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Abstract
It is shown that using the Hutchison prescription to account for inelastic effects
on surface resonances can be partially justified when sticking is taken into
account. The prescription is to multiply each elastic matrix element for collision
with the repulsive potential by the appropriate 'square root of the Debye–Waller
factor'. It is shown that, under certain assumptions, it is correct to do so for the
collisions entering and exiting the resonant surface state.

1. Introduction

Atom–surface scattering is reasonably well described by approximate formulae over a wide
range of conditions, ranging from the extreme quantum limit of diffraction of light atoms
(usually He^4) from an ordered, low-temperature surface, to the classical limit of the collision of
a heavy atom with a room-temperature surface, possibly a disordered one. Detailed numerical
calculations are of course needed for a full explanation, and one hopes a prediction, of the
distribution in energy and angle of the atoms scattered from a particular surface. Numerical
methods work very well in the extreme quantum limit, when surface dynamics can be neglected.
On the other hand, full numerical treatments of inelastic quantum scattering are very time
consuming, if they are to be used to reveal dependence on several parameters, such as energy and
angles of the incident atom and surface temperature. Further, they also involve approximations,
such as the imperfect knowledge of the atom–surface potential, and a very simplified treatment
of surface dynamics. Thus, there is still a need for effective approximations.

Inelastic effects can be accurately computed for a realistic surface dynamics when they can
be treated as a small perturbation, using the distorted-wave Born approximation (DWBA) [1].
However, even at low temperature, the DWBA does not account properly for inelastic effects
on resonant scattering [2], either elastic or inelastic [3], because in a resonant process the atom
undergoes repeated collisions with the surface. In particular, the DWBA does not predict the
temperature dependence of the resonance lineshapes, i.e., the signature of a resonance (whether
a dip or a peak, possibly asymmetric), as well as its strength and width.

A class of approximations [4] that covers the full range, from the quantum limit of mostly elastic scattering to the classical limit of purely inelastic scattering, consists of variations of the exponentiated DWBA (EBA) and the closely related trajectory approximation (TA) [5]. However, for resonant scattering, the EBA inherits the limitations of the DWBA, and the simple TA is manifestly invalid, because the resonant lineshapes result from interference between different trajectories. One must sum the amplitude of direct scattering to the amplitudes of trajectories in which the atom is temporarily trapped in a surface-bound state.

A procedure for doing this in elastic scattering was introduced by Celli, Garcia and Hutchison [6] and has been successfully applied both to an isolated resonance and to the crossing and mixing of resonances [7]. The atom–surface potential is written as the sum of a repulsive part and an attractive part that depends only on z, the coordinate perpendicular to the surface. The effect of the attractive part on an incoming particle is to increase its kinetic energy along z by the well depth D (Beeby correction), so $E_z = \hbar^2 p_z^2 / 2M + D$ for an atom of mass M and incoming momentum $-\hbar p_z$ (with z pointing away from the surface and p_z positive). When the parallel momentum changes from $\mathbf{K}$ to $\mathbf{K} + \mathbf{G}$, the perpendicular energy changes from E_{0z} to $E_{Gz} = E_{0z} + K^2/2M - (\mathbf{K} + \mathbf{G})^2/2M$.

Considering an elastic process first, the S-matrix element for scattering from the repulsive part alone is denoted by $S(F, 0)$ if $E_{Fz} > D$ (the atom escapes) and by $S(N, 0)$ if $0 < E_{Nz} < D$ (the atom is reflected back by the attractive potential). For an isolated resonance, the scattered amplitude, summed over all trajectories, has the form

$$B_F^+ = S(F, 0) + \frac{S(F, N) R_N S(N, 0)}{1 - R_N S(N, N)} \tag{1.1}$$

where $R_N = \exp(\mathrm{i}\phi(N))$, ϕ being the phase accrued in a round trip in the surface well. Manifestly, $S(F, N)$ describes escape from the well and $S(N, N)$ describes the reflection from the hard wall back into the surface-trapped trajectory. Unitarity requires that $|S(N, N)|^2 + |S(F, N)|^2 \leqslant 1$ (other channels may be available); hence $|S(N, N)| < 1$. We note for later reference that the resonant part of equation (1.1) results from the sum of a multiple-scattering series:

$$\frac{S(F, N) R_N S(N, 0)}{1 - R_N S(N, N)} = S(F, N) R_N S(N, 0) + S(F, N) R_N S(N, N) R_N S(N, 0) + \cdots. \tag{1.2}$$

The effect of inelastic scattering on equation (1.1) is fairly well described by the following prescription, introduced by Hutchison [8]: replace each matrix element S by its average value in the presence of inelastic scattering. If each scattering from the repulsive wall is treated in the EBA or TBA, this amounts to multiplying each S by the corresponding e^{-W}, where e^{-2W} is the Debye–Waller factor for the transition involved. This prescription seems intuitive enough, and it derives from an analysis by Duke and Laramore [9] of inelastic effects on multiple scattering in electron diffraction. However, Duke and Laramore do not discuss the case of resonant scattering, where the effect of inelasticity is crucial, and it is not obvious that the multiple-scattering series in the surface well can really be replaced by

$$S(F, N)\mathrm{e}^{-W_{FN}} R_N S(N, 0)\mathrm{e}^{-W_{0N}} + S(F, N)\mathrm{e}^{-W_{FN}} R_N S(N, N)\mathrm{e}^{-W_{NN}} R_N S(N, 0)\mathrm{e}^{-W_{0N}} + \cdots. \tag{1.3}$$

The aim of this paper is to extend the EBA and related approximations to resonant scattering by discussing the 'square root of Debye–Waller' prescription in the context of equation (1.1). This prescription has also been applied to the more general case of many elastic resonances [8], as well as to inelastic resonances with one-phonon exchange [10], but only the isolated elastic resonance will be treated in detail in this paper.

Other approaches to resonant scattering have been developed and have their merits. For purely elastic scattering, one can of course solve the problem numerically for any chosen potential; then analysis is needed only to interpret the computed results. Some of the early work of this kind was done by Chow and Thompson [11], who also introduced an optical potential to account for inelastic effects. A consistent theory can be developed by treating both the static corrugation and the inelastic interaction as perturbations [6, 12]; this method has been extended to higher orders by Manson and collaborators [13], and has also been used by Böheim [15] to discuss the effect of resonances on sticking. Recent work by Miret-Artés and collaborators [14] emphasizes the use of the coupled channels formalism and the possibility of a fully numerical treatment of inelasticity.

2. Elastic and inelastic processes

Within the EBA or TA, the matrix element for scattering from the repulsive potential contains the factor e^Q, where Q is linear in the displacements u of the surface atoms. The scattered intensity is proportional to the integral over time of $\langle\exp(Q_1)\exp(Q_2)\rangle$, where Q_1 is computed at time 0, Q_2 is computed at time t, and $\langle\cdots\rangle$ denotes the thermal average. In the simplest approximation, $Q_1 = \mathrm{i}q\cdot u$, where q is the momentum transfer and u is the displacement of a surface atom, and $Q_2 = -\mathrm{i}q\cdot u(t)$. Quite generally, one can use the relation

$$\langle\exp(Q_1)\exp(Q_2)\rangle = \exp(\tfrac{1}{2}\langle Q_1^2\rangle + \tfrac{1}{2}\langle Q_2^2\rangle + \langle Q_1 Q_2\rangle) \tag{2.1}$$

and note that all the t-dependence is contained in $\langle Q_1 Q_2\rangle$, which is proportional to a displacement–displacement correlation function $\langle u_1(0)u_2(t)\rangle$ and vanishes for large t. By definition, the Debye–Waller exponent is $W = -\tfrac{1}{2}\langle Q_1^2\rangle = -\tfrac{1}{2}\langle Q_2^2\rangle$; in the simplest approximation $2W = \langle(q\cdot u)^2\rangle$. Thus the final result, for energy transfer $\hbar\omega$, contains the factor

$$e^{-2W}\delta(\omega) + e^{-2W}\int_{-\infty}^{\infty}[\exp(\langle Q_1 Q_2\rangle) - 1]e^{\mathrm{i}\omega t}\,\mathrm{d}t/2\pi \tag{2.2}$$

and the strength of the elastic peak is reduced by e^{-2W}.

For the extension to resonant scattering, there are two lessons to be learned from these well-known results. First, to compute elastic scattering one can simply take the square of $\langle\exp(Q_1)\rangle$, without going through the exercise of computing $\langle\exp(Q_1)\exp(Q_2)\rangle$ and then picking out the elastic peak. Second, the central result that simplifies the analysis, equation (2.1), is a particular case of

$$\langle\exp(Q_1)\cdots\exp(Q_n)\rangle = \exp\left(\frac{1}{2}\sum_{k=1}^{n}\langle Q_k^2\rangle + \sum_{k=1}^{n-1}\sum_{k'=k+1}^{n}\langle Q_k Q_{k'}\rangle\right), \tag{2.3}$$

for any integer $n > 0$. This is explicitly derived in appendix A of [9] and can be checked by series expansion of both sides: the essential point is that $k < k'$ in the double sum on the right.

When inelastic processes are neglected, equation (1.1) for an isolated resonance is obtained from the general equations

$$B_F^+ = S(F, 0) + \sum_N S(F, N)R_N B_N^+ \tag{2.4}$$

$$B_N^+ = S(N, 0) + \sum_{N'} S(N, N')R_{N'}B_{N'}^+ \tag{2.5}$$

by assuming that there is only one N-type beam (or only one that couples to the incident and final beam). One would expect that a general process, elastic or inelastic, starting from a state

$|0\{n_0\}\rangle$ with some set $\{n_0\}$ of phonon modes, would go through all possible intermediate states $|N\{n_N\}\rangle$ and end up with $|F\{n_F\}\rangle$, resulting in the equations

$$B^+_{F\{n_F\}} = S(F\{n_F\}, 0\{n_0\}) + \sum_{N\{n\}} S(F\{n_F\}, N\{n\}) R_{N\{n\}} B^+_{N\{n\}} \qquad (2.6)$$

$$B^+_{N\{n\}} = S(N\{n\}, 0\{n_0\}) + \sum_{N'\{n'\}} S(N\{n\}, N'\{n'\}) R_{N'\{n'\}} B^+_{N'\{n'\}}. \qquad (2.7)$$

These equations describe a unitary theory, as can be shown in the same way as in appendix A of [6], for the elastic equations (2.4) and (2.5). Unitarity, i.e. flux conservation, seems to be a virtue, but it misses the possibility of sticking. As discussed by Brivio and Grimley [17] and by Clougherty and Kohn [18], the unitary amplitudes correctly describe experiments in which one waits an infinite time for atoms returning from the surface and assumes that there is no decoherence of the phonon states. Under actual experimental conditions, atoms that fall into surface-bound states desorb incoherently, mostly after the experiment has ended, and are in effect adsorbed. In classical calculations of adsorption, it is customary to count as 'sticking trajectories' only those in which the total energy of the atom becomes negative. Surface resonances come from trajectories in which the total atom energy remains positive, even though the perpendicular energy is negative in the surface resonant state. However, if the phonon occupation numbers are altered while going through the resonant state, one should not simply allow for the restoration of the original phonons in a later collision, as implied by equations (2.6) and (2.7).

To see what approximations can be developed, consider again the case of an isolated (elastic) resonance. Then in the unitary theory we must sum the series

$$\sum_{\{n\}} S(F\{n_F\}, N\{n\}) R_{N\{n\}} S(N\{n\}, 0\{n_0\})$$

$$+ \sum_{\{n\}\{n'\}} S(F\{n_F\}, N\{n'\}) R_{N\{n'\}} S(N\{n'\}, N\{n\}) R_{N\{n\}} S(N\{n\}, 0\{n_0\}) + \cdots. \qquad (2.8)$$

Already the first term is difficult to evaluate, even if we take $\{n_F\} = \{n_0\}$. The sum over $\{n\}$ should include only states such that the atom has energy between 0 and $-D$ and the phase ϕ of $R_{N\{n\}}$ depends on this energy through the energy loss or gain to phonons, $E(\{n\}) - E(\{n_0\})$. Further, if we want to introduce dephasing, it is not clear how much of it occurs in the effective time for a round trip in the surface well. Finally, we must average over $\{n_0\}$. The difficulties increase with the next term in equation (2.8), where the phonon sums and averages involve three inelastic factors. The Nth term of the series involves $N + 2$ such factors and thus, according to equation (2.3), $N(N - 1)$ correlation functions $\langle Q_k Q_{k'} \rangle$ in the exponent. It seems impossible to proceed without further approximations.

One thing we can do is to assume that near a resonance with a surface-bound state of energy $D + \varepsilon_b$ the series (2.8), for $\{n_F\} = \{n_0\}$, can be approximated by

$$S(F\{n_0\}, N\{n_0\}) \frac{\mathrm{i}}{(\mathrm{d}\phi/\mathrm{d}E)(E_{Nz} - \varepsilon_b + \mathrm{i}\Gamma/2)} S(N\{n_0\}, 0\{n_0\}). \qquad (2.9)$$

This means that we use a bound-state propagator with a width Γ, which is general enough, and, further, that we do not allow phonons to be exchanged, because any phonon emitted or absorbed during the $S(N, 0)$ collision cannot be coherently reabsorbed or re-emitted in the $S(F, N)$ collision, which happens a time $\hbar/\Gamma$ later. Note that the Hutchison prescription, applied to $S(N, N)$ only, amounts to introducing the bound-state propagator with

$$(\mathrm{d}\phi/\mathrm{d}E)\Gamma/2 = 1 - S(N, N)\mathrm{e}^{-W_{NN}}. \qquad (2.10)$$

The remaining task is to average $S(F\{n_0\}, N\{n_0\})S(N\{n_0\}, 0\{n_0\})$ over initial phonon states. We show in the next section that this averaging gives precisely the Hutchison prescription, that is, if $\rho(\{n\})$ are the thermal weights,

$$\sum_{\{n\}} \rho(\{n\})S(F\{n\}, N\{n\})S(N\{n\}, 0\{n\}) = S(F, N)\mathrm{e}^{-W_{FN}}S(N, 0)\mathrm{e}^{-W_{N0}}. \tag{2.11}$$

This means that the average of a product can be replaced by the product of the averages, since by definition

$$S(F, N)\mathrm{e}^{-W_{FN}} = \sum_{\{n\}} \rho(\{n\})S(F\{n\}, N\{n\}) \tag{2.12}$$

and similarly for $S(N\{n\}, 0\{n\})$.

3. Thermal averaging

This section is purely mathematical and will show that equation (2.11) is true for a large number of oscillators, although not for a single oscillator. We start however with a single oscillator of mass m and angular frequency ω_0 and compute the thermal average

$$A = (1 - \mathrm{e}^{-x}) \sum_{n=0}^{\infty} \mathrm{e}^{-nx} \langle n| \exp(\mathrm{i}p_1\hat{u})|n\rangle \langle n| \exp(\mathrm{i}p_2\hat{u})|n\rangle \tag{3.1}$$

where $x = \hbar\omega_0/k_BT$ and $\hat{u}$ is the displacement operator in units of

$$x_0 = \sqrt{\frac{\hbar}{m\omega_0}}. \tag{3.2}$$

We recall first that the basic Debye–Waller result is, for any p,

$$\mathrm{e}^{-W} = (1 - \mathrm{e}^{-x}) \sum_{n=0}^{\infty} \mathrm{e}^{-nx} \langle n|\exp(\mathrm{i}p\hat{u})|n\rangle = \exp(-\tfrac{1}{2}p^2\langle\hat{u}^2\rangle), \tag{3.3}$$

where

$$\langle\hat{u}^2\rangle = \langle\hat{n}\rangle + \frac{1}{2} = \frac{1}{2}\coth\frac{x}{2}. \tag{3.4}$$

To evaluate A, start by writing the sum in equation (3.1) as

$$\sum_{nn'} \langle n|\exp(\mathrm{i}p_1\hat{u})|n'\rangle \langle n'|\exp(\mathrm{i}p_2\hat{u})|n\rangle \mathrm{e}^{-nx}\delta_{nn'} \tag{3.5}$$

and use

$$\delta_{nn'} = \int_{-\pi}^{\pi} \exp(\mathrm{i}\tau(n' - n))\,\mathrm{d}\tau/2\pi. \tag{3.6}$$

The sum over n' can be carried out by closure [16] and gives

$$A = \int_{-\pi}^{\pi} \langle\exp(\mathrm{i}p_1\hat{u}) \exp(\mathrm{i}p_2\hat{u}(t))\rangle \frac{\mathrm{d}\tau}{2\pi}, \tag{3.7}$$

where $t = \tau/\omega_0$. Now use the thermal averages

$$\langle\exp(\mathrm{i}p_1\hat{u}) \exp(\mathrm{i}p_2\hat{u}(t))\rangle = \exp(-\tfrac{1}{2}(p_1^2 + p_2^2)\langle\hat{u}^2\rangle - p_1p_2\langle\hat{u}(0)\hat{u}(t)\rangle) \tag{3.8}$$

and

$$\langle\hat{u}(0)\hat{u}(t)\rangle = \tfrac{1}{2}(\langle\hat{n}\rangle\mathrm{e}^{-\mathrm{i}\tau} + \langle\hat{n} + 1\rangle\mathrm{e}^{\mathrm{i}\tau}). \tag{3.9}$$

The τ-integral is computed by series expansion and resummation and gives a modified Bessel function:

$$\int_{-\pi}^{\pi} \exp(-p_1 p_2 \langle \hat{u}(0)\hat{u}(t) \rangle) \frac{\mathrm{d}\tau}{2\pi} = \sum_{r=0}^{\infty} \frac{1}{(r!)^2} \left(\frac{y^2}{4} \right)^r = I_0(y) \tag{3.10}$$

where $y = p_1 p_2 \sqrt{\langle \hat{n} \rangle \langle \hat{n} + 1 \rangle}$. Then, using

$$\langle \hat{n} \rangle \langle \hat{n} + 1 \rangle = \frac{1}{4} \left(\coth^2 \frac{x}{2} - 1 \right) = \frac{1}{4 \sinh^2(x/2)} \tag{3.11}$$

we obtain

$$A = \exp\left(-\frac{1}{2}(p_1^2 + p_2^2)\langle \hat{u}^2 \rangle \right) I_0 \left(\frac{p_1 p_2}{2 \sinh(x/2)} \right). \tag{3.12}$$

Consider now the average on the left side of equation (2.11). It is the product of $\mathcal{N}$ averages of type A, one for each normal mode of the surface. For each normal mode both p_1 and p_2 are of order $1/\sqrt{\mathcal{N}}$, so the sum of $\frac{1}{2}p_1^2 \langle \hat{u}^2 \rangle$ for all the normal modes gives a finite result, which is nothing but $W_{F,N}$, and similarly the sum of $\frac{1}{2}p_2^2 \langle \hat{u}^2 \rangle$ gives $W_{N,0}$. However, the product of the I_0-factors gives 1, because

$$I_0(y) = 1 + \frac{y^2}{4} + \cdots = 1 + \mathcal{O}(1/\mathcal{N}^2). \tag{3.13}$$

This completes the proof of equation (2.11).

4. Conclusions

We have seen that the Hutchison prescription can be given some justification, at least as it applies to the matrix elements for entering and exiting the surface state. More importantly, we have argued that the lack of unitarity of the Hutchison approximation is not a bad thing, because it is consistent with the presence of sticking. New, more stringent tests of the approximation would be useful. In these tests one should correctly compute the elastic S-matrix elements and not use the eikonal approximation, and also use more accurate expressions for the Debye–Waller exponents, from the EBA and the like, rather than simply $\frac{1}{2}q^2 \langle \hat{u}^2 \rangle$. These corrections are likely to be more significant when one computes $S(N, N)$, or more generally $S(N, N')$, and its Debye–Waller factor. The separability of the potential into a static attractive part and a dynamic repulsive part is also least justified when dealing with $S(N, N)$.

We see in this paper that the Hutchison prescription comes from averaging elastic processes over initial phonon numbers, while neglecting inelastic processes that pass through a surface-bound state. In an earlier paper [19], we obtained approximate expressions for the elastic amplitudes that include one-phonon emission on entry into a surface-bound state and reabsorption on exit, or vice versa (rather than simply neglecting all inelastic processes of this type as we do in this paper). Those expressions give corrections to the Hutchison prescription that remain to be evaluated.

Acknowledgments

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