

Multiphonon scattering from surfaces

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We consider the relationship between several different formalisms for treating the multiphonon inelastic scattering of atomic projectiles from surfaces. Starting from general principles of formal scattering theory, the trajectory approximation to the scattering intensity is obtained. From the trajectory approximation, the conditions leading to the fast-collision approximation for multiquantum inelastic scattering are systematically derived.

I. INTRODUCTION

With the advent of atom-surface scattering, and particularly He-surface scattering, as a standard experimental method for measuring surface phonon-dispersion relations,¹ it becomes important to understand all features which can appear in the experimental time-of-flight data. These features can be roughly grouped into four components: elastic diffraction peaks arising as a result of the underlying periodicity of the crystal substrate, the diffuse elastic intensity caused by defects, single surface phonon peaks, and the diffuse inelastic background. The diffraction intensities² and the single phonon excitation intensities³ are relatively well understood and tractable calculations are readily carried out.⁴ Less well understood are the origins of the diffuse elastic peak, although recently it has been shown to yield important information about the differential cross sections of defects⁵⁻⁷ or adsorbates⁸ on the surface. The object of this paper is the diffuse inelastic background which is a strong component observed in the time-of-flight intensities, and which must be properly subtracted in order to correctly interpret the intensities of the single phonon peaks. The diffuse inelastic background consists of two parts, incoherent inelastic scattering from defects⁹ and the coherent multiphonon contribution. For clean, well-ordered surfaces the multiphonon contribution usually dominates, and although diffuse, it is not featureless. Structure appears in the multiphonon contribution and peaks can occur which resemble single phonon features,¹⁰ thus it is important to have a good understanding of these processes.

There have been a number of general approaches to the inelastic surface scattering problem that are capable, in principle, of describing the complete picture of multiquantum exchanges upon collision,¹¹⁻²¹ or at least within the confines of the trajectory approximation.^{22,23} Recently, two of these approaches by the present authors have proven to be quite successful in quantitatively explaining the shapes, as well as the temperature and energy dependence, of the multiphonon intensities observed

in He-surface scattering experiments.^{10,24} Although these two different approaches appear quite disparate, they are fundamentally very similar. The object of this paper is to show how the two approaches can be drawn from a common theoretical basis, to compare them to other formalisms, and then to clarify their similarities and differences.

II. FORMALISM OF LEVI AND BORTOLANI

In a very comprehensive and excellent review of the theory of atom-surface scattering, Levi and Bortolani present a general multiphonon formalism based on the time-evolution operator approach to solutions of the many-body Schrödinger equation.²⁵ Consider the total system to be described by a Hamiltonian of the form

$$H^{\text{tot}} = H + H^c + V, \quad (1)$$

where H is the Hamiltonian of the free particle, H^c is the Hamiltonian of the unperturbed crystal, and V is the interaction coupling the projectile and crystal. A standard approach is to start from the probability density of the particle to lose an amount of energy Δ given by

$$N(\Delta) = \langle\langle (\mathbf{k}_i | S^\dagger \delta(H - E_i + \Delta) S | \mathbf{k}_i) \rangle\rangle, \quad (2)$$

where the symbol $\langle\langle \rangle\rangle$ defines an ensemble average over the initial crystal states $|n_i\rangle$, and the scattering operators S are defined by

$$S = \lim_{t \rightarrow \infty} U(+t, -t), \quad (3)$$

where $U(s_2, s_1)$ is the time-evolution operator. For considerations of parallel momentum exchange, a standard approach, following Brako and Newns¹⁴ is to start from the probability density of the particle to lose an amount Δ of energy and an amount $\hbar\mathbf{K}$ of parallel momentum.

$$N(\mathbf{K}, \Delta) = \langle\langle \{ [\mathbf{k}_i | S^\dagger \delta(H - E_i + \Delta) \times \delta(\mathbf{P}/\hbar - \mathbf{K}_i - \mathbf{K})] S | \mathbf{k}_i \} \rangle\rangle, \quad (4)$$

where \mathbf{P} is the momentum operator for the projectile. The differential reflection coefficient, which is usually compared to the experimentally measured intensities, is related to (4) by a simple density of states:

$$\frac{dR}{d\Delta d\Omega} = k_f k_{fz} N(\mathbf{K}, \Delta), \quad (5)$$

where $\hbar \mathbf{k}_f$ is the final projectile momentum and $\hbar k_{fz}$ is its component in the direction normal to the surface.

Using the global energy conservation between the projectile and the surface, $E_f^c - E_i^c + E_f - E_i = 0$, the energy δ function in Eq. (4) can be converted to one involving the

crystal Hamiltonian, $\delta(H^c - E_i^c - \Delta)$. The δ functions are rewritten as integral representations in the transformation usually ascribed to Glauber²⁶ and Van Hove,²⁷ and after defining time-dependent operators in a somewhat more generalized interaction picture according to

$$S(\mathbf{R}, t) = \exp\{-i[\mathbf{R} \cdot \mathbf{P} - H_c t]/\hbar\} \\ \times S \exp\{i[\mathbf{R} \cdot \mathbf{P} - H_c t]/\hbar\}, \quad (6)$$

the differential reflection coefficient appears in the general form

$$\frac{dR}{d\Delta d\Omega} = \frac{k_f k_{fz}}{(2\pi)^3 \hbar L^2} \int_{-\infty}^{+\infty} dt \int d\mathbf{R} \int d\mathbf{R}' \exp\{i[\mathbf{K} \cdot (\mathbf{R} - \mathbf{R}') - t\Delta/\hbar]\} \\ \times \langle\langle (\mathbf{k}_i | S^\dagger(\mathbf{R}, 0) S(\mathbf{R}', t) | \mathbf{k}_i) \rangle\rangle. \quad (7)$$

Equation (7) is formally without approximation, and is a quite general expression for describing the scattering. However, in order to make progress towards tractable calculations, approximations must be applied.

The inelastic eikonal formula of Levi and Bortolani can be obtained if we assume that the spatial matrix elements of the generalized scattering operator can be written in the simple form

$$\langle n_j | (\mathbf{k}_j | S(\mathbf{R}) | \mathbf{k}_i) | \eta_i \rangle = -\frac{1}{L} \int d\mathbf{R}' \exp[i(\mathbf{K}_i - \mathbf{K}_j) \cdot \mathbf{R}'] \langle n_j | b(\mathbf{R} + \mathbf{R}') \exp[i\eta(\mathbf{R} + \mathbf{R}')] | n_i \rangle \delta_{k_{jz}, \alpha}, \quad (8)$$

where $b(\mathbf{R})$ is the source function, which reduces to $\sqrt{k_{iz}/k_{jz}}$ in the simple eikonal approximation, and α is the magnitude of the perpendicular wave vector consistent with energy conservation between the projectile and the crystal. The phase $\eta(\mathbf{R}, t)$ can be developed in a series in terms of the vibrational displacements $\mathbf{u}_j(t)$ of the atoms making up the crystal.

$$\eta(\mathbf{R}, t) = \eta_0(\mathbf{R}) + \delta\eta(\mathbf{R}, t)$$

$$= \eta_0(\mathbf{R}) - \frac{1}{\hbar} \sum_j \int_{-\infty}^{\infty} ds \mathbf{f}_j(\mathbf{R}, s) \cdot \mathbf{u}_j(s + t), \quad (9)$$

where the series has been truncated at the linear term in \mathbf{u}_j , and the force \mathbf{f}_j is the negative gradient of the interaction potential with respect to the small displacement \mathbf{u}_j .

Under the assumption that the phase η of Eq. (9) de-

pends linearly on the displacements \mathbf{u}_j , and that the displacements are harmonic and appear only in the $\delta\eta$ term, then the average over crystal states in (7) is readily evaluated.

$$\langle\langle \exp\{-i\delta\eta(\mathbf{R}, 0)\} \exp\{i\delta\eta(\mathbf{R}', t)\} \rangle\rangle \\ = \exp\{-W(\mathbf{R}) - W(\mathbf{R}') + 2\mathcal{W}(\mathbf{R}, \mathbf{R}', t)\}, \quad (10)$$

where $\mathcal{W}(\mathbf{R}, \mathbf{R}', t)$ is the generalized time-dependent displacement correlation function

$$\mathcal{W}(\mathbf{R}, \mathbf{R}', t) = \frac{1}{2} \langle\langle \delta\eta(\mathbf{R}, 0) \delta\eta(\mathbf{R}', t) \rangle\rangle \quad (11)$$

and $W(\mathbf{R})$ is the generalized Debye-Waller exponent, with the relation $W(\mathbf{R}) = \mathcal{W}(\mathbf{R}, \mathbf{R}, 0)$. Then, in the trajectory approximation, the differential reflection coefficient appears in the form

$$\frac{dR}{d\Delta d\Omega} = \frac{k_f k_{fz}}{(2\pi)^3 \hbar L^2} \int d\mathbf{R} \int d\mathbf{R}' b(\mathbf{R}') b^*(\mathbf{R}) \exp\{i\mathbf{K} \cdot (\mathbf{R} - \mathbf{R}') + i\eta_0(\mathbf{R}') - i\eta_0(\mathbf{R})\} \\ \times \exp\{-W(\mathbf{R}) - W(\mathbf{R}')\} \int_{-\infty}^{+\infty} dt \exp\{-it\Delta/\hbar\} \exp\{2\mathcal{W}(\mathbf{R}, \mathbf{R}', t)\}. \quad (12)$$

Within the confines of the eikonal approximation and the harmonic approximation, Eq. (12) describes the complete elastic and inelastic scattering by the interaction potential V . The elastic and single phonon inelastic contributions are obtained upon expanding the displacement correlation phase function $\exp\{2\mathcal{W}(\mathbf{R}, \mathbf{R}', t)\}$ to zeroth and first order in its argument, respectively. The form of Eq. (12), particularly the fact that it is expressed as a double integral over the surface, is especially useful for application to the corrugated hard wall potential.²⁸

The differential reflection coefficient of Eq. (12) has been averaged over this thermal motion, hence it must reflect the perfect periodicity of the lattice. This periodicity is expressed, for example, in the relation

$$\eta_0(\mathbf{R} + \mathbf{R}_l) = \eta_0(\mathbf{R}) \quad (13)$$

with similar relations valid for $b(\mathbf{R})$ and for $W(\mathbf{R})$. In Eq. (13) \mathbf{R}_l is a lattice vector along the surface, with the index l

labeling surface unit cells, and for simplicity in notation we have made the (unnecessary) assumption that the crystal is a Bravais lattice with only one atom per surface unit cell (uc). Similarly, the displacement correlation function obeys the relation

$$\mathcal{W}(\mathbf{R} + \mathbf{R}_l, \mathbf{R}' + \mathbf{R}_l, t) = \mathcal{W}(\mathbf{R}, \mathbf{R}', t). \quad (14)$$

The translational symmetry allows us to rewrite the differential reflection coefficient (12) as an integral over a single unit cell together with a summation over all lattice vectors

$$\begin{aligned} \frac{dR}{d\Delta d\Omega} &= \frac{k_f k_{fz}}{(2\pi)^3 \hbar L^2} \int_{uc} d\mathbf{R} \int_{uc} d\mathbf{R}' b(\mathbf{R}') b^*(\mathbf{R}) \exp\{i\mathbf{K} \cdot (\mathbf{R}' - \mathbf{R}) + i\eta_0(\mathbf{R}') - i\eta_0(\mathbf{R}) - W(\mathbf{R}) - W(\mathbf{R}')\} \\ &\quad \times \sum_l \sum_{l'} \exp\{i\mathbf{K} \cdot (\mathbf{R}_{l'} - \mathbf{R}_l)\} \int_{-\infty}^{+\infty} dt \exp\{-it\Delta/\hbar\} \exp\{2W(\mathbf{R} + \mathbf{R}_l, \mathbf{R}' + \mathbf{R}_{l'}, t)\}. \end{aligned} \quad (15)$$

With the use of Eqs. (13) and (14) the double summation in (15) reduces to a single summation, and letting ρ be the surface density of unit cells, the differential reflection coefficient becomes

$$\begin{aligned} \frac{dR}{d\Delta d\Omega} &= \frac{k_f k_{fz} \rho}{(2\pi)^3 \hbar} \int_{uc} d\mathbf{R} \int_{uc} d\mathbf{R}' b(\mathbf{R}') b^*(\mathbf{R}) \exp\{i\mathbf{K} \cdot (\mathbf{R}' - \mathbf{R}) + i\eta_0(\mathbf{R}') - i\eta_0(\mathbf{R}) - W(\mathbf{R}) - W(\mathbf{R}')\} \\ &\quad \times \sum_n \exp\{i\mathbf{K} \cdot \mathbf{R}_n\} \int_{-\infty}^{+\infty} dt \exp\{-it\Delta/\hbar\} \exp\{2\mathcal{W}(\mathbf{R}, \mathbf{R}' + \mathbf{R}_n, t)\}. \end{aligned} \quad (16)$$

The major simplification which permits the relatively tractable expression (16) for the differential reflection coefficient is the trajectory approximation. Crudely speaking, the trajectory approximation has the property of treating the particle operators semiclassically while treating the crystal degrees of freedom quantum mechanically.

III. FAST-COLLISION LIMIT

One of the authors has developed a theory of multiple phonon scattering based on the transition rate $w(\mathbf{k}_f, \mathbf{k}_i)$ for scattering from a projectile state of momentum $\hbar\mathbf{k}_i$ to a state of momentum $\hbar\mathbf{k}_f$, which is essentially the time derivative of the probability density of Eq. (4).

$$w(\mathbf{k}_f, \mathbf{k}_i) = \frac{2\pi}{\hbar} \left\langle \left\langle \sum_{n_f} |T_{fi}|^2 \delta(\mathcal{E}_f - \mathcal{E}_i) \right\rangle \right\rangle, \quad (17)$$

where T_{fi} is the transition matrix, \mathcal{E}_p is the total energy of the system, and the summation is over the final states of the crystal. Upon making a transformation to the interaction picture in which the time evolution of the transition operator is defined according to

$$\hat{T}(t) = \exp\{iH_c t/\hbar\} \hat{T} \exp\{-iH_c t/\hbar\} \quad (18)$$

and for a periodic surface it is natural to write the matrix elements of (18) taken with respect to particle eigenstates as follows:

$$(\mathbf{k}_f | \hat{T}(t) | \mathbf{k}_i) = \sum_{l;\kappa} \exp\{-i\mathbf{k} \cdot [\mathbf{r}_{l,\kappa} + \mathbf{u}_{l,\kappa}(t)]\} \tau_{fi}^\kappa, \quad (19)$$

where $\mathbf{r}_{l,\kappa}$ is the equilibrium position of the κ th element of the l th unit cell and $\hbar\mathbf{k}$ is the momentum exchange, $\mathbf{k} = \mathbf{k}_f - \mathbf{k}_i = (\mathbf{K}, k_{fz} + k_{iz})$. Note that the index κ is not necessarily associated specifically with atoms making up the unit cell; because atomic projectiles scatter from the electron cloud and not directly from the crystal atomic cores, it may be convenient to divide the unit cell into arbitrary subunits which we refer to as elements. In order to make further progress, a major approximation is made in which it is assumed that the scattering amplitude τ_{fi}^κ is independent of the crystal displacements $\mathbf{u}_{l,\kappa}(t)$, and consequently independent of time. Such an approximation can only be valid if the local environment of each unit cell is identical at all times, which implies that the coherence region for scattering associated with the neighborhood of each unit cell is vibrating rigidly, with no distortion that might arise from short vibrational wavelengths. This approximation is basically a fast-collision assumption of the sort that has been used very successfully in the scattering of x rays and neutrons. It is argued that such an approximation should be good for a description of multiphonon atom-surface scattering, since the energy and momentum exchanges involved will be dominated by low-energy and long-wavelength phonons.

Once the approximation of (19) is made, the transition rate (17) can be readily evaluated leading to the following expression in terms of the displacement correlation function.

$$\begin{aligned} w(\mathbf{k}_f, \mathbf{k}_i) &= \frac{N}{\hbar^2} \int_{-\infty}^{+\infty} dt \exp\{-it\Delta/\hbar\} \sum_n \sum_\kappa \sum_{\kappa'} (\tau_{fi}^\kappa)^\dagger \tau_{fi}^{\kappa'} \exp\{-i\mathbf{K} \cdot \mathbf{R}_n\} \exp\{i\mathbf{k} \cdot (\mathbf{r}_{\kappa'} - \mathbf{r}_\kappa)\} \exp\{-W_\kappa(\mathbf{k})\} \\ &\quad \times \exp\{-W_{\kappa'}(\mathbf{k})\} \exp\{\langle \langle \mathbf{k} \cdot \mathbf{u}_{0;\kappa}(0) \mathbf{k} \cdot \mathbf{u}_{n;\kappa'}(t) \rangle \rangle\}. \end{aligned} \quad (20)$$

The Debye-Waller factor appearing in (20) is of the classic form, depending on the time-independent self-correlation function:

$$W_{\kappa}(\mathbf{k}) = \frac{1}{2} \langle [\mathbf{k} \cdot \mathbf{u}_{n;\kappa}(t)]^2 \rangle. \quad (21)$$

Using simple models for the displacement correlation function, the transition rate of Eq. (20) has demonstrated its ability to describe quantitatively the shape, energy dependence, and temperature dependence of a rather large range of He-surface scattering systems.^{29,30} However, a basic derivation of the approximation embodied in Eq. (19), together with a justification of its applicability is lacking. We now show that Eq. (19) arises naturally from the Levi-Bortolani form of Eq. (16) above in the limit of small frequency and long-wavelength vibrational displacements.

If the collision is fast compared to the vibrational period, then the trajectory approximation phase of Eq. (9) becomes

$$\begin{aligned} \frac{dR}{d\Delta d\Omega} &= \frac{k_f k_{fz} \rho}{(2\pi)^3 \hbar} \exp\{-2W(\mathbf{k})\} \left| \int_{uc} d\mathbf{R} b(\mathbf{R}) \exp\{-i\mathbf{K} \cdot \mathbf{R} + i\eta_0(\mathbf{R})\} \right|^2 \\ &\times \sum_n \exp\{-i\mathbf{K} \cdot \mathbf{R}_n\} \int_{-\infty}^{+\infty} dt \exp\{-it\Delta/\hbar\} \exp\{\langle \mathbf{k} \cdot \mathbf{u}_0(0) \mathbf{k} \cdot \mathbf{u}_n(t) \rangle\}. \end{aligned} \quad (24)$$

Equation (24) is identical in form to (20) above, in the case of a Bravais lattice, if we make the following association [after first accounting for the appropriate density of final states to convert the transition rate (20) to a differential reflection coefficient]:

$$|\tau_{fi}| = \frac{\hbar^2 \sqrt{k_{fz} k_{iz}}}{L^3 m} \left| \int_{uc} d\mathbf{R} b(\mathbf{R}) \exp\{-i\mathbf{K} \cdot \mathbf{R} + i\eta_0(\mathbf{R})\} \right|. \quad (25)$$

The reduced transition matrix τ_{fi} is identified as the off-energy-shell transition-matrix element of the elastic part of the interaction potential (here taken in the trajectory approximation).

The summation over unit cells over the surface appearing in (24) as well as in (16) gives rise to coherent effects that appear even in the multiphonon intensity.³¹ These effects appear as broad structure in the coherent multiphonon background under quantum-mechanical conditions. At high temperatures and large projectile energies this coherence structure disappears as only one term in the summation dominates, signifying that the incoming projectile is interacting over a coherence region that encompasses only one crystal unit cell.

The discussion leading to Eq. (24) provides one justification of the assumption of the form of the transition matrix of Eq. (20). Such an assumption, basically a neutron-scattering approximation, is definitely not good in the case of low-energy electrons interacting with a surface because the interaction is strong and collisions with multiple-scattering centers are important. Since atoms also interact strongly with the surface, it could be argued

$$\delta\eta = -\frac{1}{\hbar} \sum_j \mathbf{u}_j \cdot \int_{-\infty}^{+\infty} \mathbf{f}_j(s) ds. \quad (22)$$

If, in addition only long-wavelength vibrations are considered, then all \mathbf{u}_j are effectively identical over the coherence area of the scattering event and \mathbf{u}_j can be taken out of the sum. The remaining time integral of the force $\mathbf{f}_j(s)$ is the momentum imparted to the j th crystal atom, and we are left with

$$\delta\eta = -\frac{1}{\hbar} \mathbf{u}_0 \cdot \sum_j \int_{-\infty}^{+\infty} \mathbf{f}_j(s) ds = -\mathbf{u}_0 \cdot \mathbf{k}. \quad (23)$$

[Equation (23) can also be obtained from (22) upon assuming that all of the momentum of the incoming projectile is imparted to a single crystal atom.] If we apply the further approximation embodied in (23) to the Levi-Bortolani differential coefficient of Eq. (16), after first properly accounting for the translational displacements in space and time arising from the interaction picture transformation (6), the result is

that the momentum exchange approximation should fail in that case also. However, this derivation shows that the reason why it works successfully for atom-surface scattering is because the scattering is basically a two-dimensional process. It will fail when the scattering can no longer be considered a quick collision, such as when diffraction is very strong and resonances with the physisorption bound states can occur. We discuss again the validity of such a model in the section below where we provide a second justification of Eq. (20) starting from somewhat more fundamental principles.

IV. RELATIONSHIP TO OTHER THEORIES

We would now like to address once again the results of the previous section, but this time to derive them in a more rigorous fashion. We will begin from a general form for the scattering probability and then systematically obtain the scattering intensities derived previously by others. A convenient starting point is the formally exact expression of Eq. (7). In the interaction picture the scattering operator (3) can be written as

$$S(\alpha) = T \lim_{t_0 \rightarrow -\infty} \exp \left\{ \frac{-i}{\hbar} \int_{-t_0}^{t_0} ds V(\alpha; s) \right\}, \quad (26)$$

where $\alpha = (\mathbf{R}, t)$ signifies the supplementary variables of the driving operators as in Eq. (6) and T is the time-ordering operator. Before inserting (26) into the general scattering probability (7) it is of interest to discuss the form of the interaction potential $V = V(\mathbf{r}, \{\mathbf{u}_{j;\kappa}\})$, where

$\{\mathbf{u}_{j;\kappa}\}$ symbolizes the set of displacement variables of the crystal. Here we use the same notation as in (19) in which for the set of indices $(j;\kappa)$, j is a two-dimensional variable that counts unit cells of the surface and κ is a three-dimensional variable that counts elements of the basis set within the unit cell including those in all the layers below the surface. We write the interaction as the sum of two parts

$$V = V^0 + V^1, \quad (27)$$

where the "strong" part V^0 contains the terms which backscatter the projectile and prevent it from penetrating appreciably into the bulk, and the remainder V^1 contains the major terms describing interactions with the lattice vibrations. A logical assignment is provided by expanding in a Taylor series in the lattice vibrations:

$$V = V(\mathbf{r}, \{\mathbf{u}_{j;\kappa}\}) \Big|_{\{\mathbf{u}_{j;\kappa}=0\}} + \sum_{j;\kappa} \nabla_{j;\kappa} V(\mathbf{r}, \{\mathbf{u}_{j;\kappa}\}) \Big|_{\{\mathbf{u}_{j;\kappa}=0\}} \cdot \mathbf{u}_{j;\kappa} + \cdots, \quad (28)$$

where $\nabla_{j;\kappa}$ is the gradient operator with respect to the $(j;\kappa)$ displacement. The logical choice is to associate V^0 with the leading term of (28) which is now independent of the displacement, and let V^1 be the sum of all higher-order terms. A great simplification occurs in the case in which the potential is a summation of pairwise atomic interactions:

$$V = \sum_{j;\kappa} v(\mathbf{r} - \mathbf{r}_j - \mathbf{r}_\kappa - \mathbf{u}_{j;\kappa}), \quad (29)$$

where the position of the $(j;\kappa)$ element in the lattice as a function of time is written as $\mathbf{r}_{j;\kappa}(t) = \mathbf{r}_j + \mathbf{r}_\kappa + \mathbf{u}_{j;\kappa}(t)$ with \mathbf{r}_j and \mathbf{r}_κ the equilibrium positions of the j th unit cell and the κ th element within the cell, respectively:

$$\begin{aligned} V &= \sum_{j;\kappa} v(\mathbf{r} - \mathbf{r}_j - \mathbf{r}_\kappa) - \nabla_{\mathbf{r}} \sum_{j;\kappa} v(\mathbf{r} - \mathbf{r}_j - \mathbf{r}_\kappa) \cdot \mathbf{u}_{j;\kappa} + \cdots \\ &= V^0 + \sum_{j;\kappa} \mathbf{f}_{j;\kappa} \cdot \mathbf{u}_{j;\kappa} + \cdots, \end{aligned} \quad (30)$$

where we have made the further association, as in Eq. (9) above, that $\mathbf{f}_{j;\kappa} = -\nabla_{\mathbf{r}} v(\mathbf{r} - \mathbf{r}_j - \mathbf{r}_\kappa)$ is the classical force on the projectile due to the $(j;\kappa)$ crystal atom fixed in the crystal.

However, separation of the form of (28) or (30) is certainly not unique, and for certain purposes it may be more convenient to make the distinction between displacements of the unit cell taken as a whole and the additional displacements of the elements of the basis. For example, writing $\mathbf{r}_{j;\kappa}(t) = \mathbf{r}_j + \mathbf{r}_\kappa + \mathbf{u}_j(t) + \mathbf{u}'_{j;\kappa}(t)$ the potential can be expanded in the $\{\mathbf{u}_j(t)\}$ only, according to

$$\begin{aligned} V &= \sum_{j;\kappa} v(\mathbf{r} - \mathbf{r}_j - \mathbf{r}_\kappa + \mathbf{u}'_{j;\kappa}) \\ &\quad - \nabla_{\mathbf{r}} \sum_{j;\kappa} v(\mathbf{r} - \mathbf{r}_j - \mathbf{r}_\kappa + \mathbf{u}'_{j;\kappa}) \cdot \mathbf{u}_j + \cdots \end{aligned} \quad (31)$$

which may be convenient when one wishes to examine the internal distortions of the unit cell due to vibrations.

Taking account of the expansion of the interaction potential in (27) and the form of the scattering operator (26), the differential reflection coefficient (7) becomes

$$\begin{aligned} \frac{dR}{d\Delta d\Omega} &= \frac{k_f k_{fz}}{(2\pi)^3 \hbar L^2} \int_{-\infty}^{+\infty} dt \int d\mathbf{R} \int d\mathbf{R}' \exp\{i[\mathbf{K} \cdot (\mathbf{R} - \mathbf{R}') - t\Delta/\hbar]\} \\ &\quad \times \left\langle \left\langle \left[\mathbf{k}_i \right] T \exp \left\{ \frac{i}{\hbar} \int_{-\infty}^{+\infty} ds V^0(\alpha; s) + \frac{i}{\hbar} \int_{-\infty}^{+\infty} ds V^1(\alpha; s) \right\} \right| \left[\mathbf{k}_f \right] \right\rangle \\ &\quad \times \left[\left[\mathbf{k}_f \right] T \exp \left\{ \frac{-i}{\hbar} \int_{-\infty}^{+\infty} ds' V^0(\alpha'; s') + \frac{-i}{\hbar} \int_{-\infty}^{+\infty} ds' V^1(\alpha'; s') \right\} \right| \left[\mathbf{k}_i \right] \right\rangle, \end{aligned} \quad (32)$$

where the additional driving parameters are $\alpha = (\mathbf{R}, 0)$ and $\alpha' = (\mathbf{R}', t)$. In spite of the complicated appearance of Eq. (32), the effect of the average over initial crystal states will be to produce an operator which is periodic with the symmetry of the static lattice. This means that in the matrix elements, the spatial integrals can be reduced to integrals over single unit cells, together with discrete summation over all unit cells. Using the expansion (28) for the interaction potential, the differential reflection coefficient then becomes

$$\begin{aligned}
\frac{dR}{d\Delta d\Omega} &= \frac{k_f k_{fz}}{(2\pi)^3 \hbar L^2} \int_{-\infty}^{+\infty} dt \int d\mathbf{R} \int d\mathbf{R}' \exp\{i[\mathbf{K} \cdot (\mathbf{R} - \mathbf{R}') - t\Delta/\hbar]\} \\
&\quad \times \sum_{l;l'} \exp\{i\mathbf{K} \cdot [\mathbf{R}_{l'} - \mathbf{R}_l]\} \\
&\quad \times \left\langle \left\langle \left[\mathbf{k}_i \left| T \exp \left\{ \frac{i}{\hbar} \int_{-\infty}^{+\infty} ds V^0(s) \right. \right. \right. \right. \\
&\quad \left. \left. \left. + \frac{i}{\hbar} \int_{-\infty}^{+\infty} ds \sum_{j;\kappa} \mathbf{f}_{j;\kappa} \cdot \mathbf{u}_{j+l;\kappa}(\alpha; s) \right\} \right| \mathbf{k}_f \right]_{uc} \right. \\
&\quad \times \left[\mathbf{k}_f \left| T \exp \left\{ \frac{-i}{\hbar} \int_{-\infty}^{+\infty} ds' V^0(s') \right. \right. \right. \\
&\quad \left. \left. \left. + \frac{-i}{\hbar} \int_{-\infty}^{+\infty} ds' \sum_{j';\kappa'} \mathbf{f}_{j';\kappa'} \cdot \mathbf{u}_{j'+l';\kappa'}(\alpha'; s') \right\} \right| \mathbf{k}_i \right]_{uc} \left. \right\rangle \right\rangle .
\end{aligned} \tag{33}$$

In order to make further progress toward explicit calculations with (32) it is necessary to deal with the commutation of the various terms of the potential in the exponentials. A convenient way of treating this is through the trajectory approximation in which the force is evaluated along a single classical trajectory of the potential V^0 characterized by the time-dependent path $\mathbf{r}(s)$.^{14,25} With the trajectory approximation the potential V^1 depends only on the crystal displacements, while by choice V^0 depends only on the particle coordinates, and the two terms commute. The differential reflection coefficient simplifies to

$$\begin{aligned}
\frac{dR}{d\Delta d\Omega} &= \frac{k_f k_{fz}}{(2\pi)^3 \hbar L^2} \int_{-\infty}^{+\infty} dt \int d\mathbf{R} \int d\mathbf{R}' \exp\{i[\mathbf{K} \cdot (\mathbf{R} - \mathbf{R}') - t\Delta/\hbar]\} \\
&\quad \times \sum_{l;l'} \exp\{i\mathbf{K} \cdot [\mathbf{R}_{l'} - \mathbf{R}_l]\} |\sigma_{fi}|^2 \\
&\quad \times \left\langle \left\langle \exp \left\{ \frac{i}{\hbar} \int_{-\infty}^{+\infty} ds \sum_{j;\kappa} \mathbf{f}_{j;\kappa}[\mathbf{r}(s)] \cdot \mathbf{u}_{j+l;\kappa}(\alpha; s) \right\} \right. \right. \\
&\quad \left. \left. \times \exp \left\{ \frac{-i}{\hbar} \int_{-\infty}^{+\infty} ds' \sum_{j';\kappa'} \mathbf{f}_{j';\kappa'}[\mathbf{r}(s')] \cdot \mathbf{u}_{j'+l';\kappa'}(\alpha'; s') \right\} \right\rangle \right\rangle ,
\end{aligned} \tag{34}$$

where σ_{fi} is defined below in Eq. (36).

The thermal average in (34) can now be carried out, for operators linear in the harmonic displacements the commutations are handled with the relation $e^A e^B = e^{A+B} e^{[A,B]/2}$, and $\langle\langle e^A \rangle\rangle = \exp(\langle\langle A^2/2 \rangle\rangle)$. The result is

$$\begin{aligned}
\frac{dR}{d\Delta d\Omega} &= \frac{\rho k_f k_{fz}}{(2\pi)^3 \hbar} \int_{-\infty}^{+\infty} dt \int d\mathbf{R} \int d\mathbf{R}' \exp\{i[\mathbf{K} \cdot (\mathbf{R} - \mathbf{R}') - t\Delta/\hbar]\} \\
&\quad \times |\sigma_{fi}|^2 \sum_l \exp\{i\mathbf{K} \cdot \mathbf{R}_l\} \exp\{-W(\mathbf{R}; \mathbf{k})\} \exp\{-W(\mathbf{R}'; \mathbf{k})\} \exp\{2\mathcal{W}_l(\mathbf{R}, \mathbf{R}', t)\} ,
\end{aligned} \tag{35}$$

where

$$\sigma_{fi} = \left[\mathbf{k}_f \left| T \exp \left\{ \frac{-i}{\hbar} \int_{-\infty}^{+\infty} ds V^0(s) \right\} \right| \mathbf{k}_i \right]_{uc} . \tag{36}$$

The displacement correlation function is similar to Eq. (11) and depends only on the relative distance $l - l'$ between unit cells

$$\mathcal{W}_l(\mathbf{R}, \mathbf{R}', t) = \frac{1}{2\hbar^2} \left\langle \left\langle \int_{-\infty}^{+\infty} ds \sum_{j;\kappa} \mathbf{f}_{j;\kappa}[\mathbf{r}(s)] \cdot \mathbf{u}_{j;\kappa}(\alpha; s) \int_{-\infty}^{+\infty} ds' \sum_{j';\kappa'} \mathbf{f}_{j';\kappa'}[\mathbf{r}(s')] \cdot \mathbf{u}_{j'+l';\kappa'}(\alpha'; s') \right\rangle \right\rangle \tag{37}$$

and $W(\mathbf{R}, \mathbf{k}) = \mathcal{W}_{l=0}(\mathbf{R}, \mathbf{R}, t=0)$.

Equation (35) is a quite general expression in which the only major approximations, aside from the harmonic approximation, are the expansion of the interaction potential through linear terms only and the application of the trajectory approximation. It is essentially identical to the result presented by Bortolani and co-workers^{12,13,25} of Eq. (12) with two minor exceptions; we have accounted for the periodicity of the lattice which is recovered after averaging over the initial states of the crystal and the scattering amplitude σ_{fi} does not depend on the variable \mathbf{R} . This latter difference is simply due to the choice of separation of the interaction potential into the parts V^0 and V^1 , a different choice in which V^0 contains displacements of the basis elements which distort the unit cell such as in Eq. (31), which will lead to

$$|\sigma_{fi}|^2 \rightarrow \sigma_{fi}^\dagger(\mathbf{R}) \sigma_{fi}(\mathbf{R}') \quad (38)$$

after making a reasonable set of simplifying assumptions.

We note here that the spatial integrals over \mathbf{R} and \mathbf{R}' in the differential reflection coefficient of (35) can be replaced by integrals over a single unit cell. Translation through a lattice vector such as in the operation $\mathbf{R} \rightarrow \mathbf{R} + \mathbf{R}_j$ simply changes the phase of the displacement vector. The correlation function (37) depends only on the phase difference, and this phase difference is summed over in (35). Thus the reduction of the spatial integrals to integrals over single unit cells merely multiplies (35) by a constant equal to the corresponding density of states.

General theories of inelastic surface scattering based on the powerful S -matrix formalism have been developed earlier by Brenig¹⁸ and by Brako and Newns¹⁴ and even much earlier by Beebe.¹¹ Equation (35) is more general than these earlier theories in two aspects; interference in multiphonon scattering arising from contributions from different surface unit cells is accounted for in the summation over lattice sites, and there is a multiplicative form

factor $|\sigma_{fi}|^2$ which shows that the scattering from a single unit cell provides an envelope for the overall scattering distribution. For example, the theory of Brako and Newns in the form as developed by Celli *et al.*^{10,32} is recovered exactly if in Eq. (35) only the term $l=0$ is retained and if $|\sigma_{fi}|^2$ is set equal to unity.

The remaining task is to clarify the relation of the fast-collision approximation presented in Eq. (20) to the more general result of (35). For this we need only consider the phase generated by the trajectory approximation as appears in the correlation function of (37):

$$I = \frac{1}{\hbar} \int_{-\infty}^{+\infty} ds \sum_{j;\kappa} \mathbf{f}_{j;\kappa}[\mathbf{r}(s)] \cdot \mathbf{u}_{j+l;\kappa}(\mathbf{R}, t; s) \quad (39)$$

and assuming that the collision is rapid compared to the important and dominant vibrational frequencies, this goes to

$$I \rightarrow \frac{1}{\hbar} \sum_{j;\kappa} \mathbf{u}_{j+l;\kappa}(\mathbf{R}, t) \cdot \int_{-\infty}^{+\infty} ds \mathbf{f}_{j;\kappa}[\mathbf{r}(s)] \\ = \sum_{j;\kappa} \mathbf{u}_{j+l;\kappa}(\mathbf{R}, t) \cdot \mathbf{k}_{j;\kappa}, \quad (40)$$

where $\hbar \mathbf{k}_{j;\kappa}$ is the momentum exchanged by a classical projectile with the $(l;\kappa)$ surface atom as in (23) above:

$$\hbar \mathbf{k}_{j;\kappa} = \int_{-\infty}^{+\infty} ds \mathbf{f}_{j;\kappa}[\mathbf{r}(s)]. \quad (41)$$

The next and final assumption is that all atoms in the neighborhood of the classical point of collision have approximately the same phase and amplitude of displacement:

$$I \rightarrow \mathbf{u}_l(\mathbf{R}, t) \cdot \sum_{j;\kappa} \mathbf{k}_{j;\kappa} = \mathbf{u}_l(\mathbf{R}, t) \cdot \mathbf{k}. \quad (42)$$

Inserting the approximate form (42) into the differential reflection coefficient of (35) above gives

$$\frac{dR}{d\Delta d\Omega} = \frac{\rho k_f k_{fz}}{(2\pi)^3 \hbar} \int_{-\infty}^{+\infty} dt \int_{uc} d\mathbf{R} \int_{uc} d\mathbf{R}' \exp\{i[\mathbf{K} \cdot (\mathbf{R} - \mathbf{R}') - t\Delta/\hbar]\} \\ \times \sigma_{fi}^\dagger \sigma_{fi} \sum_l \exp\{i\mathbf{K} \cdot \mathbf{R}_l\} \exp\{-W(\mathbf{R}; \mathbf{k})\} \\ \times \exp\{-W(\mathbf{R}'; \mathbf{k})\} \exp\{\langle \mathbf{k} \cdot \mathbf{u}_0(\mathbf{R}, 0) \mathbf{k} \cdot \mathbf{u}_l(\mathbf{R}', t) \rangle\}. \quad (43)$$

The differential reflection coefficient in Eq. (43) is now remarkably similar to that of Eq. (20). If, in Eq. (20) we take the limit in which the unit-cell elements denoted by the index κ become small, and replace the summations over (κ, κ') by integrals over a single surface layer, the result is identical to (43) except that the form factor $|\sigma_{fi}|^2$ takes on the $(\mathbf{R}, \mathbf{R}')$ dependence discussed in Eq. (38). The final connection between the two results lies in the relation between scattering amplitudes τ_{fi} and σ_{fi} , which is a special case of (25):

$$|\tau_{fi}| = \frac{\hbar^2 \sqrt{k_{fz} k_{iz}}}{L^3 m} |\sigma_{fi}|. \quad (44)$$

At this point we have clearly spelled out a complete set of approximations necessary to obtain the rather simple form of the transition rate of Eq. (20) from formal scattering theory; or in other words, this presents a systematic justification of the rapid scattering assumption of Eq. (19) from which (20) is directly obtained. The approximations made explicit in Eqs. (40)–(42) show that only small-frequency and long-wavelength phonon modes are considered, and optical modes enter only as a possible temperature and position dependence of the scattering amplitude as in (38). The first approximation to the scattering amplitude τ_{fi} is clearly identified in Eq. (36) as the off-energy-shell transition-matrix element of the elastic part of the interaction potential. Although τ_{fi} (or, al-

ternatively σ_{fi}) is a matrix element taken only over a single unit cell, it includes multiple scattering with all neighboring unit cells which can occur via the first-order interaction potential V^0 .

From the calculational point of view, this justification is important because of the great calculational simplicity afforded by the multiphonon scattering intensity of Eq. (20) as opposed to the full trajectory approximation of Eq. (35), and this advantage becomes particularly pronounced when Eq. (20) is coupled with simple models for the vibrational displacements, such as Debye or Einstein models. The success of this simpler approach in explaining the multiphonon intensities for numerous systems ranging from the quantum-mechanical regime³⁰⁻³² to nearly classical scattering³³ shows that these assumptions have a broad range of practical applicability.

The appearance and clear definition of a scattering amplitude τ_{fi} (or σ_{fi}) in the trajectory approximation of (35) shows that the neutronlike scattering assumption of (19) can indeed be applied to atom-surface scattering in the case of multiple quantum exchanges. Normally such an approximation is not considered valid for systems in which there is multiple scattering with different scattering centers. However, in the atom-surface case, in spite of its strong and multiple-scattering nature, such an assumption again becomes useful because of the two-dimensional character of the scattering zone. However, there are clear limitations to such an approximation. For example, this approximation is not expected to give a good description of single surface phonon exchange except possibly in the long-wavelength acoustic limit, and it is not valid when the wave packet of the probe has components which reside for long times near the surface such as in selective adsorption resonances.

Finally, it is noted that the reduction of the full trajectory approximation limit of Eq. (35) to the fast-collision expression of (41) provides, in the intervening steps, a hierarchy of different stages of approximation which may prove to be useful in special cases.

V. CONCLUSIONS

Starting from the general formalism of surface scattering in the form popularized by Levi and Bortolani we have presented a derivation of the quick collision model for the multiphonon intensities observed in atom-surface scattering. This model, which is essentially contained in the statement of Eq. (19), is basically an application of x-ray or neutron-scattering models to the atom-surface problem. As suspected, the model is valid under the assumptions that the multiphonon scattering is dominated by long-wavelength and small-frequency phonon exchange processes. This means that the collision must be fast compared to the dominant vibrational periods and the scattering coherence length must be short compared to the dominant phonon wavelengths, conditions which seem to be satisfied for a large variety of surface systems measured with He-atom scattering. It appears that the neutron-scattering type of approximation is reasonably valid for atom-surface scattering because of the two-dimensional nature of the scattering process, that is to say because of the fact that the atomic projectiles scatter strongly only from the topmost layer of the surface. In this derivation, the scattering amplitude τ_{fi} (or form factor $|\tau_{fi}|^2$) for scattering from a unit cell is identified, to a first approximation, as the off-energy-shell transition-matrix element for scattering by the elastic part of the atom-surface interaction potential. This justifies approximations that have been used for τ_{fi} and provides ways of making better theoretical approximations for its functional form.

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