

INTERPRETATION OF SELECTIVE ADSORPTION IN ATOM–SURFACE SCATTERING *

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The elastic theory for resonant atom–surface scattering is shown to explain simply the occurrence of both minima and maxima at resonance and the strength and shape of the absorption lines, on the assumption that the repulsive part of the potential is of the form $V(z - \xi)$, where ξ is the surface corrugation and V can be regarded as a hard wall at the locus of turning points. Explicit formulae are obtained in the semiclassical limit. For a simple sinusoidal corrugation with rectangular symmetry, the signature of an isolated resonance is determined unambiguously by the parity of $|m| + |m' - m| - |m'| + |n| + |n' - n| - |n'|$, where (m, n) is the resonant vector and (m', n') the scattering vector, in reciprocal lattice units. The predicted signatures of isolated resonances agree with experiments and more elaborate calculations for the systems He/LiF and He/Graphite. Calculated splittings in the surface band structure also show reasonably good agreement. An alternative formulation of resonant scattering, as suggested by Wolfe and Weare, can be based in an appropriate sorting of successive orders of distorted wave perturbation theory. For small corrugations there is good correspondence between the two approaches.

1. Introduction

The basis for the interpretation of selective adsorption phenomena in atom–surface diffraction was given long ago by Lennard-Jones and Devonshire [1]. It involves simple kinematic considerations of energy and momentum and allows a direct determination of the energies E_n of surface-bound adsorbed states. If $\mathbf{k} = (K, k_z)$ is the incident momentum of a particle of mass M and \mathbf{G} are the reciprocal lattice vectors of the surface, the resonance condition is

$$k^2 = (\mathbf{K} + \mathbf{G})^2 + 2ME_n/\hbar^2 \quad (1.1)$$

The incident angles (θ_i, ϕ_i) for which adsorption occurs for a given E_n are determined by (1.1) with $K = k \sin \theta_i$ ($\cos \theta_i, \sin \phi_i, 0$) (the z axis is perpendicular to the

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surface). Conversely, E_n can be determined and the experiments correlated.

Simple kinematics does not determine, however, whether a given resonance will give rise to a maximum or a minimum in the diffracted intensity. It was often thought that inelastic processes would play an important role at resonance and that as a result a theory of the intensities would be difficult. Chow and Thompson [2], however, pointed out that the observed features could be reproduced by model calculations using a purely elastic theory (except for an overall Debye–Waller correction). Recent calculations [3,4] with simple but realistic atom–surface potentials show remarkable agreement with experiment [5,6].

We shall take here the point of view that an elastic theory is completely adequate, at least as a starting point. The primary aim will be to explain in simple and physical terms the reason for the occurrence of maxima or minima at selective adsorption and the strength and width of the adsorption lines. Much of the discussion is based on the use of a potential of the type ($r = (R, z)$):

$$V(\mathbf{r}) = V_r(z - \zeta(\mathbf{R})) + V_a(z), \quad (1.2)$$

where V_r is a short-range repulsion, $\zeta(\mathbf{R})$ is an effective surface corrugation profile and $V_a(z)$ is a long-range attraction (see fig. 1). This choice is strongly indicated, at least for the prototype case of He/LiF(100), by comparisons with experiment of calculations using different types of potentials [7]. It provides a very convenient parametrization of $V(\mathbf{r})$, since the functional forms of V_r and V_a are roughly known and $\zeta(\mathbf{R})$ can be guessed from geometrical considerations. In fact, V_r can often be well approximated by an effective hard wall and $\zeta(\mathbf{R})$ by a simple sinusoid. In this case explicit formulae can be obtained in the semiclassical or eikonal [8] limit, which corresponds to the Kirchhoff approximation. These formulae are quite accurate, as long as no double-scattering or shadowing occurs for the classical trajectories [9], and will be used in our discussion. Thus this paper is in good part an extension to resonant scattering of the basic work of Levi et al. on the interpreta-

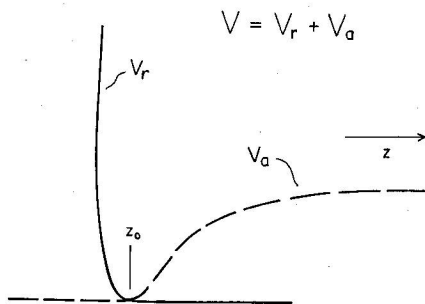


Fig. 1. Schematic plot of the potential $V(\mathbf{r})$, eq. (1.2), for a fixed value of \mathbf{R} as a function of z , showing the decomposition into the attractive part V_a (dotted line) and the repulsive part V_r (solid line). The basic simplifying assumption of the theory presented in sections 2, 3 and 4 is that V_a depends on z alone, while V_r shifts rigidly in the z direction with changing \mathbf{R} .

tion of diffraction intensities in terms of a hard wall model [10]. Much guidance and support in developing the theory is provided by the results of extensive calculations [3,4,11] that not only agree with the available data [5,6] (showing that the model potential (1.2) is good), but also provide many additional results.

In addition to the question of maxima and minima for isolated resonances, there is also the interesting question of the mixing of resonances arising from different values of G and E_n [2]. In other words, for each E_n there is a complete band structure of surface resonant states $E_n(\mathbf{K})$, which is periodic with period G and not simply parabolic in \mathbf{K} as implied by (1.1). The gaps in this band structure are also determined by the potential (1.2). Attempts have been made, with limited success, to correlate these band gaps with the diffraction intensity profiles on the basis of the Distorted Wave Born Approximation (DWBA), by expanding $V(\mathbf{r})$ in a series [12],

$$V(\mathbf{r}) = \sum_G V_G(z) \exp(i\mathbf{G} \cdot \mathbf{R}), \quad (1.3)$$

and treating the Fourier components for $G \neq 0$ as a perturbation. The advantage of this approach is that a given band gap is determined to a first approximation directly by a single $V_G(z)$. Elaborate numerical calculations based on the potential (1.3) should in principle be able to fit all the data, if enough G components are kept in the expansion. We found, however, that the form (1.2), where $\zeta(\mathbf{R})$ may then be Fourier-expanded, gives a better parametrization and is applicable both to the details of the resonant structure, such as band gaps, and to the overall calculation of the intensities. Further, semiclassical considerations can be applied to obtain correlations between data with a minimum of computations, as shown in this paper. Nevertheless, the parametrization (1.3) may well be better for "soft" surfaces, and historically it was used by Chow and Thompson to demonstrate first many of the effects that are discussed in this paper [2].

The formalism on which most of the discussion is based is presented in section 2. Section 3 gives the criteria for the occurrence of maxima or minima at resonance and discusses the shapes of isolated resonance lines and the line width, section 4 deals with interacting resonances and band gaps. Section 5 discusses an alternative approach, which is formally exact but does not lead to explicit approximations, except in the limit where the DWBA can be applied. Examples of applications for He/LiF and He/graphite are given in each section. We have selected these systems because complete data and corresponding calculations have recently become available for them.

2. Formalism

To develop the theory in its simplest form, we assume that there are two planes, $z = z_0$ and $z = z_0 - \delta$ (with $\delta > 0$), such that (see fig. 1)

$$V_r(z - \zeta(\mathbf{R})) = 0 \quad \text{for } z > z_0 - \delta, \quad (2.1)$$

$$V_a(z) = -D \quad \text{for } z < z_0. \quad (2.2)$$

This means that the attractive well has a flat bottom of depth D and width $>\delta$, with δ arbitrarily small. This assumption can be relaxed, as discussed in section 4, but at the cost of a loss of simplicity in the theory. The implication of (2.1.) and (2.2.) is that we can solve separately for the wave functions of V_r and V_a and then match at $z = z_0$.

For incident energy E and parallel momentum \mathbf{K} , the eigenfunction of $V = V_r + V_a$ for $z_0 - \delta < z < z_0$ is a linear combination of plane waves

$$\sum_G [B_G^+ |\mathbf{K} + \mathbf{G}, p_G\rangle + B_G^- |\mathbf{K} + \mathbf{G}, -p_G\rangle], \quad (2.3)$$

where

$$|\mathbf{K} + \mathbf{G}, \pm p_G\rangle = \exp[i(\mathbf{K} + \mathbf{G}) \cdot \mathbf{R} \pm ip_G z], \quad (2.4)$$

$$(\mathbf{K} + \mathbf{G})^2 + p_G^2 = 2M(E + D)/\hbar^2. \quad (2.5)$$

(We use G instead of \mathbf{G} as a subscript for simplicity.) The plane waves (2.4) are also separately eigenfunctions of $V_r - D$ and of V_a for $z_0 - \delta < z < z_0$.

Similarly, for $z \rightarrow \infty$ the eigenfunction of V is

$$|\mathbf{K}, -k_{0z}\rangle + \sum_G A_G |\mathbf{K} + \mathbf{G}, k_{Gz}\rangle, \quad (2.6)$$

with

$$(\mathbf{K} + \mathbf{G})^2 + k_{Gz}^2 = 2ME/\hbar^2. \quad (2.7)$$

The scattering problem for V amounts to a determination of the coefficients A_G .

Let us assume that the scattering problem for $V_r - D$ has been solved. The wave $|\mathbf{K} + \mathbf{G}, -p_G\rangle$ is an incident wave on $V_r - D$. Then

$$B_G^+ = \sum_{G'} S(\mathbf{G}, \mathbf{G}') B_{G'}^-, \quad (2.8)$$

with known coefficients $S(\mathbf{G}, \mathbf{G}')$. Let us also assume that the scattering problem for V_a has been solved. This is easy to do because of the conservation of parallel momentum. The wave $|\mathbf{K} + \mathbf{G}, p_G\rangle$ is incident from the left on V_a while $|\mathbf{K} + \mathbf{G}, -p_G\rangle$ and $|\mathbf{K} + \mathbf{G}, k_{Gz}\rangle$ are the only outgoing waves corresponding to it. We have then for $G \neq 0$

$$A_G = T_G B_G^+, \quad (2.9)$$

$$B_G^- = R_G B_G^+, \quad (2.10)$$

where R_G and T_G (with $k_{Gz}|T_G|^2 + p_G|R_G|^2 = p_G$) are known reflection and transmission coefficients for incidence from the left. For $G = 0$ we must also

include $|K, -k_{0z}\rangle$ as an incident wave and consequently

$$A_0 = R'_0 + T_0 B_0^*, \quad (2.11)$$

$$B_0^- = T'_0 + R_0 B_0^*, \quad (2.12)$$

where R'_0 and T'_0 are coefficients for incidence from the right. From (2.8), (2.10) and (2.12)

$$B_G^* = S(\mathbf{G}, \mathbf{0}) T'_0 + \sum_{\mathbf{G}'} S(\mathbf{G}, \mathbf{G}') R_{\mathbf{G}'} B_{\mathbf{G}'}^*. \quad (2.13)$$

When this is solved for B_G^* , A_G can be obtained from (2.9) and (2.11). In principle, the summation in (2.13) extends over all \mathbf{G}' , but we can distinguish three types of waves: (a) above continuum threshold, open channels, allowed final states, denoted by F, F' , (b) below continuum threshold, in the well, closed channels leading to possible resonances with bound states, denoted by N, N' ; (c) below the bottom of the well, denoted by A, A' . Explicitly, the above conditions give, from (2.5) and (2.7)

$$k_{Fz}^2 > 0, \quad p_F^2 > 0, \quad (2.14a)$$

$$k_{Nz}^2 < 0, \quad p_N^2 > 0, \quad (2.14b)$$

$$k_{Az}^2 < 0, \quad p_A^2 < 0. \quad (2.14c)$$

For a smoothly varying V_a , the coefficients R_F are very small, except near threshold; for $V_a \sim z^{-3}$, R_F is always small. (This is unlike the case, previously considered, where V_a is a square well [13]). Also, the product $S(\mathbf{G}, A)R_A$ vanishes rapidly below the well bottom. Therefore the sum in (2.13) can be extended over N vectors only unless we are specifically interested in threshold effects (in which case we can suitably enlarge the set of N vectors). Then (2.13) becomes a matrix equation of finite size involving only the B_N^* .

As a first example, suppose there is only one N vector. Then

$$B_N^* = [1 - S(N, N)R_N]^{-1} S(N, \mathbf{0}) T'_0. \quad (2.15)$$

Since $|R_N| = 1$, we can put $S(N, N)R_N = |S| \exp(i\delta)$ with δ real and $|S| < 1$. $|S|^2$ is the specular reflection coefficient for $|K + N, -p_N\rangle$ from the potential V_r alone. A resonance occurs when $|S| - \exp(-i\delta)$ is small. It must be noted that $|S|$ and δ are functions of E only through p_G , or equivalently through $\epsilon = \hbar^2 p_G^2 / 2M$, the energy of perpendicular motion measured from the bottom of the well. The condition $\exp[-i\delta(\epsilon)] = 1$ gives the bound state energies ϵ_b in the well, or the binding energies $D - \epsilon_b$. For ϵ near ϵ_b we can expand

$$\delta(\epsilon) = 2\pi n_b + \frac{d\delta}{d\epsilon} (\epsilon - \epsilon_b), \quad n_b \text{ integer} > 0, \quad (2.16)$$

and then, using the unitarity condition

$$|S|^2 = 1 - \sum_{\mathbf{F}} \frac{p_F}{p_N} |S(\mathbf{F}, N)|^2, \quad (2.17)$$

we find,

$$B_N^* \simeq i S(N, \mathbf{0}) T_0' \exp(i\delta) \left[\frac{d\delta}{d\epsilon} \left(\epsilon - \epsilon_b + i \frac{\Gamma}{2} \right) \right]^{-1}, \quad (2.18)$$

which is a typical resonance with a width

$$\Gamma = 2 \left(\frac{d\delta}{d\epsilon} \right)^{-1} (1 - |S|) \simeq \left(\frac{d\delta}{d\epsilon} \right)^{-1} \sum_F \frac{p_F}{p_N} |S(F, N)|^2. \quad (2.19)$$

Then, from (2.9) and (2.13) with $\mathbf{G} = \mathbf{F}$ and $\mathbf{G}' = \mathbf{N}$, using $|T_F|^2 \simeq p_F/k_{Fz}$, $|T_0|^2 \simeq k_{0z}/p_0$,

$$|A_F|^2 = \frac{p_F k_{0z}}{k_{Fz} p_0} \left| S(\mathbf{F}, \mathbf{0}) + i S(\mathbf{F}, N) R_N S(N, \mathbf{0}) \left[\frac{d\delta}{d\epsilon} \left(\epsilon - \epsilon_b + i \frac{\Gamma}{2} \right) \right] \right|^2. \quad (2.20)$$

This is also valid for $\mathbf{F} = \mathbf{0}$, since R_0' is negligible in the present approximation scheme. Further discussion of (2.20) is postponed to sections 3 and 4, but it should be noted that it is only valid, of course, for $|\epsilon - \epsilon_b| < (d\delta/d\epsilon)^{-1}$.

The general case can be handled in a similar way. Define

$$b_N = R_N'^{1/2} (p_N/p_0)^{1/2} B_N^*, \quad (2.21)$$

$$s_{GG'} = R_G'^{1/2} p_G'^{1/2} S(\mathbf{G}, \mathbf{G}') p_G'^{-1/2} R_G'^{1/2}. \quad (2.22)$$

Then (2.13) becomes

$$b_N = s_{N0} T_0' + \sum_{N'} s_{NN'} b_{N'}. \quad (2.23)$$

The matrix $s_{NN'}$ obeys the condition, analogous to (2.17),

$$s^\dagger s = 1 - g, \quad (2.24)$$

with

$$g_{NN'} = \sum_F s_{FN}^* s_{FN'}. \quad (2.25)$$

We also have $ss^\dagger = s^\dagger s$ on account of the time-reversal symmetry

$$p_G S(\mathbf{G}, \mathbf{G}') = p_{G'} S(\mathbf{G}', \mathbf{G}). \quad (2.26)$$

Then s is a normal matrix and can be diagonalized. Let the eigenvectors be $e_{N\nu}$ and write the eigenvalues in the form $(1 - g_\nu)^{1/2} \exp(i\delta_\nu)$, where g_ν are the eigenvalues of g . Repeating the steps leading to (2.20), we arrive at

$$|A_F|^2 = \frac{k_{0z}}{k_{Fz}} \left| s_{F0} + \sum_\nu \frac{s_{F\nu} s_{\nu 0} \exp(-i\delta_\nu)}{\exp(-i\delta_\nu) - 1 + \frac{1}{2} g_\nu} \right|^2, \quad (2.27)$$

for $g_\nu \ll 1$, where

$$s_{F\nu} = \sum_{N'} s_{FN'} e_{N'\nu}^*, \quad s_{\nu 0} = \sum_N e_{N\nu} s_{N0}. \quad (2.28)$$

Near an isolated resonance, the relevant δ_ν can be expanded, yielding a formula like (2.20), with $\Gamma = (d\delta_\nu/dE)^{-1}g_\nu$, if the non-resonant transitions can be neglected.

The theory given here is fully unitary, as shown in the Appendix. Even the crudest approximation, $|A_F|^2 = (p_F k_{0z}/k_{Fz} p_0) |S(F, \mathbf{0})|^2$ is nearly unitary if $E > D$ and several diffracted beams are allowed, since in this approximation

$$\sum_F \frac{k_{Fz}}{k_{0z}} |A_F|^2 = \sum_F \frac{p_F}{p_0} |S(F, \mathbf{0})|^2. \quad (2.29)$$

3. Resonance maxima and minima

The treatment of the general case in section 2 is rather formal and requires a numerical diagonalization of $s_{NN'}$. A major simplification occurs if $|s_{NN'}|$ is nearly unity, in which case B_N^+ is still given approximately by (2.15), except near the crossing of two resonances, and isolated resonances are described by (2.20). We show here that much of the existing experimental data and the corresponding calculations using hard corrugated wall (HCW) potentials are explained by (2.20), where further $S(G, G')$ is computed in the Kirchhoff approximation.

To be specific, we consider in detail the case of He/LiF(001) with $ka = 16$ [5]. The surface profile is well approximated by

$$\zeta(x, y) = \frac{1}{2} \zeta_0 [\cos(2\pi x/a) + \cos(2\pi y/a)], \quad (3.1)$$

with $\zeta_0 = 0.307 \text{ \AA}$ [11]. For this simple surface

$$S(G, G') = -\exp[i(p_G + p_{G'})z_0] i^{-|m| - |n|} |S(G, G')|, \quad (3.2)$$

where z_0 is defined in (2.1) and m and n are integers defined by $m = m_G - m_{G'}$, $n = n_G - n_{G'}$ with

$$G = (2\pi/a)(m_G, n_G, 0). \quad (3.3)$$

The magnitude of S is given explicitly in terms of Bessel functions:

$$|S(G, G')| = P(G, G') J_{|m|}((p_G + p_{G'})\zeta_0/2) J_{|n|}((p_G + p_{G'})\zeta_0/2). \quad (3.4)$$

$P(G, G')$ is the "obliquity prefactor" (of order unity) given by [10]

$$P(G, G') = \frac{p_{G'} \cdot (p_{G'} - p_G)}{p_G(p_{G'} + p_G)} = \frac{1 + \cos \theta \cos \theta' - \sin \theta \sin \theta' \cos(\phi - \phi')}{\cos \theta (\cos \theta + \cos \theta')}, \quad (3.5)$$

where $\theta, \phi, \theta', \phi'$ are the angles of the vectors $p_G = (K + G, -p_G)$ and $p_{G'} = (K + G', p_{G'})$. Using (3.2), eq. (2.20) becomes

$$\frac{k_{Fz}}{k_{0z}} |A_F|^2 = \frac{p_F}{p_0} |S(F, \mathbf{0})|^2 \left| 1 + \frac{i^{2l+1} |S(F, N)| |S(N, \mathbf{0})| / |S(F, \mathbf{0})|^2}{(d\delta/d\epsilon) (\epsilon - \epsilon_b + i\Gamma/2)} \right|^2, \quad (3.6)$$

with the sign of the resonant term determined by

$$2l = |m_N| + |m_F - m_N| - |m_F| + |n_N| + |n_F - n_N| - |n_F| \quad (3.7)$$

We have used the fact that in this case $\exp(i\delta) = -R_N \exp(2ip_N z_0)$ to cancel out all other phase factors, leaving only $i^{2l} = (-1)^l$. Note that P and $d\delta/de$ are positive by nature and that all the Bessel functions in (3.4) turn out to be positive in our case.

Let us define the ratio b of resonant to elastic amplitude, in this case

$$b = (-1)^l 2 |S(F, N)| |S(N, 0)| \left[\Gamma \left(\frac{d\delta}{de} \right) |S(F, 0)| \right]^{-1}. \quad (3.8)$$

The main results for the profile (3.1) are:

- (i) b is real, hence *isolated resonances have a symmetric, lorentzian shape*;
- (ii) for resonances that do not overwhelm the background ($b > -2$) the factor $(-1)^l$ determines uniquely that an *isolated resonance gives rise to a maximum for l even, a minimum for l odd*;
- (iii) in a region where the background is small ($|b| > 2$) all resonances give rise to maxima.

To clarify these statements, we recall that for general, complex $b = b_1 + ib_2$, the line shape of an isolated resonance as a function of $x = 2(\epsilon - \epsilon_b)/\Gamma$ is given by

$$\left| 1 + \frac{ib}{x+i} \right|^2 = 1 + \frac{b_1^2 + b_2^2 + 2b_1 + 2b_2 x}{x^2 + 1}. \quad (3.9)$$

For $b_2 = 0$, the line is always lorentzian, and the intensity at resonance is a maximum if $b_1 > 0$, a minimum if $0 > b_1 > -2$ and a maximum again for $b_1 < -2$. For $b_1 = -2$ the resonance is unnoticeable.

The parameter x in (3.9) can be related to an angle instead of the energy by the replacement $\epsilon - \epsilon_b = (d\epsilon/d\theta)(\theta - \theta_b)$: thus the considerations given here apply directly to the shape of structure seen in plots of diffracted intensity in beam F as a function of incident polar (θ_i) or azimuthal (ϕ_i) angle.

The azimuthal plots at $\theta_i = 70^\circ$ are available [5] to test this simple theory. For the specular beam $(m_F, n_F) = (0, 0)$, we find $l = |m_N| + |n_N|$, and indeed N beams $(0, 1)$ and $(0, \bar{1})$ give minima, while $(0, \bar{2})$, $(1, \bar{1})$ and $(\bar{1}, 1)$ give maxima. In fact, table 1 shows that (3.7) gives correct predictions for all the azimuthal plots reported in ref. [4]. It also predicts correctly the structure in the polar plots for the $(\bar{1}, 0)$ and $(\bar{1}, 1)$ beams, and for the $(0, 2)$ resonance at 60° in the $(0, 0)$ beam. The other resonances in the $(0, 0)$ beam, at $\theta_i < 50^\circ$, are stronger than the background and thus cannot be but maxima according to (3.9).

Since the dominant resonances have $m_N = 0$, (3.7) correctly predicts that the overall pattern for a beam is to be determined by n_F alone, as remarked in ref. [4].

The width Γ of an isolated resonance is correctly predicted by (2.19) to depend only on the resonant state itself and not on the particular initial and final states involved in the scattering. Γ contains the factor $(d\delta/de)^{-1}$, which is inversely proportional to the density of bound states and is small for states near the top the well,

Table 1

Ratio of resonance to background amplitude (eq. (3.8)) for He/LiF at $\Theta_i = 70^\circ$, $k_i = 5.76 \text{ \AA}^{-1}$; because the intensity at resonance is proportional to $(1 + b)^2$, negative b implies a resonance minimum

Resonance		b for output beam (m_F, n_F)						
		0, 0	$\bar{1}, 0$	$\bar{1}, 1$	$\bar{1}, \bar{1}$	$\bar{2}, 0$	$\bar{2}, 1$	$\bar{1}, \bar{2}$
2	0, $\bar{1}$	-0.97	-1.29	0.88	-0.44	-1.44	0.73	-0.23
3	0, $\bar{1}$	-0.61	-0.83	-0.28	0.54	-0.93	-0.29	1.37
0	0, $\bar{2}$	0.15	0.21	0.04	-0.38	0.21	0.03	1.13
1	0, $\bar{1}$	-1.10	-1.39	1.07	-0.47	-1.49	0.87	-0.24
1	0, $\bar{2}$	0.16	0.24	0.04	-0.40	0.27	0.05	0.88
0	$\bar{1}, \bar{2}$	-0.06	0.15	-0.30	0.03	0.29	-0.45	0.01
2	0, $\bar{2}$	0.16	0.25	0.05	-0.39	0.28	0.05	0.75
3	0, $\bar{2}$	0.16	0.25	0.05	-0.40	0.29	0.05	0.72
0	0, $\bar{1}$	-1.39	-1.49	1.54	-0.50	-1.38	1.17	-0.24
0	$\bar{1}, \bar{1}$	0.56	0.35	0.05	-0.37	0.22	0.03	-0.61
0	$\bar{1}, \bar{2}$	-0.06	-0.04	0.00	0.11	-0.03	0.00	-0.23
2	$\bar{1}, \bar{1}$	0.68	-0.90	1.32	-0.32	-2.07	2.18	-0.20
2	$\bar{2}, \bar{1}$	-0.08	0.28	-0.31	0.12	-0.53	0.98	0.07
1	$\bar{1}, \bar{1}$	0.64	-0.95	1.65	-0.33	-1.94	2.55	-0.20

especially if the potential is long range. (This factor can also be estimated semiclassically, since $\delta = 2p_N w$, where w is the effective width of the well and $\hbar d\delta/d\epsilon = 2Mw/hp_N$ is the period of bound motion). The other factor in Γ gives the total scattering probability out of state N and usually increases as ϵ approaches continuum threshold, but $(d\delta/d\epsilon)^{-1}$ is dominant and the states near threshold are correctly predicted to have narrow widths.

The numerical value of b for isolated resonance lines is also well approximated by (3.8). For the azimuthal plots at $\theta_i = 70^\circ$, the order of magnitude of the Bessel functions appearing in $S(F, N)S(N, \mathbf{0})$ is $J_0 \simeq 0.70, J_1 \simeq 0.45, J_2 \simeq 0.15$; in $S(F, \mathbf{0})$ the orders of magnitude are $J_0 \simeq J_1 \simeq 0.6$ and $J_2 \simeq 0.2$; g is roughly the same ($\simeq 0.6$) for all bound states. This readily explains in a qualitative way the relative magnitude of the peaks. Table 1 gives the values of b from eq. (3.8) for a qualitative comparison with figs. 1–3 of ref. [4].

If a second harmonic $\xi_1 \cos(2\pi x/a)\cos(2\pi y/a)$ is added to the profile (3.1), then $S(G, G')$ has both real and imaginary components. Expanding for small ξ_1 , one finds that $J_{|m|}J_{|n|}$ is replaced by

$$J_{|m|}J_{|n|} + \frac{1}{4}i\xi_1 (i^{|m|-|m+1|} J_{|m+1|} + i^{|m|-|m-1|} J_{|m-1|}) \times (m \rightarrow n). \quad (3.10)$$

The shape of the resonances is thus affected by the admixture of ξ_1 , as can be seen by comparing figs. 1 and 4 of ref. [4]. (Overlapping lorentzian peaks can also give rise to asymmetric line shapes.)

An example with asymmetric line shapes is provided by He/graphite scattering. The corrugation is

$$\zeta(x, y) = 2\xi_{10} \{ \cos(2\pi x/a) + \cos(2\pi y/a) + \cos[2\pi(x - y)/a] \}, \quad (3.11)$$

with $\xi_{10} = -0.023 \text{ \AA}$ [14]. For $k = 7 \text{ \AA}^{-1}$, a typical value of $c = |\xi_{10}|(p_G + p_{G'})$ is 0.15, so that $\exp[i(p_G + p_{G'})\zeta]$ can be expanded.

To display the results, we define

$$\begin{aligned} J_{mn}(c) &= \int \frac{dx dy}{a^2} \exp \left[-i \left(\frac{2\pi mx}{a} + \frac{2\pi ny}{a} \right) - i(p_G + p_{G'}) \zeta(\mathbf{R}) \right] \\ &= \sum_{l=-\infty}^{\infty} i^{|l|+|m+l|+|n-l|} J_{|m+l|}(2c) J_{|n-l|}(2c) J_{|l|}(2c). \end{aligned} \quad (3.12)$$

To order c^2 (within the Kirckhoff approximation, which is not exact even for small $|p_0 \xi_{10}|$):

$$J_{00} = 1 - 3c^2, \quad (3.13)$$

$$J_{10} = J_{1\bar{1}} = +ic - c^2, \quad (3.14)$$

$$J_{11} = J_{2\bar{1}} = 2J_{20} = 2J_{2\bar{2}} = -c^2. \quad (3.15)$$

Inserting in (3.6), we conclude that the (1, 0) and (1, $\bar{1}$) resonances give asymmetric minima, those in (3.15) give weak maxima in the specular intensity, and so on, in agreement with recent experiments [14] and with calculations we have performed by the method of ref. [4]. Calculations by Chow [15], also give resonances with signatures that are predicted correctly by the above considerations [it must be noted that in the (01) and (0, $\bar{1}$) beams, in his notation, there are resonances strong enough to overwhelm the background].

4. Interacting resonances

To keep the discussion simple, we consider first the case where two beams N, N' have exactly the same energies and matrix elements by symmetry. This occurs, for instance, for the (1, 0) and (0, 1) beams when scattering is done in the $\phi = 45^\circ$ azimuth for He/LiF. The two coupled equations for b_N and $b_{N'}$ are

$$b_N = s_{NN}b_N + s_{N'N'}b_{N'} + s_{N0}T'_0, \quad (4.1)$$

$$b_{N'} = s_{N'N}b_N + s_{N'N'}b_{N'} + s_{N'0}T'_0, \quad (4.1')$$

and, when $s_{NN'} = s_{N'N}$ and $s_{N'N'} = s_{NN}$, the solution is

$$b_N = b_{N'} = s_{N0}T'_0 / (1 - s_{NN} - s_{N'N'}). \quad (4.2)$$

In the language of section 2, this amounts to say that resonant transitions occur

only [16] to the state given by the symmetric eigenvector of the matrix s , which has eigenvalue $s_{NN} + s_{NN'}$. The shift due to the mixing can be discussed most simply in terms of the relation between the phases of s_{NN} and $s_{NN'}$. In the Kirchhoff approximation for He/LiF, the relative phase is given by i^{-l} , where $l = |m_N - m_{N'}| + |n_N - n_{N'}|$. Then, for the profile (3.1):

$$b_N = b_{N'} = \frac{s_{N0} T_0}{1 - i(d\delta/d\epsilon)(\epsilon - \epsilon_0) - (|s_{NN}| + i^{-l}|s_{NN'}|)}, \quad (4.3)$$

where ϵ_0 is the unshifted energy at crossing, δ is the phase of s_{NN} and $d\delta/d\epsilon$ is evaluated at $\epsilon = \epsilon_0$. With these approximations

- (i) for even l the resonance is not shifted,
- (ii) for odd l the resonance is shifted to

$$\epsilon_0 \pm |s_{NN'}|(d\delta/d\epsilon)^{-1}, \quad (4.4)$$

where the $-$ sign applies for $l = 1, 5, \dots$ and the $+$ sign for $l = 3, 7, \dots$.

More generally, if δ_N and $\delta_{N'}$ are the phases of s_{NN} and $s_{NN'}$, we have

$$s_{NN'} = s_{N'N} = i^l |s_{NN'}| \exp[i(\delta_N + \delta_{N'})/2], \quad (4.5)$$

and the resonance crossing occurs when δ_N and $\delta_{N'}$ are both multiples of 2π . One finds again that there is no splitting, to lowest order, for even l . For odd l there is a symmetric splitting and the shift, for $|s_{NN} - s_{N'N'}| \ll |s_{NN'}|$ is

$$\pm 2 |s_{NN'}| (d\delta_{N'}/d\epsilon + d\delta_N/d\epsilon)^{-1}. \quad (4.6)$$

This approximate theory predicts no splitting when $N - N'$ is a $\{1, 1\}$ or $\{2, 0\}$ vector. Experimentally, Frankl's group reports [17] shifts $V(1, 1)$ that are not inconsistent with zero and $\langle 0|V(1, 0)|0\rangle \simeq 0.25$ meV for the ground state band at $\theta_i \simeq 70^\circ$ and $k_i = 5.8 \text{ \AA}^{-1}$. The predictions of (4.6), using the Kirchhoff values for $s_{NN'}$ are reported in table 2. The values of $d\delta/d\epsilon$ were determined simply by fitting the formula [18]

$$E = -D[1 - \lambda(n + \frac{1}{2})]^\alpha \quad (4.7)$$

to the observed bound states and setting $\delta = 2\pi n$. A good fit is obtained for $\alpha = 5.8$, which corresponds to a 6-3 potential [18], or for $\alpha = 6$, which corresponds

Table 2

Splittings for He/LiF; the matrix elements (in 10^{-2} meV) connecting bound states i, j for $N - N' = \{1, 0\}$ are calculated from (4.4), using the Kirchhoff approximation for $s_{NN'}$; the surface parameters used are a lattice constant of 2.817 Å and a corrugation of 0.307 Å; the well parameters are given in the text

ij	00	11	22	33	01	02	03	04	12	13	23
V	30	15	6	2	21	10	4	1	8	3	3

Table 3

Splittings for He/graphite, the matrix elements (in 10^{-2} meV) connecting bound states i, j for $N - N' = (1, 0)$ are calculated from eq. (4.4) using the Kirchhoff approximation for $|s_{NN'}|$; the surface parameters used are a lattice constant of 2.465 Å and a peak to peak corrugation of 0.21 Å

ij	00	11	22	33	44	01	02	03	04	12	13	23
V	17	15	10	5	2	16	12	7	2	2	7	7

to a 9–3 potential [19]; the well depth D is around 9.3 meV. For a flat-bottom well with a repulsive wall [4] the best fit is obtained for $D = 8$ meV. If this value is D is used, $\langle 0|V(1,0)|0\rangle$ changes to 0.28 and the other values of table 2 are unchanged. It should be noted that the Kirchhoff approximation gives an overestimate for the low-lying states, due to neglect of shadowing and double scattering. For the ground state, using the exact hard-wall value $|s_{NN'}| = 0.26$ instead of the Kirchhoff value $|s_{NN'}| = 0.35$, we obtain $\langle 0|V(1, 0)|0\rangle = 0.22$ meV.

The bound states for He⁴/graphite seem to be best fitted by (4.7) with α near the value 3.25 that corresponds to a 10–5 potential [18]. The simple estimate of matrix elements given in (3.13)–(3.15) should be fairly accurate. It is evident that only the (1, 0) and (1, $\bar{1}$) vectors give sizeable splittings, because their matrix elements are the largest and are almost pure imaginary. Formula (4.6) gives the values reported in table 3, which are generally somewhat smaller than the experimental values [20]. Simple estimates show that the remainder can be attributed to the fact that the bottom of the attractive well is not flat, as assumed so far, but varies periodically as shown in fig. 2 of the paper by Carlos and Cole [21]. This “well bottom” effect, unlike the “hard wall” effect, can certainly be treated by perturbation theory (see next section) and in this case the two effects are simply additive to first order. A more complete theory of He scattering from graphite will be published separately, including resonance broadening due to inelastic effects, which can be handled phenomenologically through an imaginary part of the potential [15].

5. Distorted wave theory

An alternative approach to the resonant scattering problem is through the use of eigenstates of the flat surface (distorted waves) as a basis set [12]. The flat surface potential $V_0(z)$ is taken to be the x – y average of $V(r)$, which coincides with the $G = 0$ Fourier component of expansion (1.3). The real eigenfunctions of V_0 include continuum states labeled by q ($q > 0$) and F , or simply by f :

$$\chi_f = |\chi; \mathbf{K} + \mathbf{F}, q\rangle = \chi_q(z) \exp[i(\mathbf{K} + \mathbf{F}) \cdot \mathbf{R}], \quad (5.1)$$

with energy $E_f = \hbar^2 [(\mathbf{K} + \mathbf{F})^2 + q^2]/2M$. There are also bound states

$$\chi_b = |\chi; \mathbf{K} + \mathbf{N}, n\rangle = \chi_n(z) \exp[i(\mathbf{K} + \mathbf{N}) \cdot \mathbf{R}], \quad (5.2)$$

with energy $E_b = \hbar^2 (\mathbf{K} + \mathbf{N})^2/2M + E_n$ and discrete $E_n < 0$.

Exact eigenstates of V include scattering states

$$\psi_f^{(\pm)} = |\psi;^{(\pm)} \mathbf{K} + \mathbf{F}, \mp q\rangle. \quad (5.3)$$

The state $\psi_f^{(+)}$ evolves from a free wave $|\mathbf{K} + \mathbf{F}, -q\rangle$ with outgoing wave boundary conditions; the state $\psi_f^{(-)}$ evolves into $|\mathbf{K} + \mathbf{F}, q\rangle$ with incoming wave boundary conditions. One can similarly define states $\chi_f^{(\pm)}$; however we have simply

$$\chi_q^{(\pm)}(z) = \exp(\pm i\phi) \chi_q(z), \quad (5.4)$$

and the phases ϕ all cancel at the end. In terms of χ, ψ we have

$$\frac{k_{Fz}}{k_{0z}} |A_F|^2 = \left| \delta_{F0} \exp(i\phi_0) - \frac{im}{\hbar^2 k_{0z}} \langle \chi; \mathbf{K} + \mathbf{F}, k_{Fz} | V | \psi^{(+)}; \mathbf{K}, -k_{0z} \rangle \right|^2. \quad (5.5)$$

We must still determine ψ , or equivalently the t -matrix, defined by

$$t_{f0} = \langle \chi; \mathbf{K} + \mathbf{F}, q | V | \psi^{(+)}; \mathbf{K}, -k_{0z} \rangle, \quad (5.6)$$

and similarly for t_{b0} . The matrix element in (5.5) is t_{f0} evaluated "on the energy shell", i.e. for $q = k_{Fz}$. The equation obeyed by t is [22,23,24]

$$t_{g0} = v_{g0} \exp(i\phi_0) + \sum_{g'} v_{gg'} \frac{1}{E - E_{g'}} t_{g'0}, \quad (5.7)$$

where $E = E_0 + i0^+$ and g, g' run over both f and b states. The DWBA is obtained by taking $t_{f0} = v_{f0} \exp(i\phi_0)$. Near an isolated resonance ($E \simeq E_b$) one finds approximately

$$\exp(-i\phi_0) t_{f0} = v_{f0} + \frac{v_{fb} v_{b0}}{E - E_b - \Sigma}, \quad (5.8)$$

where

$$\Sigma = \sum_f |v_{bf}|^2 / (E - E_f). \quad (5.9)$$

The imaginary part of Σ gives the width:

$$-\text{Im } \Sigma = \frac{\Gamma}{2} = \sum_F \frac{m}{2\hbar^2 k_{Fz}} |v_{Fb}|^2, \quad (5.10)$$

where the sum is over the "open channels" and explicitly

$$v_{Fb} = \langle \chi; \mathbf{K} + \mathbf{F}, k_{Fz} | V | \chi; \mathbf{K} + \mathbf{N}, n \rangle. \quad (5.11)$$

Then, from (5.10), neglecting the real part of Σ and using $v_{00} = 0$,

$$|A_0|^2 = \left| 1 - \frac{i(m/\hbar^2 k_{0z}) |v_{b0}|^2}{E - E_b + i\Gamma/2} \right|^2, \quad (5.12)$$

$$|A_F|^2 = \frac{m^2}{\hbar^4 k_{0z} k_{Fz}} \left| v_{F0} + \frac{v_{Fb} v_{b0}}{E - E_b + i\Gamma/2} \right|^2. \quad (5.13)$$

The resonance line shapes given by these formulae are those discussed in section 3 [23,24]. For a surface with x - y inversion symmetry, all the matrix elements are real. The prediction of (5.12), (5.13) is that, excluding the case when v_{Fb} is (nearly) zero for all $F \neq 0$:

(i) All resonances in the specular beam are symmetric minima, with b_1 (eq. (3.9)) given by $-2|v_{0b}|^2/\Sigma_F|v_{Fb}|^2$. Clearly $0 > b_1 > -2$, with $b_1 \simeq -2$ only in the case we have excluded.

(ii) Resonances in the non-specular beams are asymmetric, with b_2 (eq. (3.9)) given by $2v_{Fb}v_{b0}/v_{F0}\Gamma$. The maximum dominates for $|b_2| \gtrsim 1$.

The exceptional case, when the bound state couples (almost) only to the incident (and specular) beams, can be treated by an approximation that preserves unitarity [12]. Then b is no longer real and for $b_1 \simeq -2$ the specular intensity displays an asymmetric maximum and the other intensities have corresponding minima. (The exceptional nature of this case was not recognized in ref. [12], where the results (5.12) and (5.13) are said incorrectly to apply only when inelastic processes are present).

The results of straight perturbation theory are thus quite different from those obtained in section 3 which agree with experiments and full numerical calculations. The discrepancy has been ascribed correctly to the neglect of higher order terms in perturbation theory and rules have been suggested to recognize when such terms are important [2,25]. Recently such rules have been put on a firm formal basis by Wolfe and Weare [24], who start from the exact formula of the same structure as (5.8):

$$\exp[-i(\phi_0 + \phi_f)] t_{f0} = \tau_{f0} + \tau_{fb}\tau_{b0}/(E - E_b - \Sigma), \quad (5.14)$$

where Σ is now given by (5.9) with τ replacing v , and τ obeys the equation:

$$\exp(-i\phi_g) \tau_{gg'} = v_{gg'} \exp(i\phi_{g'}) + \sum_f v_{gf} \frac{1}{E - E_f} \tau_{fg'} + \sum_{b' \neq b} v_{gb'} \frac{1}{E - E_{b'}} \tau_{b'g'}. \quad (5.15)$$

The sum over bound states $b' \neq b$ will be neglected in the following. (The state b must be singled out because it is near resonance, and the method is easily extended to the case of two or more "near resonant" bound states).

The correct signature of isolated resonances for LiF is predicted by assuming: (i) the only non-zero matrix elements $v_{gg'}$, are those in which $\mathbf{G}' - \mathbf{G}$ is a $\{1, 0\}$ vector, (ii) only the leading term in a perturbation expansion of (5.9) is to be kept and (iii) the "on-shell" part of the sum over intermediate states dominates, i.e.

$$\sum_f v_{gf} \frac{1}{E - E_f} v_{fg'} \simeq -i \frac{m}{2\hbar^2} \sum_F \frac{1}{k_{Fz}} v_{gF} v_{Fg'}. \quad (5.16)$$

Within this framework, the effective $\{1, 0\}$ matrix elements $\tau(1, 0) = V(1, 0)$ are

real for any surface with inversion symmetry, the effective $\tau(1, 1)$ and $\tau(2, 0)$ are proportional to $-iV(1, 0)^2$ by (5.16) and are thus imaginary, the effective $\tau(2, 1)$ and $\tau(3, 0)$ are real again and so on. To express these results in terms of s -matrix elements, one must recall that the s -matrix corresponding to the t -matrix τ is $\sigma_{f_0} = -2\pi i \delta(E_f - E) \tau_{f_0}$ and that, within perturbation theory, the reflected amplitude is real (and $\simeq 1$). Thus $\alpha(0, 0)$ is real, $\alpha(1, 0)$ imaginary, $\alpha(2, 0)$ and $\alpha(1, 1)$ are real again and so on, in agreement with (3.2). (It should be noted that the s -matrix σ is not the same as the matrix s of section 3 but there is a formal correspondence nevertheless). The main difficulty with this perturbation-theory approach is that it is not possible to reproduce the observed intensities off-resonance for He/LiF by including only a $(1, 0)$ Fourier component in the expansion (1.3) for the potential. On the other hand, for He/Graphite it is consistent to assume that only the fundamental harmonic ($V(1, 0) = V(1, \bar{1})$ in this case) is significant, at least at $\theta_i = 70^\circ$. However, perturbation theory would predict symmetric resonance lines in the specular beam, whereas the observed lines are more asymmetric than in He/LiF.

Perturbation theory is probably most applicable to treat the energy shifts and splittings of interacting resonances, especially in the lowest bound states for which the repulsive part of the potential is effectively rather soft. Indeed, it has been applied with some success to this end [2,25]. A more refined theory should incorporate the results of section 3 for the "hard wall" part of the potential and use perturbation theory for the effects due to the shift of the "well bottom", as discussed briefly in section 4 for the band splittings. Further development along these lines and applications to other systems are left for future work.

The theory of section 3 can be applied with a minimum of computation to data analysis. In a survey of the literature, we have found that it provides a basis for the interpretation of existing data in all cases, but the number of independent data on systems other than He/LiF and He/graphite is not much larger than the number of adjustable parameters in the potential, so that the test of theory is not very stringent. In particular, the effective surface corrugations for H and D on alkali halides [26] seem to be described by two Fourier components of comparable size, instead of the simple corrugation (3.1).

Appendix

Using the approximate form for (2.13)

$$B_N^* \simeq T'_0 S(N, \mathbf{0}) + \sum_{N'} S(N, N') R_{N'} B_{N'}^*, \quad (\text{A.1})$$

and assuming $R'_0 \simeq 0$ yields the scattered amplitudes

$$A_F = T_F [S(F, \mathbf{0}) T'_0 + \sum_N S(F, N) R_N B_N^*]. \quad (\text{A.2})$$

With the approximate relations

$$|T_0'|^2 \simeq k_{0z}/p_0, \quad |T_F|^2 \simeq p_F/k_{Fz}, \quad |R_N|^2 \simeq 1, \quad (\text{A.3})$$

the desired unitary sum can then be written

$$\sum_F \frac{k_{Fz}}{k_{0z}} |A_F|^2 = \sum_F \frac{p_F}{k_{0z}} \left\{ \frac{k_{0z}}{p_0} |S(F, \mathbf{0})|^2 + \left| \sum_N S(F, N) R_N B_N^* \right|^2 + [T_0'^* S^*(F, \mathbf{0}) \sum_N S(F, N) R_N B_N^* + \text{c.c.}] \right\}. \quad (\text{A.4})$$

Since the $S(\mathbf{G}, \mathbf{G}')$ obey the unitarity condition

$$\sum_F p_F S^*(F, \mathbf{G}) S(F, \mathbf{G}') + \sum_N p_N S^*(N, \mathbf{G}) S(N, \mathbf{G}') = \delta_{GG'} p_G, \quad (\text{A.5})$$

this becomes

$$\begin{aligned} \sum_F \frac{k_{Fz}}{k_{0z}} |A_F|^2 &= 1 - \sum_N \frac{p_N}{p_0} |S(N, \mathbf{0})|^2 + \sum_N \frac{p_N}{k_{0z}} |B_N^*|^2 \\ &\quad - \sum_N \frac{p_N}{k_{0z}} \left| \sum_{N'} S(N, N') R_{N'} B_{N'}^* \right|^2 - \sum_N \frac{p_N}{k_{0z}} [T_0'^* S^*(N, \mathbf{0}) \\ &\quad \times \sum_{N'} S(N, N') R_{N'} B_{N'}^* + \text{c.c.}]. \end{aligned} \quad (\text{A.6})$$

Substituting (A.1) for the third term in (A.6) gives

$$\sum_F \frac{k_{Fz}}{k_{0z}} |A_F|^2 = 1. \quad (\text{A.7})$$

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