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Multiphonon atom–surface scattering from corrugated surfaces: derivation of the inelastic scattering spectrum for diffraction states

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Abstract
A strictly quantum mechanical derivation of the energy and parallel momentum resolved scattering spectrum formula that combines the effects of the diffraction of atoms from corrugated surfaces and multiple inelastic scattering by dispersive phonons is presented. The final result is expressed in the compact and numerically tractable form of a Fourier transform of a cumulant expansion in which each term embodies an interplay between the processes of projectile diffraction and multiphonon scattering to all orders in the respective interaction potentials. The Debye–Waller reduction of the intensities of diffraction peaks is explicitly formulated.

1. Introduction

Thermal energy He atom scattering (HAS) has established itself as one of the most sensitive techniques for studying the structural and vibrational properties of surfaces, dominantly due to the unprecedented energy and angular resolution attainable in HAS experiments. The large amount of high quality data acquired in these studies has also motivated the development of theoretical models for interpretation of the various HAS experiments. The impressive achievements of HAS in the investigations of surfaces carried out in the past few decades and the concomitant theoretical interpretations have been reviewed in a series of articles, monographs and books (see [1–26] and references therein). Owing to the versatile use of HAS, this literature is usually focused on the investigations of specific surface properties like the structure of clean crystal surfaces and imperfect, rough and nanostructured surfaces, on the dynamical properties of periodic surfaces and adlayers, on the mobility and surface diffusion of adsorbed atoms and molecules, etc.

One of the long lasting challenges in the theory of HAS has been that of the development of a unified interpretation of vibrationally or phonon-induced inelastic atom scattering from corrugated and periodically ordered surfaces, either clean or covered with adlayers. In this situation one expects a strong interplay between the effects caused by two very different components of atom–surface interactions. The first one is the static interaction of the projectile atom with the crystal lattice which, in the case of strong surface corrugation, gives rise to diffraction effects in the angularly resolved scattering distributions. The second one, which is complementary to the first one, is the dynamical interaction of the projectile with delocalized (propagating) or localized vibrational modes or phonons that have nonvanishing amplitude in the surface region. This interaction gives rise to inelastic scattering in which the momentum and energy are exchanged between the projectile and the phonons. The situation in which the scattering event is governed by two potentials of different spatial and dynamical characteristics poses a complicated problem in the interpretations of concrete experiments. The formal solution of the two-potential collision problem is obtainable in a closed form [27], and is commonly presented in the context of calculations of the total scattering matrix S. To introduce the notation we denote by $H_0 = H_0^{\mathrm{p}} + H_0^{\mathrm{ph}}$ the sum of the kinetic energy operator of the projectile and the unperturbed phonon

field, the corresponding eigenstates are denoted by $|j\rangle$, and U and V are the static and dynamic atom–surface potentials, respectively. The diffraction part of the Hamiltonian is $H^{\rm p}_{\rm diff} = H^{\rm p}_0 + U$, and $\phi^{(\pm)}_j$ are the eigenstates of the Hamiltonian $\mathcal{H}_0 = H^{\rm p}_{\rm diff} + H^{\rm ph}_0$ that have evolved from the unperturbed state $|j\rangle$ and satisfy the outgoing $(+)$ and incoming $(-)$ wave boundary conditions. In a similar fashion we denote by $\psi^{(\pm)}_j$ the outgoing and incoming scattered waves that are the eigenstates of the full Hamiltonian $H = H^{\rm p}_{\rm diff} + H^{\rm ph}_0 + V$. Then, the full S-matrix element for scattering from the initial asymptotic state $|i\rangle$ to the final asymptotic state $|f\rangle$ is obtained in the general form [27]

$$\begin{aligned} S_{\rm fi} &= \langle \psi^{(-)}_{\rm f} | \psi^{(+)}_{\rm i} \rangle = \langle \psi^{(+)}_{\rm f} | S | \psi^{(+)}_{\rm i} \rangle \\ &= \langle \phi^{(-)}_{\rm f} | \phi^{(+)}_{\rm i} \rangle - 2\pi {\rm i} \delta(E_{\rm i} - E_{\rm f}) \langle \phi^{(-)}_{\rm f} | V \\ &\quad + V \frac{1}{E_{\rm i} - H + {\rm i}\eta} V | \phi^{(+)}_{\rm i} \rangle. \end{aligned} \tag{1}$$

Here $E_{\rm i}$ and $E_{\rm f}$ are the total initial and final state energies and $\eta = 0^+$. The term

$$\langle \phi^{(-)}_{\rm f}, \phi^{(+)}_{\rm i} \rangle = S^{\rm diff}_{\rm fi} = \delta_{{\rm f},i} - 2\pi {\rm i} \delta(E_{\rm f} - E_{\rm i}) T^{\rm diff}_{{\rm f},i} \tag{2}$$

is a component of the S-matrix element which for $V = 0$ describes diffractive scattering on the basis of eigenstates of H_0. However, direct implementations of (1) to multiphonon atom scattering from corrugated surfaces are usually connected with computational difficulties in the treatment of the intermediate propagation contained in the last term on the RHS of (1). This necessitates approximations in the calculations of scattering amplitudes in the regime of strong diffraction and multiphonon excitations. Quite generally, approximations can be introduced on the levels of U or V, or both. An important step in the application of (1) was made in [9] and [10] in which the atom–phonon scattering from corrugated surfaces was treated in the distorted wave Born approximation (DWBA), i.e. by approximating the last term on the RHS of (1) by $-2\pi {\rm i} \delta(E_{\rm i} - E_{\rm f}) \langle \phi^{(-)}_{\rm f} | V | \phi^{(+)}_{\rm i} \rangle$. In that calculation the projectile–phonon interaction V was assumed linear in phonon displacements and therefore could induce only one-phonon transitions in the DWBA. For V nonlinear in phonon displacements the DWBA can also induce multiphonon transitions, but in the regime of HAS their amplitudes are small in comparison with those of consecutive one-phonon transitions of the same multiplicity [28], and hence they cannot appreciably affect the scattering spectra. On the other hand, going beyond the DWBA in applications of (1), and thereby encompassing multiphonon excitations, seems to be a formidable task. To the best of our knowledge, a computationally amenable quantum mechanical (QM) treatment of multiphonon atom–surface scattering based on expression (1) and including the effects of U and V to all orders has not been achieved yet. In the following we shall outline an alternative route towards the solution of this problem which is based on the extension of the QM theory of multiphonon scattering from smooth surfaces presented in sections 4–8 of [19].

2. The scattering spectrum formalism

Elastic diffraction of atoms from corrugated surfaces has been a subject of great interest since the very beginning of atom–surface scattering experiments. One of the most exploited theoretical descriptions of these processes is based on the solution of close coupled (CC) equations for scattering from periodic potentials. These calculations can nowadays be carried out numerically with high precision. On the other hand, several algorithms have been developed for the description of single-phonon and multiphonon atom scattering from smooth planar surfaces. One of these approaches, based on the formalism of angularly and energy resolved scattering spectrum [19], has demonstrated remarkable interpretational and predictive power in revealing surface dynamical properties in the extreme quantum regime of HAS, including also the global (macroscopic) quantities deriving from the microscopic properties of gas–surface interactions [29]. However, the descriptions of combined diffractive and phonon-induced inelastic scattering have not yet reached a comparable level of accuracy to the ones achieved in separate treatments of the diffraction and inelastic events. This is mainly due to severe complications associated with the treatment of two kinds of scattering potentials on an equivalent footing.

In several earlier publications we have studied the diffractive and resonant multiphonon He atom scattering from benchmark systems consisting of commensurate Xe monolayers adsorbed on graphite [32] C(0001) and copper [36] Cu(111) surfaces. The adlayers of Xe support, besides the in-surface-plane longitudinal and shear horizontal vibrational modes, in both systems, also the vertically polarized $\rm FT_z$ or S modes with negligible dispersion. These optical-like modes couple most strongly to the scattered He atoms and hence play the major role in the energy and momentum transfer in the course of projectile–target interaction. However, as regards the surface corrugation amplitude of Xe adlayers revealed by HAS, these two systems exhibit markedly different properties.

The system He → Xe/C(0001) exhibits strong surface corrugation [30] and to bring the calculated HAS diffraction intensities into a relation with the measured ones, a three-dimensional (3D) multichannel CC approach was required to yield reliable fully converged theoretical values for comparison with experiments [31, 32]. Vibrational excitations in Xe/graphite adlayers were studied earlier using HAS in the one-phonon scattering regime [33] and also modelled theoretically [34, 35]. However, no attempt has been made to model the multiphonon scattering spectra due to the lack of corresponding experimental data.

By contrast, the He → Xe/Cu(111) system exhibits relatively strong multiphonon excitations but weak diffraction intensities even at low incident energies of the projectile atoms [36]. Both of these features can be successfully interpreted theoretically through separate calculations [36, 37]. In this context the use of the CC approach to ascertain the bound state resonant and inelastic multiphonon scattering in this paradigmatic system seemed a natural

method of choice. This was successfully carried out in [38] by constructing the restricted Fock-space coupled channel (RFCC) equations which for linear projectile–phonon coupling [28] and nondispersive phonon modes can be solved numerically with sufficient accuracy. This approach can reproduce well the earlier results obtained from the scattering spectrum formalism but also provides additional information on and new insight into the resonant scattering [24, 39] not contained in the previous calculations. Vibrational properties of a generically similar Kr/Pt(111) monolayer system were also studied by using HAS [40] but the effects of surface corrugation were neither presented nor accounted for in the interpretation of inelastic scattering intensities.

The two successful applications of the CC method referred to above raise the question of whether a conveniently formulated CC formalism could be utilized to describe the interplay between diffractive and multiphonon inelastic scattering from surfaces. However, for dispersive phonon modes the construction of scattered states as carried out in [38] is no longer feasible in three dimensions and different or improved approaches are needed. In the following we shall follow an alternative route and propose a description of this problem by investigating the effect of phonons on particular diffraction states. This corresponds to the experimental situation in the studies of inelastic atom–surface scattering. To this end we start from the earlier introduced formalism for the lateral momentum and energy resolved atom–surface scattering spectrum [19]:

$$N_{\mathbf{k_i}}(\Delta\mathbf{K},\Delta E) = \lim_{t\to\infty}\langle\psi^{(+)}_{\mathbf{k_i}}(t)|\delta(\Delta\mathbf{K}-(\hat{\mathbf{P}}-\mathbf{K_i})) \times \delta(\Delta E-(H_0^{\mathrm{ph}}-E_{\mathrm{i}}^{\mathrm{ph}}))|\psi^{(+)}_{\mathbf{k_i}}(t)\rangle. \quad (3)$$

Here $\psi^{(+)}_{\mathbf{k_i}}(t)$ is the wavefunction of the system that has evolved from the unperturbed phonon field wavefunction and the wavefunction of the particle with initial 3D momentum $\hbar\mathbf{k_i} = (\mathbf{K_i}, k_{iz})$ and the energy $E_{\mathbf{k_i}}$. $\hat{\mathbf{P}}$ is the particle momentum operator (parallel to the surface) and $\Delta\mathbf{K} = \mathbf{K_f} - \mathbf{K_i}$ and ΔE denote the total parallel momentum and the energy transferred to the scattered particle. We assume, consistently with the scattering boundary conditions, that the dynamics of the system in the limit $t \to \pm\infty$ is governed solely by $H_0 = H_0^{\mathrm{p}} + H_0^{\mathrm{ph}}$. Due to the presence of a single projectile particle in the normalization volume L^3 at all times we have $\langle\psi^{(+)}_{\mathbf{k_i}}(t)|\psi^{(+)}_{\mathbf{k_i}}(t)\rangle = 1$, i.e. the spectrum (3) is normalized to unity.

Expression (3) provides the relevant information that can be extracted from HAS measurements and used for the evaluation of experimentally observable physical quantities. Following [19] we shall first formulate the closed form solution for the scattering spectrum and then propose the leading approximate expression that embodies the effects of multiphonon inelastic scattering pertaining to a specified diffraction state. In all of these considerations the projectile couplings to electronic excitations in the target are neglected since their role becomes important in a different regime of scattering of energetic neutral or ionized beams from metal surfaces [41].

3. Inelastic atom scattering from corrugated surfaces

3.1. Formal derivation of the scattering spectrum

The energy and lateral momentum resolved scattering spectrum (3) which combines the effects of diffraction of atoms from corrugated surfaces and inelastic scattering by phonons can be conveniently formulated within the two-potential scattering formalism. We assume that the diffraction part of the problem governed by $H^{\mathrm{p}}_{\mathrm{diff}}$ is solved, e.g. by employing the close-coupling formalism. The outgoing scattered waves $\phi^{(+)}_{\mathbf{k}}$, which are the eigenstates of $H^{\mathrm{p}}_{\mathrm{diff}}$ that have evolved from the initial plane wave $|\mathbf{k_i}\rangle$ moving towards the surface, can be expressed in the Bloch form relating to the lateral propagation [9, 10, 12]

$$\langle\mathbf{r}|\phi^{(+)}_{\mathbf{k_i}}\rangle = \sum_{\mathbf{G'}=\mathbf{0}}^{\infty}\frac{1}{L^{3/2}}\chi^{(+)}_{\mathbf{K_i}+\mathbf{G'},k_{zi}(\mathbf{G'})}(z)\mathrm{e}^{\mathrm{i}(\mathbf{K_i}+\mathbf{G'})\mathbf{R}}, \quad (4)$$

where L is the linear dimension of the quantization and normalization box and $\mathbf{G}$ represents the two-dimensional surface reciprocal lattice vectors. Likewise, the incoming scattered waves are expressed as

$$\langle\mathbf{r}|\phi^{(-)}_{\mathbf{k_f}}\rangle = \sum_{\mathbf{G''}=\mathbf{0}}^{\infty}\frac{1}{L^{3/2}}\chi^{(-)}_{\mathbf{K_f}+\mathbf{G''},k_{zf}(\mathbf{G''})}(z)\mathrm{e}^{\mathrm{i}(\mathbf{K_f}+\mathbf{G''})\mathbf{R}}. \quad (5)$$

Here the indices i and f denote the initial and final states, respectively, and $k_z^2(\mathbf{G}) = \mathbf{k}^2 - (\mathbf{K}+\mathbf{G})^2$. The summation ranges over all open scattering channels $\mathbf{G}$ for which $k_z^2(\mathbf{G}) > 0$. The amplitude of the specularly reflected beam is given by the $\mathbf{G} = 0$ term. The $\chi^{(\pm)}$ are given by the sum of appropriately weighted normalized waves $\varphi_{k_z(\mathbf{G})}(z)$ that propagate towards and away from the surface (cf (6) and (7) below). It should be noted that the scattering boundary conditions select only the subsets of eigenstates of $H^{\mathrm{p}}_{\mathrm{diff}}$ in the expressions for $\phi^{(\pm)}_{\mathbf{k}}$.

For the crystal occupying the negative half-space $z < 0$ the asymptotic forms of $\chi^{(+)}(z)$'s for $z \to \infty$, positive total energy and two directions of propagation relative to the surface are given by [9, 32]

$$\chi^{(+)}_{\mathbf{K_i}+\mathbf{G},k_{zi}(\mathbf{G})}(z) \to \mathrm{e}^{-\mathrm{i}k_{zi}z}\delta_{\mathbf{G},\mathbf{0}} + A_{\mathbf{k_i},\mathbf{G}}\mathrm{e}^{+\mathrm{i}k_{zi}(\mathbf{G})z}, \quad k_{zi}(\mathbf{G}) > 0$$
$$\chi^{(+)}_{\mathbf{K_i}+\mathbf{G},k_{zi}(\mathbf{G})}(z) \to 0, \qquad k_{zi}^2(\mathbf{G}) < 0. \quad (6)$$

The asymptotic form of $\chi^{(-)}(z)$ is obtained by changing the sign in front of k_z and $k_z(\mathbf{G})$ in expressions (6), namely

$$\chi^{(-)}_{\mathbf{K_f}+\mathbf{G},k_{zf}(\mathbf{G})}(z) \to \mathrm{e}^{+\mathrm{i}k_{zf}z}\delta_{\mathbf{G},\mathbf{0}} + A_{\mathbf{k_f},\mathbf{G}}\mathrm{e}^{-\mathrm{i}k_{zf}(\mathbf{G})z}, \quad k_{zf}(\mathbf{G}) > 0$$
$$\chi^{(-)}_{\mathbf{K_f}+\mathbf{G},k_{zf}(\mathbf{G})}(z) \to 0, \qquad k_{zf}^2(\mathbf{G}) < 0. \quad (7)$$

This implies the asymptotic behaviour $\varphi_{k_z(\mathbf{G})}(z \to -\infty) \to 0$ and $\varphi_{k_z(\mathbf{G})}(z \to \infty) \to \sqrt{2}\exp(\mathrm{i}k_z(\mathbf{G})z)$ where $k_z(\mathbf{G})$ may acquire positive and negative values.

With the box normalization in (4) and (5) the scattered waves satisfy the orthogonality and closure relations

$$\langle\phi_{\mathbf{k}}^{(\pm)}|\phi_{\mathbf{k}'}^{(\pm)}\rangle = \delta_{\mathbf{k},\mathbf{k}'}, \tag{8}$$

$$\sum_{\mathbf{k}} |\phi_{\mathbf{k}}^{(\pm)}\rangle\langle\phi_{\mathbf{k}}^{(\pm)}| = 1. \tag{9}$$

In combination with (6) and (7) this implies $\sum_{\mathbf{G}}|A_{\mathbf{k},\mathbf{G}}|^2 = 1$, meaning that after the completion of collision the unit particle density probability is distributed over all open **G**-channels.

The conservation of the asymptotic projectile current perpendicular to the surface as calculated from (6) to (7) yields

$$\sum_{\mathbf{G}} \frac{k_z(\mathbf{G})}{k_z}|A_{\mathbf{k},\mathbf{G}}|^2 = \sum_{\mathbf{G}}|S_{\mathbf{k},\mathbf{G}}^{\mathrm{diff}}|^2 = 1, \tag{10}$$

with the summation extending only over open diffraction channels for which $k_z^2(\mathbf{G}) > 0$.

Introducing the scattering operator S for distorted waves, denoting by $|ph_\mathrm{i}\rangle$ a particular initial phonon configuration with the statistical Boltzmann weight $w_{\mathrm{ph_i}}$, and by $\{ph_\mathrm{i}\}$ a set of possible initial phonon configurations, the projectile scattering spectrum can be written as

$$N_{\mathbf{k_i}}(\Delta\mathbf{K}, \Delta E) = \sum_{\{ph_\mathrm{i}\}} w_{\mathrm{ph_i}}\langle ph_\mathrm{i}|\langle\phi_{\mathbf{k_i}}^{(+)}|S^\dagger\delta(\Delta\mathbf{K} - (\hat{\mathbf{P}} - \mathbf{K_i}))$$
$$\times\,\delta(\Delta E - (H_0^{\mathrm{ph}} - E_\mathrm{i}^{\mathrm{ph}}))S|\phi_{\mathbf{k_i}}^{(+)}\rangle|ph_\mathrm{i}\rangle. \tag{11}$$

Here the particle momentum operator parallel to the surface $\hat{\mathbf{P}}$ is diagonal in the waves $\langle\mathbf{R}|\mathbf{K}+\mathbf{G}\rangle = \exp[\mathrm{i}(\mathbf{K}+\mathbf{G})\mathbf{R}]/L$ but not in the scattered waves $\langle\mathbf{r}|\phi_{\mathbf{k}}^{(\pm)}\rangle$. The scattering operator S is the limit of the full evolution operator of the system

$$S = \lim_{t_\mathrm{f}\to\infty, t_\mathrm{i}\to-\infty}\exp[-\mathrm{i}(\mathcal{H}_0 + V)(t_\mathrm{f} - t_\mathrm{i})], \tag{12}$$

where $\mathcal{H}_0 = H_{\mathrm{diff}}^{\mathrm{p}} + H_0^{\mathrm{ph}}$. For reasons to be discussed later, the limit $t_f \to \infty$ should be taken only after the various manipulations with the δ-functions acting on the state vector $S|\phi_{\mathbf{k_i}}^{(+)}\rangle|ph_\mathrm{i}\rangle = S|\phi_\mathrm{i}^{(\pm)}\rangle$ in (11) have been performed[1].

The energy resolved scattering spectrum $N_{\mathbf{k_i}}(\Delta\mathbf{K})$ is obtained from (11) by integration over all $\Delta\mathbf{K}$ and reads

$$N_{\mathbf{k_i}}(\Delta E) = \sum_{\{ph_\mathrm{i}\}} w_{\mathrm{ph_i}}\langle ph_\mathrm{i}|\langle\phi_{\mathbf{k_i}}^{(+)}|S^\dagger\delta(\Delta E - (H_0^{\mathrm{ph}} - E_0^{\mathrm{ph}}))$$
$$\times\, S|\phi_{\mathbf{k_i}}^{(+)}\rangle|ph_\mathrm{i}\rangle. \tag{13}$$

In an analogous fashion the parallel momentum resolved scattering spectrum or the angularly resolved scattering distribution $N_{\mathbf{k_i}}(\Delta\mathbf{K})$ is obtained from (11) by integration over all exchanged energies ΔE and reads

$$N_{\mathbf{k_i}}(\Delta\mathbf{K}) = \sum_{\{ph_\mathrm{i}\}} w_{\mathrm{ph_i}}\langle ph_\mathrm{i}|\langle\phi_{\mathbf{k_i}}^{(+)}|S^\dagger\delta(\Delta\mathbf{K} - (\hat{\mathbf{P}} - \mathbf{K_i}))$$
$$\times\, S|\phi_{\mathbf{k_i}}^{(+)}\rangle|ph_\mathrm{i}\rangle. \tag{14}$$

In the absence of the projectile–phonon interaction, i.e. for $V = 0$, we have $S = S^{\mathrm{diff}} = \lim_{t_\mathrm{f}\to\infty, t_\mathrm{i}\to-\infty}\exp[-\mathrm{i}\mathcal{H}_0(t_\mathrm{f} - t_\mathrm{i})]$. Since the wavefunctions $|\phi_{\mathbf{k_i}}^{(+)}\rangle$ are eigenfunctions of $H_{\mathrm{diff}}^{\mathrm{p}}$ appearing in S^{diff} we have

$$N_{\mathbf{k_i}}^{\mathrm{diff}}(\Delta\mathbf{K}) = \langle\phi_{\mathbf{k_i}}^{(+)}|\delta(\Delta\mathbf{K} - (\hat{\mathbf{P}} - \mathbf{K_i}))|\phi_{\mathbf{k_i}}^{(+)}\rangle. \tag{15}$$

Substituting (4) into (15) we find the diffraction spectrum in the form

$$N_{\mathbf{k_i}}^{\mathrm{diff}}(\Delta\mathbf{K}) = \sum_{\mathbf{G}'}|a_{\mathbf{k_i},\mathbf{G}'}|^2\delta(\Delta\mathbf{K} - \mathbf{G}'), \tag{16}$$

where

$$|a_{\mathbf{k_i},\mathbf{G}'}|^2 = \langle\mathbf{K_i} + \mathbf{G}'|\langle\chi_{\mathbf{K_i}+\mathbf{G}',k_{zi}(\mathbf{G}')}^{(+)}|\chi_{\mathbf{K_i}+\mathbf{G}',k_{zi}(\mathbf{G}')}^{(+)}\rangle$$
$$\times\,|\mathbf{K_i} + \mathbf{G}'\rangle. \tag{17}$$

For later convenience we also define the normalized **G**-components of $\phi_{\mathbf{k}}^{(\pm)}(\mathbf{r})$

$$\langle\mathbf{r}|\mathbf{K}+\mathbf{G}, k_z(\mathbf{G});^{(\pm)}\rangle = \frac{1}{|a_{\mathbf{k},\mathbf{G}}|L^{3/2}}\chi_{\mathbf{K}+\mathbf{G},k_z(\mathbf{G})}^{(\pm)}(z)\mathrm{e}^{\mathrm{i}(\mathbf{K}+\mathbf{G})\mathbf{R}}. \tag{18}$$

The scattering spectra defined in (11), (13) and (14)) are positive definite quantities. $N_{\mathbf{k_i}}(\Delta\mathbf{K}, \Delta E)$ satisfies the unitarity condition:

$$\int \mathrm{d}^2(\Delta\mathbf{K})\int \mathrm{d}(\Delta E)N_{\mathbf{k_i}}(\Delta\mathbf{K}, \Delta E) = 1, \tag{19}$$

and analogously for the spectra (13) and (14) in their respective phase spaces. In the following we shall for the sake of simplicity manipulate a somewhat simpler expression (14) in order to demonstrate the desired result and then write down by analogy the corresponding expression for (11) following the procedure described in section 4.2 of [19].

In the next step we use the exponential or Magnus representation of the evolution operator in the interaction picture with respect to $\mathcal{H}_0 = H_{\mathrm{diff}}^{\mathrm{p}} + H_0^{\mathrm{ph}}$ to write [42]

$$S = \lim_{t_\mathrm{f}\to\infty, t_\mathrm{i}\to-\infty}\exp[-\mathrm{i}\mathcal{H}_0(t_f - t_i)]\exp[-\mathrm{i}\hat{G}(t_f - t_i)], \tag{20}$$

where $\hat{G}(t_f - t_i) = \sum_{n=1}^{\infty}\hat{G}_n(t_f - t_i)$ (not to be confused with the 2D reciprocal lattice vectors **G**) is a series of time-ordered integrals of $V_I(t_j)$ in the interaction representation with respect to $\mathcal{H}_0 = H_{\mathrm{diff}}^{\mathrm{p}} + H_0^{\mathrm{ph}}$, and their ascending commutators that are explicitly written out in equations (182)–(188) of [19]. This leads to the description of inelastic processes in terms of perturbed distorted (diffracted) waves. As will be shown in section 3.2, the exponential form of the operators in the diagonal matrix elements in expressions (11), (13) and (14) will make them amenable to evaluation based on cumulant expansion. To demonstrate this on the

[1] It is possible to define the scattering spectrum (11) for transitions only into the final waves running away from the surface. This is effectuated by the replacement $\delta(\Delta E - (H_0^{\mathrm{ph}} - E_\mathrm{i}^{\mathrm{ph}}))S \to \delta(\Delta E - (H_0^{\mathrm{ph}} - E_\mathrm{i}^{\mathrm{ph}}))\Lambda^{\mathrm{out}}S$ in (11) where Λ^{out} is the corresponding projection operator [27]. However, this would complicate the following discussion far beyond the present scope.

example of (14) we employ the van Hove transformation to express the momentum δ-function as a two-dimensional Fourier transform, $\delta(\mathbf{K}) = \int \mathrm{d}^2\boldsymbol{\mathcal{R}} \exp(\mathrm{i}\mathbf{K}\boldsymbol{\mathcal{R}})/(2\pi)^2$, define $\lim_{t_\mathrm{f}\to\infty, t_\mathrm{i}\to-\infty} \exp[-\mathrm{i}\hat{G}(t_f - t_i)] = \exp(-\mathrm{i}\hat{G}) = \exp(-\mathrm{i}\sum_{n=1}^{\infty}\hat{G}_n)$, and introduce the unitary transformation

$$\exp(\mathrm{i}\hat{G})\hat{\mathbf{P}}\exp(-\mathrm{i}\hat{G}) = \hat{\boldsymbol{\mathcal{P}}} = \hat{\mathbf{P}} + \sum_{m=1}^{\infty}\frac{i^m}{m!}\hat{G}^m[\hat{\mathbf{P}}]$$
$$= \hat{\mathbf{P}} + \hat{\boldsymbol{\mathcal{W}}}, \tag{21}$$

where $\hat{G}^m[\hat{\mathbf{P}}] = [\hat{G}, [\hat{G}, \ldots, [\hat{G}, \hat{\mathbf{P}}]]]$ denotes mth-order repeated commutator of $\hat{G}$ with $\hat{\mathbf{P}}$. This procedure was described in detail in section 4.2 of [19] and enables us to write

$$N_{\mathbf{k_i}}(\Delta\mathbf{K}) = \int \frac{\mathrm{d}^2\boldsymbol{\mathcal{R}}}{(2\pi)^2}\mathrm{e}^{\mathrm{i}(\Delta\mathbf{K}+\mathbf{K_i})\boldsymbol{\mathcal{R}}}\sum_{\{ph_\mathrm{i}\}} w_{\mathrm{ph_i}}$$
$$\times \langle ph_\mathrm{i}|\langle\phi^{(+)}_{\mathbf{k_i}}|\exp(\mathrm{i}\hat{G})\exp(-\mathrm{i}\hat{\mathbf{P}}\boldsymbol{\mathcal{R}})\exp(-\mathrm{i}\hat{G})|\phi^{(+)}_{\mathbf{k_i}}\rangle|ph_\mathrm{i}\rangle$$
$$= \int \frac{\mathrm{d}^2\boldsymbol{\mathcal{R}}}{(2\pi)^2}\mathrm{e}^{\mathrm{i}(\Delta\mathbf{K}+\mathbf{K_i})\boldsymbol{\mathcal{R}}}\sum_{\{ph_\mathrm{i}\}} w_{\mathrm{ph_i}}$$
$$\times \langle ph_\mathrm{i}|\langle\phi^{(+)}_{\mathbf{k_i}}|\exp[-\mathrm{i}\exp(\mathrm{i}\hat{G})\hat{\mathbf{P}}\boldsymbol{\mathcal{R}}\exp(-\mathrm{i}\hat{G})]|\phi^{(+)}_{\mathbf{k_i}}\rangle|ph_\mathrm{i}\rangle$$
$$= \int \frac{\mathrm{d}^2\boldsymbol{\mathcal{R}}}{(2\pi)^2}\mathrm{e}^{\mathrm{i}(\Delta\mathbf{K}+\mathbf{K_i})\boldsymbol{\mathcal{R}}}\sum_{\{ph_\mathrm{i}\}} w_{\mathrm{ph_i}}$$
$$\times \langle ph_\mathrm{i}|\langle\phi^{(+)}_{\mathbf{k_i}}|\exp[-\mathrm{i}(\hat{\mathbf{P}} + \hat{\boldsymbol{\mathcal{W}}})\boldsymbol{\mathcal{R}}]|\phi^{(+)}_{\mathbf{k_i}}\rangle|ph_\mathrm{i}\rangle$$
$$= \int \frac{\mathrm{d}^2\boldsymbol{\mathcal{R}}}{(2\pi)^2}\mathrm{e}^{\mathrm{i}(\Delta\mathbf{K}+\mathbf{K_i})\boldsymbol{\mathcal{R}}}\sum_{\{ph_\mathrm{i}\}} w_{\mathrm{ph_i}}$$
$$\times \langle ph_\mathrm{i}|\langle\phi^{(+)}_{\mathbf{k_i}}|\exp(-\mathrm{i}\hat{\mathbf{P}}\boldsymbol{\mathcal{R}})\mathcal{U}_I(\hat{\boldsymbol{\mathcal{W}}}, \boldsymbol{\mathcal{R}})|\phi^{(+)}_{\mathbf{k_i}}\rangle|ph_\mathrm{i}\rangle. \tag{22}$$

Here we have defined the $\hat{\boldsymbol{\mathcal{W}}}$-generated 'evolution' operator in the $\boldsymbol{\mathcal{R}}$-space by

$$\mathcal{U}_I(\hat{\boldsymbol{\mathcal{W}}}, \boldsymbol{\mathcal{R}}) = T_{\boldsymbol{\mathcal{R}}}\exp\left[-\mathrm{i}\int_0^{\boldsymbol{\mathcal{R}}}\mathrm{d}^2\boldsymbol{\mathcal{R}}'\,\hat{\boldsymbol{\mathcal{W}}}_I(\boldsymbol{\mathcal{R}}')\right] \tag{23}$$

where $\hat{\boldsymbol{\mathcal{W}}}_I(\boldsymbol{\mathcal{R}}) = \exp(\mathrm{i}\hat{\mathbf{P}}\boldsymbol{\mathcal{R}})\hat{\boldsymbol{\mathcal{W}}}\exp(-\mathrm{i}\hat{\mathbf{P}}\boldsymbol{\mathcal{R}})$ is expressed in the interaction picture with respect to the unperturbed 'translation' operator $\exp(-\mathrm{i}\hat{\mathbf{P}}\boldsymbol{\mathcal{R}})$. Here $T_{\boldsymbol{\mathcal{R}}}$ denotes the $\boldsymbol{\mathcal{R}}$-ordering operator which acts on the powers of $\hat{\boldsymbol{\mathcal{W}}}_I(\boldsymbol{\mathcal{R}}')$ arising from the expansion of exponential function $\exp[-\mathrm{i}\int_0^{\boldsymbol{\mathcal{R}}}\mathrm{d}^2\boldsymbol{\mathcal{R}}'\,\hat{\boldsymbol{\mathcal{W}}}_I(\boldsymbol{\mathcal{R}}')]$ into a series ($T_{\boldsymbol{\mathcal{R}}}$ is an analogue of the time-ordering operator appearing in the definition of the standard evolution operator in real time). In a completely analogous fashion we may introduce in (11) the van Hove transformation in the energy space through the Fourier transform $\delta(E) = \int \mathrm{d}\tau\exp(-\mathrm{i}E\tau)/2\pi$, define $\mathrm{e}^{\mathrm{i}\hat{G}}H_0^{\mathrm{ph}}\mathrm{e}^{-\mathrm{i}\hat{G}} = H_0^{\mathrm{ph}} + \hat{\mathcal{V}}$, and obtain the analogue of (23) in the τ-space

$$\mathcal{U}_I(\hat{\mathcal{V}}, \tau) = T_\tau\exp\left[-\mathrm{i}\int_0^{\tau}\mathrm{d}\tau\hat{\mathcal{V}}_I(\tau')\right]. \tag{24}$$

Owing to the fact that $\hat{\mathbf{P}}$ and H_0^{ph} commute, we obtain the following representation of the momentum and energy resolved scattering spectrum:

$$N_{\mathbf{k_i}}(\Delta\mathbf{K}, \Delta E) = \int \frac{\mathrm{d}^2\boldsymbol{\mathcal{R}}}{(2\pi)^2}\mathrm{e}^{\mathrm{i}(\Delta\mathbf{K}+\mathbf{K_i})\boldsymbol{\mathcal{R}}}\int\frac{\mathrm{d}\tau}{2\pi}\mathrm{e}^{-\mathrm{i}(\Delta E + E_0^{\mathrm{ph}})\tau}$$
$$\times \sum_{\{ph_\mathrm{i}\}} w_{\mathrm{ph_i}}\langle ph_\mathrm{i}|\langle\phi^{(+)}_{\mathbf{k_i}}|\exp[-\mathrm{i}(\hat{\mathbf{P}}\boldsymbol{\mathcal{R}} - H_0^{\mathrm{ph}}\tau)]$$
$$\times \mathcal{U}_I(\hat{\boldsymbol{\mathcal{W}}}, \hat{\mathcal{W}}, \boldsymbol{\mathcal{R}}, \tau)|\phi^{(+)}_{\mathbf{k_i}}\rangle|ph_\mathrm{i}\rangle, \tag{25}$$

where $\mathcal{U}_I(\hat{\boldsymbol{\mathcal{W}}}, \hat{W}, \boldsymbol{\mathcal{R}}, \tau)$ is a product of (23) and (24). It is seen that for $V = 0$, and hence $\hat{\boldsymbol{\mathcal{W}}} = 0$ and $\hat{\mathcal{W}} = 0$, one immediately retrieves the elastic diffraction spectrum. On the other hand, in the case of smooth surfaces for which $U = 0$ and consequently all $\mathbf{G} = 0$, the scattering spectrum pertinent to a flat vibrating surface is retrieved. Note also that $\boldsymbol{\mathcal{R}}$ and τ serve here only as dummy integration variables and are not associated with the dynamical properties of the system otherwise contained in the operators $\hat{\boldsymbol{\mathcal{W}}}_I$ and $\hat{\mathcal{W}}_I$.

3.2. Approximate treatments

3.2.1. Intrachannel scattering by phonons. Expression (25) is exact insofar as the sets $\{|\phi^{(\pm)}_{\mathbf{k}}\rangle\}$ are complete because no approximations have been made in its derivation. However, the advantage of using this expression in the description of multiphonon scattering processes instead of the more standard approach based on the Born expansion of the T-matrix remains to be demonstrated. One-phonon processes can be accurately described in the first-order distorted wave Born approximation in terms of $|\phi^{(\pm)}_{\mathbf{k}}\rangle$ defined in (4) and (5) [9, 12]. However, already the two-phonon processes are very difficult to treat within the standard Born expansion formalism due to the mathematical complications, on the one hand, and due to the convergence and unitarity problems when the series for the scattering matrix is truncated, on the other hand. By contrast, the interplay between diffraction and multiphonon processes can be treated within the scattering spectrum formalism efficiently and to a high degree of accuracy. To illustrate this on a tractable example which allows the intermediate steps in calculations to be easily visualized we shall assume in the first instance that the projectile–phonon interaction V does not give rise to Umklapp processes, i.e. that the changes of projectile wavevectors in phonon excitation processes are restricted to the first Brillouin zone. This assumption is well justified in a large number of systems because the projectile–phonon matrix elements may be very small for large momentum transfers [43]. Thereby the phonon emissions and absorptions take place in the course of projectile $\mathbf{G}$-intrachannel propagation only. In this case the last line in equation (25) can be written in terms of diagonal matrix elements over the normalized $\mathbf{G}$-components (18) of the scattered waves

$$N_{\mathbf{k_i}}(\Delta\mathbf{K}) = \sum_{\mathbf{G}}|a_{\mathbf{k_i},\mathbf{G}}|^2\int\frac{\mathrm{d}^2\boldsymbol{\mathcal{R}}}{(2\pi)^2}\mathrm{e}^{\mathrm{i}(\Delta\mathbf{K}-\mathbf{G})\boldsymbol{\mathcal{R}}}\sum_{\{ph_\mathrm{i}\}} w_{\mathrm{ph_i}}$$
$$\times \langle ph_\mathrm{i}|\langle\mathbf{K_i}+\mathbf{G}, k_{zi}(\mathbf{G});^{(+)}|\mathcal{U}_I(\hat{\boldsymbol{\mathcal{W}}}, \boldsymbol{\mathcal{R}})$$
$$\times |\mathbf{K_i}+\mathbf{G}, k_{zi}(\mathbf{G});^{(+)}\rangle|ph_\mathrm{i}\rangle. \tag{26}$$

For $V = 0$ one has $\hat{G} = 0$ and $\hat{\mathcal{W}} = 0$, and (26) reduces to (16). To further treat $N_{\mathbf{k_i}}(\Delta\mathbf{K})$ we define averaging of an operator $\hat{O}$ over the normalized states in (26) by

$$\langle\langle\hat{O}\rangle\rangle_{\mathbf{G}} = \sum_{\{ph_i\}} w_{\mathrm{ph_i}} \langle ph_i|\langle\mathbf{K_i}+\mathbf{G}, k_{zi}(\mathbf{G});^{(+)}| \times \hat{O}|\mathbf{K_i}+\mathbf{G}, k_{zi}(\mathbf{G});^{(+)}\rangle|ph_i\rangle. \quad (27)$$

This averaging procedure satisfies the necessary requirement that it averages the unit operator to unity. When applied to generalized exponential operators of the type (23) it can be carried out by means of cumulant expansion [44]

$$\langle\langle\mathcal{U}_I(\hat{\mathcal{W}},\boldsymbol{\mathcal{R}})\rangle\rangle_{\mathbf{G}} = \exp\left\langle\left\langle T_{\boldsymbol{\mathcal{R}}}\exp\left[-\mathrm{i}\int_0^{\boldsymbol{\mathcal{R}}}\mathrm{d}^2\boldsymbol{\mathcal{R}}'\hat{\mathcal{W}}_I(\boldsymbol{\mathcal{R}}')\right]-1\right\rangle\right\rangle_{\mathrm{c}(\mathbf{G})}, \quad (28)$$

where the subscript c means that the average $\langle\langle\cdots\rangle\rangle_{\mathrm{c}(\mathbf{G})}$ is the cumulant average based on the definition (27) (for details of taking cumulant averages see [44] and equation (6.10) therein) which is applied to the series expansion of (23) after substitution on the RHS of (28). This yields

$$\exp\left\langle\left\langle T_{\boldsymbol{\mathcal{R}}}\exp\left[-\mathrm{i}\int_0^{\boldsymbol{\mathcal{R}}}\mathrm{d}^2\boldsymbol{\mathcal{R}}'\hat{\mathcal{W}}_I(\boldsymbol{\mathcal{R}}')\right]-1\right\rangle\right\rangle_{\mathrm{c}(\mathbf{G})} = \exp\left[\sum_{n=1}^{\infty}C_n(\mathbf{G},\boldsymbol{\mathcal{R}})\right] \quad (29)$$

where $C_n(\mathbf{G},\boldsymbol{\mathcal{R}})$ are the cumulants generated by the averaging procedure (28). Hence

$$N_{\mathbf{k_i}}(\Delta\mathbf{K}) = \sum_{\mathbf{G}}|a_{\mathbf{k_i},\mathbf{G}}|^2\int\frac{\mathrm{d}^2\boldsymbol{\mathcal{R}}}{(2\pi)^2}\mathrm{e}^{\mathrm{i}(\Delta\mathbf{K}-\mathbf{G})\boldsymbol{\mathcal{R}}} \times \exp\left[\sum_{n=1}^{\infty}C_n(\mathbf{G},\boldsymbol{\mathcal{R}})\right]. \quad (30)$$

To calculate higher order cumulant averages (i.e. for $n > 1$) we need to specify some basic characteristics of the dynamic interaction V which generates the operators $\hat{\mathcal{W}}_I(\boldsymbol{\mathcal{R}})$, and particularly its representability in terms of the projectile operators. A convenient way to do this is to represent V in the second-quantization (SQ) representation which is a standard procedure in the scattering theory of many-body systems (cf chapter 10.3 in [27] and section 4.3 in [19]). Denoting by $\mathbf{r}$ the projectile coordinate, and by $\hat{\Psi}^{\dagger}(\mathbf{r})$ and $\hat{\Psi}(\mathbf{r})$ the particle field creation and annihilation operators, respectively, the SQ representation of this interaction as regards the projectile particle operators is obtained from

$$V^{\mathrm{SQ}} = \int\mathrm{d}^3\mathbf{r}\hat{\Psi}^{\dagger}(\mathbf{r})V(\mathbf{r})\hat{\Psi}(\mathbf{r}), \quad (31)$$

where $V(\mathbf{r})$ comprises also the phonon coordinates. To facilitate cumulant averaging and calculation of cumulants in (29) we shall expand the field operators $\hat{\Psi}^{\dagger}(\mathbf{r})$ and $\hat{\Psi}(\mathbf{r})$ in a complete set of states that would most conveniently represent particle propagation in the intermediate states between successive actions of the perturbation V. Among the natural choices of such manifolds the first one is a complete set of normalized $\mathbf{G}$-channel running eigenstates of $H^{\mathrm{p}}_{\mathrm{diff}}$

$$\langle\mathbf{r}|\mathbf{K}+\mathbf{G}, k_z\rangle = \exp[\mathrm{i}(\mathbf{K}+\mathbf{G})\mathbf{R}]\varphi_{k_z}(z) \quad (32)$$

with $\mathbf{K}$ restricted to a single surface Brillouin zone, e.g. that of $\mathbf{K_i}$, and unconstrained positive and negative values of k_z so as to allow for both directions of propagation relative to the surface. This also enables a simple representation of $|\mathbf{K}+\mathbf{G}, k_z(\mathbf{G});^{(\pm)}\rangle$ in terms of $|\mathbf{K}+\mathbf{G}, k_z\rangle$. The second choice is the expansion of $\hat{\Psi}(\mathbf{r})$ and $\hat{\Psi}^{\dagger}(\mathbf{r})$ in the normalized scattered states $\phi^{(\pm)}_{\mathbf{k}}(\mathbf{r})$ defined in (4) and (5). The rationale for the first choice is that irrespective of the history of populations of particular diffraction channels, here embodied in $A_{\mathbf{k_i},\mathbf{G}}$ defined in (6), once the projectile moves in a $\mathbf{G}$-channel, it couples as a single particle (i.e. described by a normalized wavefunction) to the phonons. The second choice may in our opinion lead to overcounting of diffraction channel amplitudes in intrachannel scattering. Hence, we define

$$\hat{\Psi}(\mathbf{r}) = \sum_{\mathbf{K}',\mathbf{G}',k_z'>0}[c_{\mathbf{K}'+\mathbf{G}',k_z'}\langle\mathbf{r}|\mathbf{K}'+\mathbf{G}', k_z'\rangle + c_{\mathbf{K}'+\mathbf{G}',-k_z'}\langle\mathbf{r}|\mathbf{K}'+\mathbf{G}', -k_z'\rangle]/\sqrt{2}, \quad (33)$$

where $c_{\mathbf{K}'+\mathbf{G}',k_z'}$ is the annihilation operator for a particle in the normalized running eigenstate $\langle\mathbf{r}|\mathbf{K}'+\mathbf{G}', k_z'\rangle$ of $H^{\mathrm{p}}_{\mathrm{diff}}$, and analogously for the adjoint $\hat{\Psi}^{\dagger}(\mathbf{r})$. Likewise, the initial states $\langle\mathbf{r}|\mathbf{K_i}+\mathbf{G}, k_{zi}(\mathbf{G});^{(+)}\rangle$ over which the averaging in (28) is carried out, should be expressed through the operators $c^{\dagger}_{\mathbf{K}'+\mathbf{G}',k_z'}$ and the corresponding wavefunctions $\langle\mathbf{r}|\mathbf{K}'+\mathbf{G}', k_z'\rangle$. Thereby we obtain the representation of V_I, and accordingly of $\hat{\mathcal{W}}_I(\boldsymbol{\mathcal{R}}')$, that facilitates the calculation of cumulant averages in the exponent on the LHS of (29) using the methods of quantum field theory. Generalization of (30) to the momentum and energy resolved scattering spectrum yields

$$N_{\mathbf{k_i}}(\Delta\mathbf{K},\Delta E) = \sum_{\mathbf{G}}|a_{\mathbf{k_i},\mathbf{G}}|^2\int\frac{\mathrm{d}^2\boldsymbol{\mathcal{R}}}{(2\pi)^2}\mathrm{e}^{\mathrm{i}(\Delta\mathbf{K}-\mathbf{G})\boldsymbol{\mathcal{R}}} \times \int\frac{\mathrm{d}\tau}{2\pi}\mathrm{e}^{-\mathrm{i}\Delta E\tau}\exp\left[\sum_{n=1}^{\infty}C_n(\mathbf{G},\boldsymbol{\mathcal{R}},\tau)\right], \quad (34)$$

in which the generalized cumulants $C_n(\mathbf{G},\boldsymbol{\mathcal{R}},\tau)$ can be written down by inspection of the above expressions and [19] and [44].

With the derivation of formulae (26), (30) and (34) we have reformulated the problem of calculation of multiphonon processes from expression (1)—whose solution is usually presented in the form of a Born or geometric-like series in powers of V—in a form in which the interaction generates an exponentiated cumulant series in ascending powers of V. Since the calculation of higher order terms in either type of series is not feasible in practice, except in very special cases, one may still question the advantage of using (30) and (34) instead of (1). However, this becomes clear once approximations of the same type are invoked in the calculations of multiphonon processes. A usual approximation consists of truncating the Born or perturbation series for S in powers of V after a finite number of terms, say n. Now, the truncation of

the series yields phonon excitation or annihilation amplitudes up to the order n whose sum, as a rule, produces a non-unitary result for the S-matrix unless some sort of unitarity corrections are introduced (for the unitarity correction of one-phonon excitation amplitudes see [3]). This is typically encountered in the situation in which the first-order Born approximation is implemented and higher order terms neglected, because they are hard to obtain, but the projectile–phonon interaction V is not weak enough to justify this. On the other hand, truncating the cumulant series in (30) or (34) always produces unitary results for the multiphonon scattering spectra. Moreover, in concrete problems the cumulant series may converge much faster than the related Born expansion because the effective small expansion parameter for a $2n$th-order cumulant ($n > 1$) is the power of the coupling constant in combination with the correlation between two successive phonon-induced scattering events. Hence, the truncation of cumulant series beyond the term quadratic in V describes multiphonon processes to all orders, albeit subject to the condition of weak intermediate correlations. In this respect the situation with multiphonon excitations is here completely analogous to the case of flat surfaces for which the second-order cumulant expansion or the exponentiated Born approximation (EBA) has proven a reliable method for successful description of inelastic scattering both at low and high projectile incident energies [19].

To demonstrate the derivation of the distorted wave EBA in the present example of Umklapp-free projectile–phonon interactions we shall systematically retain in $\hat{G}$, $\hat{\mathcal{W}}$ and $\hat{\mathcal{W}}$ only the terms that are linear and quadratic in V and hence lead to $C^{\mathrm{EBA}}(\mathbf{G}, \boldsymbol{\mathcal{R}}, \tau) = C_1(\mathbf{G}, \boldsymbol{\mathcal{R}}, \tau) + C_2(\mathbf{G}, \boldsymbol{\mathcal{R}}, \tau)$, and discard all others. In doing this we shall closely follow the recipes outlined in sections 4.2 and 4.3 of [19]. This amounts to calculating $[\hat{G}, \hat{\mathcal{P}}]$ and $[\hat{G}, H_0^{\mathrm{ph}}]$ with $\hat{G} = \hat{G}_1 + \hat{G}_2^{\mathrm{diag}}$, and using these to find the corresponding $\hat{\mathcal{W}}$ and $\hat{\mathcal{W}}$. The latter two commuting operators serve for definition of the 'evolution operators' $\mathcal{U}_I(\hat{\mathcal{W}}, \mathcal{R})$ and $\mathcal{U}_I(\hat{\mathcal{W}}, \tau)$, respectively. Their average generates a cumulant expansion in the exponent on the RHS of (34) in which again only the first two terms are retained, thus yielding an expression quadratic in V. Here the functional form of (31) and conservation of energy and parallel momentum select the appropriate scattered states $|\mathbf{K}' + \mathbf{G}', k_z'\rangle$ in (31), and thereby via $\hat{G}$ also in C^{EBA}. Finally we obtain

$$
\begin{aligned}
C^{\mathrm{EBA}}_{\mathrm{intra}}(\mathbf{G}, \boldsymbol{\mathcal{R}}, \tau) = -\sum_{\mathbf{Q},j,k_z'>0} \Big\{ & |\mathcal{V}^{j,k_z',k_{\mathrm{i}z}(\mathbf{G})}_{\mathbf{K_i}+\mathbf{G}-\mathbf{Q},\mathbf{K_i}+\mathbf{G}}(+\omega_{\mathbf{Q},j})|^2 \\
& \times [n(\omega_{\mathbf{Q},j}) + 1][1 - \mathrm{e}^{-\mathrm{i}(\omega_{\mathbf{Q},j}\tau - \mathbf{Q}\boldsymbol{\mathcal{R}})}] \\
& + |\mathcal{V}^{j,k_z',k_{\mathrm{i}z}(\mathbf{G})}_{\mathbf{K_i}+\mathbf{G}+\mathbf{Q},\mathbf{K_i}+\mathbf{G}}(-\omega_{\mathbf{Q},j})|^2 \\
& \times\ n(\omega_{\mathbf{Q},j})[1 - \mathrm{e}^{\mathrm{i}(\omega_{\mathbf{Q},j}\tau - \mathbf{Q}\boldsymbol{\mathcal{R}})}] \Big\} \qquad (35)
\end{aligned}
$$

in which the on-the-energy-shell intrachannel matrix elements for emission and absorption of one jth-mode phonon of wavevector $\mathbf{Q}$ and energy $\omega_{\mathbf{Q},j}$ are given by

$$
\begin{aligned}
& \mathcal{V}^{j,k_z',k_{\mathrm{i}z}(\mathbf{G})}_{\boldsymbol{K}+\boldsymbol{G}\mp\boldsymbol{Q},\boldsymbol{K}+\boldsymbol{G}}(\pm\omega_{\mathbf{Q},j}) \\
& \quad = 2\pi \langle \mathbf{K} + \mathbf{G} \mp \mathbf{Q}, k_z'; {}^{(\mathrm{s})} | V^j | \mathbf{K} + \mathbf{G}, k_{\mathrm{i}z}(\mathbf{G}); {}^{(+)} \rangle \\
& \qquad \times \delta(E_{\mathbf{K}+\mathbf{G}\mp\mathbf{Q},k_z'} - E_{\mathbf{K}+\mathbf{G},k_{\mathrm{i}z}(\mathbf{G})} \pm \hbar\omega_{\mathbf{Q},j}), \qquad (36)
\end{aligned}
$$

where $|\mathbf{K} + \mathbf{G} \mp \mathbf{Q}, k_{\mathrm{i}z}; {}^{(\mathrm{s})}\rangle = (|\mathbf{K} + \mathbf{G}' \mp \mathbf{Q}, k_{\mathrm{i}z}\rangle + |\mathbf{K} + \mathbf{G}' \mp \mathbf{Q}, -k_{\mathrm{i}z}\rangle)/\sqrt{2}$ is a normalized stationary combination of ingoing and outgoing waves (32), and $n(\omega_{\mathbf{Q},j})$ is the Bose–Einstein distribution function. Here the upper and lower signs in $\pm$ and $\mp$ stand for phonon emission and absorption, respectively, the E are the energies of the projectile in the diffraction channel $\mathbf{G}$, and V^j is a short for the projectile interaction with the jth phonon mode that produces the intrachannel matrix element (36). Here the energy conserving δ-function constrains the values of k_z' to the energy shell and therefore the diffraction channels for which ${k_z'}^2 < 0$ may be kinematically closed for inelastic scattering if $\hbar\omega_{\mathbf{Q},j}$ is large enough. For open channels ${k_z'}^2 > 0$ the δ-functions should be converted into Kronecker symbols before taking their squares in (35), and this is effectuated via

$$
\begin{aligned}
& |2\pi\delta(E_{\boldsymbol{K}\mp\boldsymbol{Q}\mp\boldsymbol{G},k_z'} - E_{\mathbf{K}+\mathbf{G},k_z} \pm \hbar\omega_{\mathbf{Q},j})|^2 \\
& \quad = \frac{\delta_{k_z',k_z(\pm)}}{\hbar^2 j_z j_z'} \Theta(k_z^2(\pm)), \qquad (37)
\end{aligned}
$$

where $k_z^2(\pm) = \frac{2M}{\hbar^2}(E_{\mathbf{K}+\mathbf{G}} + E_{k_z} - E_{\boldsymbol{K}\mp\boldsymbol{Q}\mp\boldsymbol{G}} \mp \hbar\omega_{\mathbf{Q},j})$, $j_z = v_z/L$ is the normal current and $\Theta(x)$ is the step function (see equations (261) and (262) of [19]).

The form of matrix elements in (36) requires special comment. An alert reader may have expected the appearance of incoming distorted waves $\langle \mathbf{K_i} + \mathbf{G} \mp \mathbf{Q}, k_z'; {}^{(-)}|$ instead of the stationary waves $\langle \mathbf{K_i} + \mathbf{G} \mp \mathbf{Q}, k_z'; {}^{(\mathrm{s})}|$ in (36), as would seemingly be in accord with expression (1) for the full S-matrix describing the scattering from two potentials [27]. However, here this does not happen for the following reasons. The matrix elements in (1) involving the incoming final distorted states $\phi^{(-)}_{\mathbf{k_f}}$ describe the contributions from all intermediate diffraction states which collapse into the final asymptotic state $|\mathbf{k_f}\rangle$ at $t_f = \infty$ after all the interactions have been completed and switched off [45, 46]. On the other hand, the δ-functions in expression (11) project out of the wavefunction $S|\phi_{\mathrm{i}}^{(+)}\rangle$ all the states satisfying the projecting energy and momentum requirements without reference to the final asymptotic states. In other words, this latter procedure gives phonon-induced corrections to the full diffraction spectrum (16) determined by distorted waves (4). The present assumption of intrachannel scattering induced by the interaction V^j confines inelastic projectile propagation for finite t_f always to the same $\mathbf{G}$-channel as appears in the cumulant average in (29). Therefore, by construction, the form of expression (11) with finite t_f does not contain the final asymptotic states that could be eliminated by the introduction of expressions involving $\phi_{\mathrm{f}}^{(-)}$. Instead, the intermediate states over which the summation in (35) is carried out belong to the set of eigenstates in which V^{SQ} is expanded and hence involve both directions of k_z (positive and negative). The restrictions on the summation appear only after the application of the energy and parallel momentum conservation, and here additionally by the requirement of $\mathbf{G}$-intrachannel scattering. Despite that, information on the completed scattering event is retrieved likewise in the derivation of the $T_{\mathrm{f},i}$ matrix elements from the time derivatives of full transition amplitudes

$\langle f|\psi_{\rm i}^{(+)}(t)\rangle e^{iE_f t}$ for finite $t > 0$ (cf equations (11)–(15) in chapter 5 of [27]).

Using expression (36) to calculate (35) and substituting that into (34) gives a closed form representation of the scattering spectrum in which each diffraction channel is affected by intrachannel multiphonon scattering. Here the intensities of the phonon peaks arise from an interplay between the channel diffraction amplitudes $A_{\mathbf{k_i},\mathbf{G}}$ and the phonon excitation amplitudes (36). Let us reiterate two assumptions and ensuing approximations invoked in deriving this result. The first was negligible interchannel scattering by phonons. Thereby we have also neglected the phonon-induced selective adsorption and prompt sticking processes involving the bound states (for a general discussion of these phenomena see [24]). The second approximation was the neglect of correlation between successive phonon excitation events which enabled truncation of the cumulant series in (34) beyond the second-order term to produce the EBA result (35). This, in turn, was compatible with the intrachannel scattering approximation because each intermediate diffraction event inevitably introduces a certain degree of correlation among subsequent phonon excitations.

The applicability of expression (34) in combination with (35) and (36) for description of HAS spectra is limited to the systems whose dynamical corrugation is not strong enough to induce Umklapp processes in phonon excitation or absorption. However, since according to the general properties of atom–surface interactions the matrix elements describing such processes are likely to be very small [43], approximate descriptions based on expressions (34)–(36) may prove useful in descriptions of HAS from a variety of concrete surfaces. This becomes particularly relevant in the situations involving diffraction and multiple excitation of dispersive phonons whose descriptions, as stated in section 1, are still beyond the reach of numerical treatments of the CC type.

3.2.2. Interchannel scattering by phonons. The treatment of intrachannel phonon-induced inelastic processes was based on expression (26) which contains only diagonal matrix elements of the generalized evolution operator $\mathcal{U}_I$ and therefore allows cumulant averaging to be applied. To investigate the applicability of cumulant averaging in the case of interchannel scattering by the dynamical potential V that may induce lateral (quasi-)momentum transfer $\mathbf{Q} + \mathbf{G}'$, it should first be shown that the off-diagonal matrix elements of the form

$$\langle ph_{\rm i}|\langle \mathbf{K_i} + \mathbf{G_1}, k_{zi}(\mathbf{G_1});^{(+)}|\mathcal{U}_I(\hat{\mathcal{W}}, \mathcal{R}) \times |\mathbf{K_i} + \mathbf{G_2}, k_{zi}(\mathbf{G_2});^{(+)}\rangle|ph_{\rm i}\rangle, \tag{38}$$

which arise from substitution of (4) for bras and kets in (25), do not contribute to the RHS of expression (25) for a particular form of V. However, this is difficult to illustrate without knowing the detailed structure of V and hence we shall limit our discussion to a simplified description of the problem in which the analysis can be carried through by invoking general arguments only. To this end we note that the projectile eigenstates of $H_{\rm diff}^{\rm p}$ and phonon eigenstates of $H_0^{\rm ph}$ exhibit the same Bloch periodicity. Exploiting this property we shall in the present discussion restrict the form of V so as to give rise only to interaction vertices in which the full lateral quasi-momentum is conserved, i.e. where in each interaction vertex the momentum $\mathbf{Q}$ of excited phonons obeys the relation $\mathbf{Q} = \mathbf{K}_{\rm in} - \mathbf{K}_{\rm out} - \mathbf{G}'$. The applicability of cumulant expansion may then be demonstrated by going back to equation (14), making use of the completeness of the scattered waves $\phi_{\mathbf{k_f}}^{(+)}$ and phonon states $|ph_f\rangle$, and inserting the appropriate closure relation in between the S-operator and the δ-functions in the matrix element on the RHS of this expression. The representation of $\phi_{\mathbf{k_f}}^{(+)}$ in the Bloch form produces nondiagonal terms in (25) which are of the form of coherences

$$\langle ph_{\rm i}|\langle \mathbf{K_i} + \mathbf{G_1}, k_z(\mathbf{G_1});^{(+)}|S^\dagger|\mathbf{K_f} + \mathbf{G_f}, k_z(\mathbf{G_f});^{(+)}\rangle|ph_{\rm f}\rangle \times \langle ph_{\rm f}|\langle \mathbf{K_f} + \mathbf{G_f}, k_z(\mathbf{G_f});^{(+)}| \times S|\mathbf{K_i} + \mathbf{G_2}, k_z(\mathbf{G_2});^{(+)}\rangle|ph_{\rm i}\rangle. \tag{39}$$

Here both S-matrix elements are taken between the same pairs of initial and final phonon configurations but different projectile states because $\mathbf{G_1} \neq \mathbf{G_2}$ by assumption. To examine the appearance of such terms involving the eigenstates of $H_{\rm diff}$ and the lateral momentum operator $\hat{\mathbf{P}}$ we assume the conservation of total energy and lateral momentum in the scattering event. Applying this we conclude that each product of the two S-matrix elements in (39) is subject to the conditions that can be expressed through the proportionality of (39) to the following δ-functions:

$$\delta(E_{\mathbf{K_i}+\mathbf{G_1},k_z(\mathbf{G_1})} - E_{\mathbf{K_f}+\mathbf{G_f},k_z(\mathbf{G_f})} - \{\hbar\omega_{\mathbf{Q}}\}) \times \delta_{\mathbf{K_i}+\mathbf{G_1},\mathbf{K_f}+\mathbf{G_f}+\{\mathbf{Q}+\mathbf{G}'\}} \times \delta(E_{\mathbf{K_i}+\mathbf{G_2},k_z(\mathbf{G_2})} - E_{\mathbf{K_f}+\mathbf{G_f},k_z(\mathbf{G_f})} - \{\hbar\omega_{\mathbf{Q}}\}) \times \delta_{\mathbf{K_i}+\mathbf{G_2},\mathbf{K_f}+\mathbf{G_f}+\{\mathbf{Q}+\mathbf{G}'\}}. \tag{40}$$

Here $\{\hbar\omega_{\mathbf{Q}}\}$ and $\{\mathbf{Q} + \mathbf{G}'\}$ denote the total change of energy and parallel wavevector in the transition $|ph_i\rangle \rightarrow |ph_f\rangle$ described by the two matrix elements of S in (39) differing only in $\mathbf{G_1}$ and $\mathbf{G_2}$, respectively, but not in the initial and final phonon phase-space configurations $|ph_{\rm i}\rangle$ and $|ph_{\rm f}\rangle$. Now, combining the conditions imposed on the lateral momentum changes through the δ-functions in expression (40) one arrives at the conclusion that $\mathbf{G_1} - \mathbf{G_2} = 0$. This is contrary to the assumption of the existence of nondiagonal matrix elements of the form (38) in the representation of the scattering spectrum (14) in the Bloch form (similar arguments were invoked in the discussion of equation (2.5) in [7]). Hence, we have $\mathbf{G_1} = \mathbf{G_2}$ and the diagonal representation (26) may then be used equally well in the case of interchannel inelastic scattering with a proviso that the interaction V^j can now induce also interchannel transitions accompanied by the change of projectile lateral momentum by the amount $\mathbf{Q} + \mathbf{G}'$ in each single-phonon emission or absorption process. This leads to the EBA expression for cumulant representation of the scattering spectrum that is generated by

$$C^{\rm EBA}(\mathbf{G}, \mathcal{R}, \tau) = -\sum_{\mathbf{Q},\mathbf{G}',k_z',j} \Big\{ |\mathcal{V}^{j,k_z',k_{\rm iz}(\mathbf{G})}_{\mathbf{K_i}+\mathbf{G}-\mathbf{Q}-\mathbf{G}',\mathbf{K_i}+\mathbf{G}}(+\omega_{\mathbf{Q},j})|^2$$

$$\times [n(\omega_{\mathbf{Q},j})+1][1-\mathrm{e}^{-\mathrm{i}(\omega_{\mathbf{Q},j}\tau-(\mathbf{Q}+\mathbf{G}')\boldsymbol{\mathcal{R}})}]$$
$$+|\mathcal{V}^{j,k_z',k_{iz}(\mathbf{G})}_{\mathbf{K_i}+\mathbf{G}+\mathbf{Q}+\mathbf{G}',\mathbf{K_i}+\mathbf{G}}(-\omega_{\mathbf{Q},j})|^2$$
$$\times\ n(\omega_{\mathbf{Q},j})[1-\mathrm{e}^{\mathrm{i}(\omega_{\mathbf{Q},j}\tau-(\mathbf{Q}+\mathbf{G}')\boldsymbol{\mathcal{R}})}]\Big\}. \qquad (41)$$

Owing to the choice of expansion of (31) in terms of the field operators (33) the $\mathbf{G}' \neq 0$ transitions are not additionally weighted by the channel amplitudes $A_{\mathbf{k_i},\mathbf{G}+\mathbf{G}'}$. This may seem counter-intuitive but the particle current arising from these interchannel scattering processes adds incoherently to the already existing current in the $(\mathbf{G}+\mathbf{G}')$-channel, whereas the $\mathbf{G}$-channel current is depleted by the Debye–Waller factor [19, 48]

$$\exp\left[-\sum_{\mathbf{Q},\mathbf{G}',k_z',j}\Big\{|\mathcal{V}^{j,k_z',k_{iz}(\mathbf{G})}_{\mathbf{K_i}+\mathbf{G}-\mathbf{Q}-\mathbf{G}',\mathbf{K_i}+\mathbf{G}}(+\omega_{\mathbf{Q},j})|^2 \times [n(\omega_{\mathbf{Q},j})+1] + |\mathcal{V}^{j,k_z',k_{iz}(\mathbf{G})}_{\mathbf{K_i}+\mathbf{G}+\mathbf{Q}+\mathbf{G}',\mathbf{K_i}+\mathbf{G}}(-\omega_{\mathbf{Q},j})|^2 n(\omega_{\mathbf{Q},j})\Big\}\right]. \qquad (42)$$

The interchannel scattering generator $C^{\mathrm{EBA}}_{\mathrm{inter}}(\mathbf{G},\boldsymbol{\mathcal{R}},\tau)$ comprises the $\mathbf{G}' \neq 0$ components of the sum (41). Hence

$$C^{\mathrm{EBA}}(\mathbf{G},\boldsymbol{\mathcal{R}},\tau) = C^{\mathrm{EBA}}_{\mathrm{intra}}(\mathbf{G},\boldsymbol{\mathcal{R}},\tau) + C^{\mathrm{EBA}}_{\mathrm{inter}}(\mathbf{G},\boldsymbol{\mathcal{R}},\tau). \qquad (43)$$

However, it should be noted that the intrachannel ($\mathbf{G}' = 0$) and interchannel ($\mathbf{G}' \neq 0$) EBA generators on the RHS of (43) may not provide equally good approximations in descriptions of multiphonon scattering because correlations between successive scattering events, which are neglected in the EBA, are likely to be much larger in interchannel transitions. Therefore, the validity of the EBA generator $C^{\mathrm{EBA}}_{\mathrm{inter}}(\mathbf{G},\boldsymbol{\mathcal{R}},\tau)$ for multiphonon interchannel scattering remains to be tested on concrete examples, as was illustrated for intrachannel scattering in figures 3 and 5 of [47]. Lastly, we note that in the absence of static surface corrugation, namely for $U = 0$, only the components $\mathbf{G}' = 0$ in (4) and $\mathbf{G}'' = 0$ in (5) remain, and $A_{\mathbf{k},\mathbf{0}} = 1$. In this case we have up to a phase factor $\langle \mathbf{r}|\mathbf{K}, k_z;^{(+)}\rangle = \langle \mathbf{r}|\mathbf{K}, k_z;^{(-)}\rangle = \langle \mathbf{r}|\mathbf{K}, k_z;^{(\mathrm{s})}\rangle$ and hence $C^{\mathrm{EBA}}(\mathbf{G}=0,\boldsymbol{\mathcal{R}},\tau)$ reduces to $C^{\mathrm{EBA}}(\boldsymbol{\mathcal{R}},\tau)$, pertinent to inelastic scattering from statically flat surfaces elaborated earlier [19].

4. Conclusions

In this paper we have emphasized the need for the development of a formalism which would enable equivalent quantum treatment of diffractive and multiple inelastic scattering of atoms from corrugated surfaces that support dispersive phonon modes. To our knowledge, a computationally tractable description of these processes that would go beyond the low order perturbational treatment of expression (1), or the various semiclassical approximations, has not been presented yet. Development of a formalism satisfying these requirements has been demonstrated in section 3. It is based on the calculation of a conveniently formulated scattering spectrum which is exactly solved for diffraction effects and is also amenable to nonperturbative treatment of multiphonon processes through the application of the cumulant expansion developed earlier [19] in the studies of inelastic scattering from flat surfaces. The present approach also enables a general formulation of the Debye–Waller factor for the reduction of diffraction peak intensities in atom–surface scattering.

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