SURFACE SCIENCE LETTERS

ON THE FOURIER COMPONENTS OF THE ATOM–SURFACE SCATTERING POTENTIAL

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In recent years there have been a number of interesting developments in the theoretical description of elastic diffraction of low energy neutral atoms by crystal surfaces. The first treatment of the problem was carried out some years ago by Lennard-Jones and coworkers [1] within the framework of the distorted wave Born approximation. However, this approximation is valid only when the scattering is very nearly entirely specular (the weak scattering limit) and recent experiments have shown this to be the exception rather than the rule for the scattering of light atoms from a large variety of surfaces [2–4].

The theory has been extended to the strong scattering limit by Cabrera et al. [5–7], using methods of the type which are called coupled channel calculations. These types of calculation have been extended and improved by Tsuchida [8], Wolken [9] and others [10–12]. The basic approach of this method is to write the atom–surface interaction potential as a Fourier series in directions parallel to the surface, i.e.

$$V = \sum_{G} V_G(z) \exp(iG \cdot R) , \tag{1}$$

where the position vector is written as $r = (R, z)$ with R parallel to the surface and z perpendicular, and G is a surface reciprocal lattice vector. The Schrödinger equation

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can then be developed into a set of linear coupled equations, with one equation for each diffracted or evanescent beam. The implicit assumption of this method is that it is reasonable to truncate the series (1) after a small number of terms.

The validity of this assumption appears to be confirmed by recent experimental results which seem to indicate, through the analysis of resonance splitting, that only the first one or two Fourier components of the potential are important [13,14].

In a typical calculation the Fourier components $V_G(z)$ are assumed to be exponential (the zero order usually being a Morse potential) with the strength of each component considered as an adjustable parameter, or the components are calculated directly from a summation of pairwise atomic potentials. From such a starting point the coupled channel calculations can be carried out in a manner which is free of further approximation. The splitting of energy levels observed in selective adsorption experiments is very well described. However, the difficulty is that away from resonance conditions, such calculations are only in qualitative agreement with the measured intensities of the diffracted peaks.

A quite different approach to the same problem has been to assume that the surface can be represented by a hard corrugated wall. This approach has been very successful as it gives, with few adjustable parameters (only one Fourier component of the shape function) results which are in quantitative agreement with experiment for the diffraction peak intensities [15]. Furthermore, the effects of resonance with the bound states are very well depicted by adding an attractive well in front of the surface [16,17].

The difference between these two approaches lies in the fact that the hard corrugated wall potential is the "steepest" of all possible potentials, and in fact is discontinuous at the surface and infinite below. Furthermore, it contains an infinity of slowly varying Fourier components in a compact manner. In order to establish this last statement, let us calculate the Fourier transform of a hard corrugated wall potential. It is usually taken to be infinite if $z < \phi(x)$ and zero if $z > \phi(x)$, where $\phi(x)$ is the corrugation function. We will assume for simplicity that the corrugations are only in one dimension. The difficulty with discussing directly the behavior of the Fourier components is that they are all infinite due to the singular nature of the potential for $z < \phi(x)$. Thus we choose to consider the finite corrugated wall potential defined by

$$V(x, z) = \begin{cases} V_0, & z < \phi(x), \\ 0, & z > \phi(x). \end{cases} \tag{2}$$

This potential becomes a hard corrugated wall in the limit $V_0 \to \infty$. Furthermore, it has been shown that the diffracted intensities produced by such a potential are very nearly the same as for the corrugated hard wall, even under conditions in which V_0 is only a factor 3 or 4 larger than the energy of the incident beam [18].

In order to write the potential of eq. (2) in the series form eq. (1), we make use of the integral representation of the Heaviside function $S(y)$, i.e.

$$V(x, z) = V_0 \, S(\phi(x) - z) , \tag{3}$$

where

$$S(y) = \lim_{\epsilon \to 0} \frac{1}{2\pi i} \int_{-\infty}^{+\infty} dq \, \frac{e^{iqy}}{q - i\epsilon} = \begin{cases} 1, & y > 0 , \\ 0, & y < 0 . \end{cases} \tag{4}$$

The Fourier components $V_G(z)$ are given by

$$V_G(z) = \frac{1}{a} \int_0^a dx \, e^{-iGx} \, V(x, z) , \tag{5}$$

where a is the period of the corrugation.

Using (3) and (4), and interchanging integrations, this becomes

$$V_G(z) = \lim_{\epsilon \to 0} \frac{V_0}{2\pi i a} \int_{-\infty}^{+\infty} dq \, \frac{e^{-iqz}}{q - i\epsilon} \int_0^a dx \, e^{-iGx} \, e^{iq\phi(x)} . \tag{6}$$

In order to go further it is necessary to choose $\phi(x)$, and we take the simplest and most often used form which is the sinusoidal corrugation,

$$\phi(x) = ha \sin(2\pi x/a) . \tag{7}$$

With this choice we can make use of the well known integral representation of the Bessel function in order to carry out the integral over x

$$\int_0^a dx \, \exp[-iGx + iqha \sin(2\pi x/a)] = aJ_g(qha) , \tag{8}$$

where $g = aG/2\pi$ is an integer. First, however, in order to avoid the appearance of Bessel functions of negative argument, it is convenient to transform the part of the integral over negative q into one over positive q. This gives

$$V_G(z) \equiv V_g(z) = \frac{V_0}{2\pi i} \int_0^\infty dq \left[\frac{e^{-iqz}}{q^2 + \epsilon^2} (q + i\epsilon) J_g(qha) + (-1)^g \frac{e^{iqz}}{q^2 + \epsilon^2} (-q + i\epsilon) J_g(qha) \right] . \tag{9}$$

We must consider separately the cases g even and g odd. Looking first at the case g even we have

$$V_g = \frac{-V_0}{\pi} \int_0^\infty dq \, \frac{q}{q^2 + \epsilon^2} J_g(qha) \sin(qz) + \frac{V_0}{\pi} \int_0^\infty dq \, \frac{\epsilon}{q^2 + \epsilon^2} J_g(qha) \cos(qz) . \tag{10}$$

Taking the limit $\epsilon \to 0$ is trivial for the first term and leads to the Lorentzian representation of the Dirac δ-function in the second term. Thus we have

$$V_g = -\frac{V_0}{\pi} \int\limits_0^\infty dq \frac{1}{q} J_g(qha) \sin(qz) + \frac{V_0}{2} J_g(0) \ . \tag{11}$$

Clearly the term involving $J_g(0)$ will contribute only for $g = 0$ since for all other cases $J_{g \neq 0}(0) = 0$. The remaining integral is a well known Fourier transform [19]. For the case $g = 0$, we have the final result

$$V_0(z) = \begin{cases} V_0 \ , & z < -ha \ , \\ \frac{1}{2}V_0 - (V_0/\pi) \sin^{-1}(z/ha) \ , & -ha < z < ha \ , \\ 0 \ , & z > ha \ ; \end{cases} \tag{12}$$

while for $g \neq 0$, we have

$$V_g(z) = \begin{cases} (-V_0/\pi g) \sin[g \sin^{-1}(z/ha)] \ , & -ha < z < ha \ , \\ 0 \ , & |z| > ha \ . \end{cases} \tag{13}$$

The situation for the case g odd is very similar and we obtain

$$V_g(z) = \frac{V_0}{\pi i} \int\limits_0^\infty dq \frac{1}{q} J_g(qha) \cos(qz) \ , \tag{14}$$

where the contribution corresponding to the δ-function term appearing in (10) is always vanishing. This is the cosine analog of the Fourier transform appearing in (11) and is

$$V_g(z) = \begin{cases} (V_0/\pi i g) \cos[g \sin^{-1}(z/ha)] \ , & -ha < z < ha \ , \\ 0 \ , & |z| > ha \ . \end{cases} \tag{15}$$

We note in passing that the expressions in eqs. (13) and (15) can obviously be written as polynomials in z/ha multiplied by $[1-(z/ha)^2]^{1/2}$. In fact, in terms of the Chebyshev polynomial of the second kind $U_g(z/ha)$ [20], we have for $g \geqslant 1$

$$V_g(z) = \begin{cases} (V_0/g)(-i)^g [1 - (z/ha)^2]^{1/2} U_{g-1}(z/ha) \ , & (z/ha)^2 < 1 \ , \\ 0 \ , & (z/ha)^2 > 1 \ . \end{cases} \tag{16}$$

For the negative reciprocal lattice vectors we have the relation

$$V_{-g}(z) = (-1)^g V_g(z) \ . \tag{17}$$

The first five of the Fourier components $V_G(z)$ are shown in fig. 1. We note that $V_0(z)$ which represents the average of the repulsive force at each point z, is zero for $z > ha$ and rises to V_0 for $z < -ha$. It is clearly a potential which gives rise to purely specular scattering for all particles incident with energy less than V_0. The higher
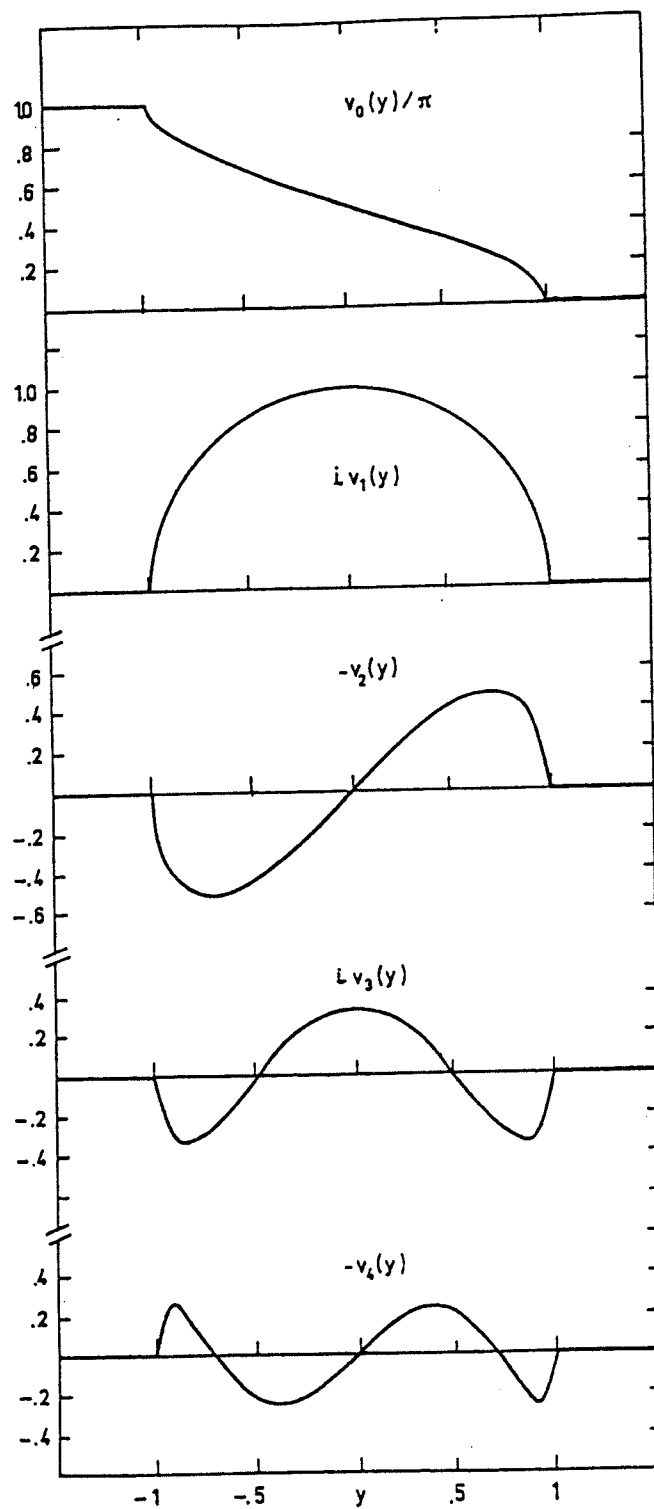
Fig. 1. The first Fourier components of the corrugated wall potential, where $v_n(y) = v_n(z/ha) = \pi V_n(z)/V_0$.

order components have an oscillatory behavior in z with the number of nodes increasing as g. The most important observation concerning these higher order components, however, is the fact that their strength decreases only as $1/g$. This is an extremely slow decay of the strength of the components and means that in order to adequately represent a corrugated wall potential, it is necessary to keep a large number of terms.

Before going further, we would like to point out that this slowly decreasing behavior of the Fourier components is not due solely to the discontinuous nature of the potential. We can demonstrate this by considering the continuous "corrugated exponential" potential defined by

$$V = C \exp[-\kappa(z - \phi(x))] . \tag{18}$$

Note that eq. (18) approaches a corrugated hard wall as $\kappa \to \infty$. With $\phi(x)$ given by (7), the Fourier expansion is straightforward giving

$$V_g(z) = (-i)^g I_g(\kappa ha) \exp(-\kappa z) , \tag{19}$$

where I_g is the modified Bessel function of the first kind. If the argument $\kappa ha > 1$ (i.e. for sufficiently "stiff" potentials), it is clear that there will be many important Fourier components.

Thus we are faced with the following problem. Calculations incorporating a hard corrugated wall potential, which contains a large number of non-negligible Fourier components, give a substantially better agreement with the experimental data than the coupled channel calculation (for all systems for which comparisons exist). On the other hand, the experimental results for resonance splitting, as interpreted by a coupled channel analysis seem to indicate that only one (for He–graphite [13]) or two (for He–alkali halide [14]) Fourier components are important.

In the light of this discrepancy it is perhaps interesting to consider again the question of level splitting in selective adsorption experiments as explained in a coupled channel analysis. Such splittings occur whenever two different reciprocal lattice vectors can provoke a transition into the same bound state while still preserving the conservation of total energy. The simplest of these calculations [10,12] assumes that the only important component of the potential is the one which directly links the two states involved and in this manner the treatment is completely analogous to the standard textbook calculation for the splitting of two degenerate states by a small perturbation. The agreement of the calculation with the observed values of the energy splitting is assured by adjusting the parameter associated with the strength of the Fourier component involved. However, if the potential has a large number of important Fourier components, a simple two-state analysis is no longer valid and one must consider the effects of all possible transitions linking the two states [10,21]. (Such effects are automatically taken into account in the hard corrugated wall calculations.) A simple calculation may be use-

ful for weakly corrugated surfaces or for merely estimating the strengths of few low order components of the potential, but it must be emphasized that the success of such calculations depends on the adjustment of parameters and in no way excludes the possibility of many other important Fourier components. Such a conclusion is supported by the previously mentioned fact that potentials determined from the coupled channel appraoch have not shown the same good quantitative agreement as the corrugated hard wall calculations for the diffracted intensities. The fact that degenerate bound state splittings are observed only for those transitions corresponding to the lowest reciprocal lattice vectors, can be explained as due to interferences between the higher order terms, or due to the fact that certain matrix elements can be small in spite of the fact that the corresponding potential components are large.

As a final remark, we should mention the fact that there have been a number of calculations of the He–alkali halide potential by summation of the pairwise atomic potentials, and in general these calculations have a small number of important Fourier components [8,10]. However, it must also be mentioned again that none of these potentials have been shown to give good quantitative agreement for both the splitting and the diffracted intensities. Thus, if we can assume, as the calculations seem to indicate, that the true interaction potential is indeed reasonably well approximated by a very stiff corrugated wall, both eqs. (19) and (16) make it clear that the true potential must contain many important terms in its Fourier expansion.

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