observe experimentally. Basically, the explanation is due to the fact that new diffraction beams, although they emerge with a very steep slope, tend to have intensities relatively small compared to the other diffracted beams while they remain in the region of large or grazing angles. In the case of molecule scattering there will be additional discrete scattered beams due to the excitation of molecular rotational modes. These inelastic rotational sidebands can

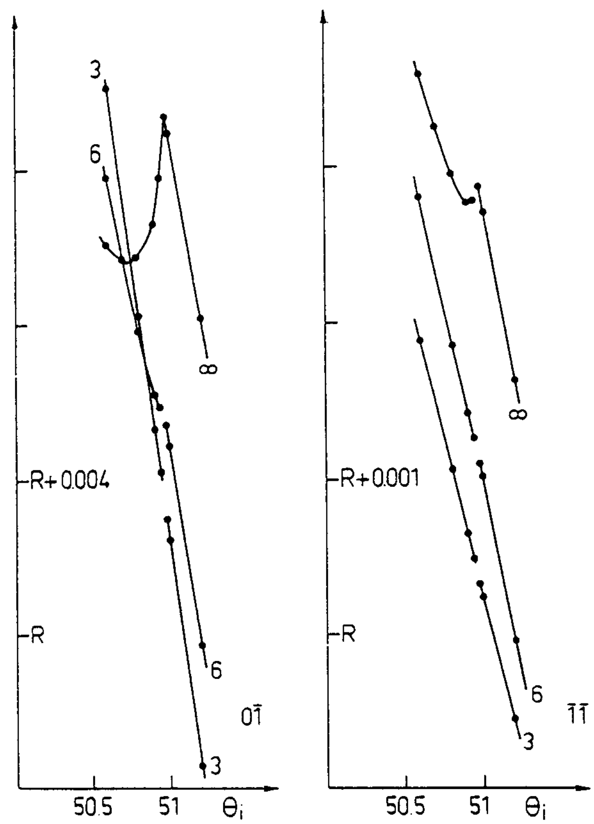

Fig. 3. Same as fig. 2 except showing the intensities of the $(0,\bar{1})$ and $(\bar{1},\bar{1})$ peaks.

also exhibit threshold resonances whenever kinematical conditions allow a new beam to appear. Experiments, for example with hydrogen molecules of various isotopic composition, show that the inelastic rotational peaks can be very intense near grazing angles [13,14]. Consequently, for such systems a threshold resonance structure may be readily observable.

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