# Quantum versus semiclassical treatment of multiphonon effects in He-atom scattering from surfaces

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We develop a formalism appropriate for studying multiple inelastic scattering of thermal-energy He atoms from surface phonons in the collision regimes in which both the motion of the particle and surface vibrations must be treated quantum mechanically. Having in mind recent experiments on He-atom scattering (HAS) from surfaces, we first point out some difficulties connected with calculating the reflection coefficients under extreme multiphonon conditions by resorting to the standard $T$-matrix approach. To circumvent these problems we make use of the connection between the reflection coefficients and angular resolved scattering spectra and show how the latter can be conveniently obtained in the form of a cumulant expansion for multiphonon-scattering amplitudes in powers of inelastic atom-surface coupling. This yields the expression for the scattering spectrum whose advantageous characteristics are the unitarity (which manifests itself through a Debye-Waller factor in exponential form with a complete Debye-Waller exponent encompassing contributions from all inelastic scattering channels) and the amenability to perturbational treatment in terms of uncorrelated and correlated atom-phonon interactions. In the scattering regimes in which the contributions of correlated multiphonon excitations become negligible relative to those of uncorrelated ones, the scattering spectrum acquires a particularly simple form of an exponentiated Born approximation (EBA). As various other semiclassical and classical approximations regarding the particle dynamics can be shown to emerge from the EBA, we estimate its validity for treating multiple He-atom scattering by Einstein- and Debye-like phonons in representative collision systems $He \rightarrow CO(\sqrt{3}\times\sqrt{3})R30°/Rh(111)$ and $He \rightarrow Cu(001)$ in which such modes have been experimentally detected. We find that under the conditions of these experiments the EBA can be considered as exact, which enables accurate calculation of the corresponding multiphonon-scattering spectra. The obtained results compare well with experimental data, thereby confirming the potentiality and applicability of the developed formalism in HAS. We also show that the semiclassical trajectory and fast collision or impulse approximations, which naturally derive as special limits of the EBA, can largely deviate from the so-defined exact EBA treatment in the considered range of the parameter space. From this we conclude that they may become unreliable in the scattering regimes in which either the validity of the EBA is violated or their deviation from the EBA is large.

## I. SINGLE-PHONON AND MULTIPHONON PROCESSES IN He-ATOM SCATTERING FROM SURFACES

Recently, a considerable interest has been aroused in connection with identification[1–6] and interpretation[7–11] of multiphonon features in the spectra of thermal-energy He atoms scattered inelastically from solid surfaces. It has been realized that a complete interpretation of single-phonon spectral features in He-atom scattering (HAS) time-of-flight (TOF) spectra, whose analyses enable the extraction of the phonon-dispersion curves, also requires a proper disentangling of multiphonon effects from the experimental data. In most cases these effects manifest themselves in the elastic or no-loss line of the spectrum through the Debye-Waller factor, as well as in the inelastic sideband, mainly as a broad and almost featureless background already detectable in the region in which the single-phonon structure dominates.[12] In contrast to this, in some systems characterized by surface phonon modes of weak or negligible dispersion, the multiphonon effects in the particle loss spectra may manifest themselves as sharp higher-order peaks or as satellites (characteristic of multiphonon and overtone losses) of the single-phonon structure.[5]

Although the number of theoretical works addressing multiphonon features of the HAS spectra has not been very large, the versatility of approaches in the treatment of this problem is indicative of its complexity. However, quite generally, they may be classified roughly into two categories: (i) calculations of the inelastic atom-surface reflection coefficient using the standard $T$-matrix approach of the stationary collision theory often carried out by utilizing the Glauber–van Hove method[13,14] to deal with phonon excitations,[7,8] and (ii) a time-dependent approach to calculate the evolution operator of the collision

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system from which the energy spectrum of the scattered particle can be derived.[9–11] This latter approach also allows for a natural extension in which the particle motion is treated by classical dynamics (for discussions of the various forms of the classical trajectory and path integral approximations, see Ref. 7).

One major problem in all theoretical treatments of multiphonon processes in HAS represents the question of which approximations to introduce to make calculations feasible, yet realistic and physically acceptable as regards the particle scattering dynamics. Approximations can be introduced in various ways and at various stages of solving the collision problem, e.g., in the order of the Born series expansion for the $T$ matrix if approach (i) is followed in approximating the generally complicated matrix elements of the interaction in each order of the expansion, or in making use of various approximate forms for the usually complicated phonon densities of states, etc.

Probably the most popular method used so far in the treatment of inelastic atom-surface scattering is based on the development of the scattering matrix in terms of the distorted waves following approach (i) above. That is, if the discussion is restricted only to flat surfaces, as is commonly done in the case of HAS from (111) and (100) surfaces of fcc metals, the problem of elastic reflections of the impinging atom (characterized by its mass $M$ and momentum and position operators $\mathbf{p}$ and $\mathbf{r}$, respectively) from the static surface potential $U^0(\mathbf{r})=U^0(z)$ can be exactly solved in a closed form. This yields distorted incoming and outgoing waves $\varphi_{\mathbf{k}}^{(-)}(\mathbf{r})$ and $\varphi_{\mathbf{k}}^{(+)}(\mathbf{r})$, respectively, where $\mathbf{k}$ denotes the set of unperturbed distorted wave quantum numbers. These states are stationary solutions of the particle Hamiltonian $H_0^p=(\mathbf{p}^2/2M)+U^0(\mathbf{r})$, and therefore describe elastic particle scattering (reflection) by $U^0(\mathbf{r})$ to all orders. Then, by treating the dissipative particle-phonon interaction $V(\mathbf{r})$ as a perturbation, one arrives at the expression for the inelastic reflection coefficient $R_{i,f}=\sigma_{i,f}/L^2\cos\theta_i$, or the scattering cross section per effective illuminated surface area $L^2\cos\theta_i$,[15] which describes scattering of the particle from its initial state characterized by the quantum number $\mathbf{k}_i$ to a final state characterized by the quantum number $\mathbf{k}_f$:[7,16,15,17]

$$R_{\mathbf{k}_i}(\mathbf{k}_f)=\frac{1}{j_{zi}}\sum_{\{n_i\}}\rho_{\mathrm{ph}}(n_i)\sum_{\{n_f\}}\frac{2\pi}{\hbar}|T_{f,i}^V|^2\delta(E_f-E_i)\ . \tag{1}$$

Here $i$ and $f$ label the initial and final states of the scattering system, respectively, $j_{zi}$ is the incident current of particles normal to the surface, and $E_i$ and $E_f$ denote the total energy of the scattering system before and after the collision, respectively. $T^V$ is the scattering matrix generated by the dissipative atom-phonon interaction $V(\mathbf{r})$ in the Hilbert space of distorted waves, and $\rho_{\mathrm{ph}}(n_i)$ is the distribution of initial phonon states $|n_i\rangle$. The summation over phonon states $\{n_f\}$ is carried out over the sets of all normal-mode quantum numbers $\{\mathbf{Q},j\}$, where $\mathbf{Q}$ is the lateral phonon momentum (parallel to the surface), and $j$ denotes the multitude of all other phonon quantum numbers (indices of the branches of the phonon spectrum, etc.).

The inelastic reflection coefficient (1) contains phonon processes to all orders in the coupling constant. By treating the dissipative atom-phonon interaction to first order,[18,16] i.e., by making a replacement $T_{f,i}^V\rightarrow V_{f,i}=\langle n_f,\varphi_f^{(-)}|V(\mathbf{r})|n_i,\varphi_i^{(-)}\rangle$, one arrives at the distorted-wave Born approximation (DWBA) expression for the $T^V$ matrix[19] and the reflection coefficient. In the case of harmonic atom-surface phonon coupling, this yields one-phonon differential inelastic reflection coefficient $dR/dk_f^3$ and the inelastic scattering intensity $dR/d\epsilon_f d\Omega_f$ which have been applied to establish single-phonon-dispersion curves for a number of solid surfaces.[17,20,21]

However, a transition from first- to higher-order distorted-wave Born approximation terms in the perturbation expansion of the $T^V$ matrix which describes multiphonon processes is far from trivial. In contrast to the first term of this expansion, viz., $V_{f,i}$, which is a local quantity describing a single inelastic-scattering event higher-order terms are generally nonlocal. Hence such terms cannot be dealt with easily unless drastic simplifications regarding the structure of $T^V$ are introduced.[7,8] This effectively limits the usefulness of this method in a general and strictly quantal treatment of higher-order correlated multiphonon-scattering processes, although the same formal Glauber–van Hove procedure as in the DWBA can be applied.[8]

The treatment of atom-phonon scattering can be considerably simplified and made much more illustrative in models in which the total atom-surface interaction potential $U(\mathbf{r})$ is assumed to be given by a pairwise sum of the scattering atom-surface atom potentials $v(\mathbf{r})$:

$$U(\mathbf{r})=U^0(\mathbf{r})+V(\mathbf{r})=\sum_{l,m}v_m(\mathbf{r}-\mathbf{R}_l-\mathbf{r}_m-\mathbf{u}_{l,m})\ , \tag{2}$$

where $\mathbf{R}_l+\mathbf{r}_m$ denotes the equilibrium position of the $m$th atom in the $l$th surface unit cell of the solid,

$$U^0(\mathbf{r})=\sum_{l,m}v_m(\mathbf{r}-\mathbf{R}_l-\mathbf{r}_m) \tag{3}$$

is the static atom-surface potential, and $\mathbf{u}_{l,m}$ denotes the displacement of the atom of the solid from its equilibrium position $\mathbf{R}_l+\mathbf{r}_m$ at point $\mathbf{r}_m$ within the $l$th surface unit cell with a basis.

From here on one can proceed in two ways in treating the dynamic component $V(\mathbf{r})$ of the total potential $U(\mathbf{r})$ given by Eq. (2). The first, most commonly followed prescription, is to assume that $\mathbf{u}_{l,m}$ is small and then expand $v_m$ up to first order in the displacements to obtain the harmonic approximation expression for $V(\mathbf{r})$:

$$V(\mathbf{r})=V(\mathbf{r},\{\mathbf{u}_{l,m}\})=\sum_{l,m}\mathbf{F}_{l,m}(\mathbf{r})\cdot\mathbf{u}_{l,m}\ . \tag{4}$$

Here

$$\mathbf{F}_{l,m}(\mathbf{r})=-\nabla v_m(\mathbf{r}-\mathbf{R}_l-\mathbf{r}_m) \tag{5}$$

is the force exerted by the $(l,m)$th atom on the impinging He atom. Quantization of $\mathbf{u}_{l,m}$ then leads to the expres-

sion for $V(\mathbf{r})$ in terms of creation and annihilation operators for substrate phonon modes. Using this, one sets up the $T^V$ matrix in terms of $V(\mathbf{r})$, which exhibits a property that only one phonon can be either created or annihilated in each interaction vertex appearing in an $n$th-order diagram of such scattering matrix [i.e., only one phonon propagator terminating in a single vertex, cf. Fig. 1(a)].

Inclusion of higher-order anharmonic terms, proportional to quadratic and higher-order powers of $\mathbf{u}_{l,m}$ [generally of $n$th-order terms which were omitted from Eq. (4)] would give rise to $n$-fold phonon vertices in the scattering matrix.[22] The problem of including such anharmonic terms is usually dealt with somewhat differently, and represents an alternative approach to the one just described. It starts by writing the matrix elements of the total interaction as

$$\langle \mathbf{k}_f | U(\mathbf{r}) | \mathbf{k}_i \rangle = U_{\mathbf{k}_f - \mathbf{k}_i} = \sum_{l,m} v_m(\mathbf{k}_f - \mathbf{k}_i) \times e^{-i(\mathbf{k}_f - \mathbf{k}_i)\cdot(\mathbf{R}_l + \mathbf{r}_m + \mathbf{u}_{l,m})}, \quad (6)$$

where now $|\mathbf{k}\rangle$ denote the particle plane-wave states of momentum $\mathbf{k}$, and then setting up the full scattering matrix $T^U$ generated by the total scattering potential $U(\mathbf{r})$ encompassing both the static surface potential and its temporal variation due to the vibrations of the atoms in the solid. As, according to (6), the matrix element $U_{\mathbf{k}_f - \mathbf{k}_i}$ contains displacements to all orders, already the first-order term in the Born expansion of $\langle \mathbf{k}_f | T^U | \mathbf{k}_i \rangle$, now given by Eq. (6), will give rise to phonon-scattering processes to all orders in the number of phonons, but each of them appearing only once [cf. Fig. 1(b)]. Higher-order Born expansion terms of $T^U$ in powers of $U$ may then give rise to any combination of repeated phonon vertices with any number of terminating phonon propagators. Again, the Glauber–van Hove method can be formally applied to calculate the reflection coefficient in terms of $T^U$, but this task usually becomes formidable beyond the standard first-order Born approximation (BA). Hence various approximate forms and ansatze for $T^U_{\mathbf{k}_f,\mathbf{k}_i}$ have been introduced in order to make calculations feasible. In particular, a separable BA-like form of the scattering operator deriving from Eq. (6), with $v_m(\mathbf{k}_f - \mathbf{k}_i)$ replaced by some effective single-center scattering operator $\tau_m(\mathbf{k}_f, \mathbf{k}_i)$, has been used in several analyses of inelastic atom-surface scattering problems.[7,8] However, such approximations, in which the particle and phonon dynamics are completely decoupled, neglect the peculiarities of the quantal particle propagation in the intermediate states of the collision event and therefore omit all quantum recoil effects which take place between successive particle interactions with phonons. This problem has been realized rather early,[23,24] but was not pursued in detail until later on.

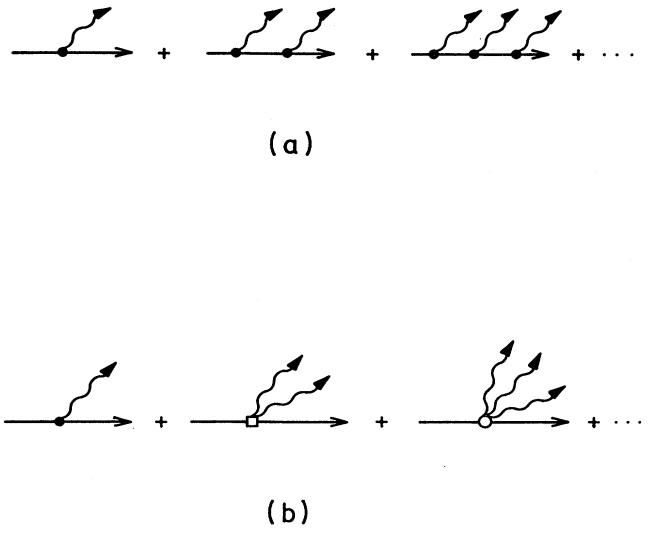


FIG. 1. (a) Series of Feynman diagrams representing He-atom scattering through emission of real phonons in the first-, second-, and third-order perturbation expansion. These types of diagrams are generated by the $T^V$ matrix (see text) in which unperturbed particle propagators are diagonal on distorted-wave states corresponding to the potential $U^0(\mathbf{r})$ of Eq. (3), and each interaction vertex derives from the application of the potential $V(\mathbf{r})$ of Eq. (4). (b) Feynman diagrams representing real phonon excitations in He-atom scattering processes which are generated by the $T^U$ matrix set up in terms of the full atom-surface potential $U(\mathbf{r})$ of Eq. (2). Here the unperturbed particle propagators correspond to the free-atom motion described by plane waves. Note the different interaction vertices denoted by dots, squares, and open circles associated with one- and simultaneous two- and three-phonon-emission processes, respectively.

As is seen from the above discussion, one can generally distinguish two types of multiphonon contributions to the atom-surface scattering processes. A multiphonon process can arise as a result of either a repeated harmonic or single-phonon emission or absorption processes (represented by single-phonon vertices in the expansion of $T^V$ or by the linear term in the first-order Born expansion of $T^U$), or from a simultaneous, anharmonic emission or absorption of phonons in a single vertex generated by anharmonic terms in the perturbation expansion of $T^U$. Thus a general multiphonon process of the $n$th order may comprise a combination of $n_1$ harmonic single-phonon processes, $n_2$ two-phonon processes, etc., where $n_1 + n_2 + \cdots + n_m = n$. However, due to different strength of the coupling matrix elements,[22,25] single and multiphonon vertices will generally bear different weights in the perturbation series expansion of the scattering matrix (cf. Fig. 1).

The extraction of phonon-dispersion curves and spectra from the experimental data is usually based on the DWBA description of real one-phonon emission and absorption processes generated by a harmonic inelastic atom-surface interaction $V(\mathbf{r})$ of the form given by Eq. (4). The matrix elements of potential (4) comprise the products of the matrix elements of force (5) and the tensor of the single phonon density of states $\mathbf{D}(\omega)$.[7,15,17] In the single-phonon-scattering regime the knowledge of these quantities enables in principle a relatively accurate reproduction of the experimentally observed single-phonon-dispersion curves.[17,20,26–28]

A substantially different situation may take place in the regime of multiphonon excitations in HAS, even in the case in which the vibrational coupling to the solid can be well described in the harmonic approximation. Here the quantum nature of the particle dynamics may begin to play a decisive role in the regimes in which the effects of the recoil of the scattered particle become important. These will occur in regions of the parameters space in which we do not expect that the conditions of either the single-center scattering regime or impulse (fast) collisions, or the classical trajectory approximation for the particle motion, would be met.[7] Our main goal in this paper is to examine and illustrate on some concrete collision systems how relevant an exact quantum treatment of scattered particle dynamics in the calculation of multiphonon He-atom scattering spectra may become.

The outline of the paper is as follows. In Sec. II we start by demonstrating some general properties of inelastic and elastic reflection coefficients, particularly the unitarity condition they must obey, and introduce the notion of the Debye-Waller factor which will be used throughout our discussions of HAS from surface phonons. Then we formulate an expression for the scattering spectrum, demonstrate its relation to the reflection coefficients, and also point out some of its most important features which will prove essential in the later elaboration of the HAS spectra. Starting from this formulation, in Sec. III A we present a detailed and rigorous quantum-mechanical derivation of the angular- or momentum-resolved scattering spectrum based on the cumulant expansion for the scattering amplitude. The main merit of this approach is that the obtained expression for the scattering spectrum is amenable to various approximate treatments, particularly perturbative ones. In Sec. III B we use these rigorous results as a point of departure for deriving the exponentiated Born approximation (EBA) formula for the angular-resolved scattering spectrum which should hold whenever the amplitudes of higher-order correlated phonon emission processes can be neglected relative to the uncorrelated ones. We also demonstrate some of the basic properties of the EBA and discuss the regimes in which other popular semiclassical and approximate descriptions may emerge from it as limiting cases. Then, in Sec. IV, we establish the criteria for estimating the validity of the EBA in HAS which enables us to define an exact treatment of atom scattering from surface excitations. The exact treatment can be established for those scattering regimes in which the EBA result makes the major contribution to the scattering spectrum, and in which the error introduced by neglecting higher-order correlated excitation processes not accounted for by the EBA can be controlled and estimated to be of the order of only a few percent. From this exact treatment a few other approximate and semiclassical ones may follow upon replacing the exact quantum-mechanical interaction matrix elements in the scattering amplitude by their quasiclassical or classical counterparts. The differences between results obtained in the exact and various semiclassical treatments for specific collision systems then demonstrate which effects such popular and widely used approximations may miss or give rise to. As typical examples of these effects and the validity of the EBA, in Secs. IV A and IV B we consider the multiphonon spectra of He atoms scattered by surface phonons of Einstein- and Debye-like character whose existence has recently been detected in a number of systems. These findings enable us to draw fairly general conclusions as to the importance of quantum versus semiclassical treatments of multiphonon processes in HAS.

## II. GENERAL PROPERTIES OF MULTIPHONON REFLECTION COEFFICIENTS AND SCATTERING SPECTRA

In this section we shall demonstrate the relation between the two quantities most frequently used in a description of atom-surface scattering experiments; the commonly discussed inelastic reflection coefficient,[7,8,16,15,17,29] and the somewhat less exploited expression for the scattering spectrum[7–10,30,31] which, however, is often easier to calculate using various approximation schemes. This relation is usually not shown explicitly for the case of two coupled quantum fields (here the fields of the particle and the substrate phonons), which may sometimes lead to ambiguities as to the very important unitarity property of the reflection coefficient itself. However, in formulations of the complete reflection coefficient and the scattering spectrum, unitarity arises naturally as an important general property and manifests itself through the so-called Debye-Waller factor (DWF) which describes the probability of elastic scattering. The standard notion of the Debye-Waller factor has usually been associated with the expression for the scattering spectrum, where it appears as a common multiplicative factor which accounts for the normalization proper of the spectrum. Its existence in the total reflection coefficient is more implicit, but can be demonstrated once an explicit connection between the two quantities describing the scattering event has been established.

Discussions of both the structural and dynamic properties of surfaces are often carried out so as to define first the unperturbed surface which, as regards the scattered particle-surface interaction, is described by a laterally averaged static potential $U^0(\mathbf{r})=U^0(z)$. This potential gives rise only to specular reflections of the scattered atoms. The wave functions corresponding to the particle motion in $U^0(z)$ are taken as a basis of distorted waves for treating either diffraction effects, if the perturbation to $U^0(z)$ is a potential describing the corrugation of the surface, or inelastic effects if the perturbing potential describes dynamic particle-surface interactions. A combined treatment is also possible and was carried out in Ref. 32 to investigate one-phonon scattering about the diffraction peaks. However, it is much less frequently used due to its extreme complexity, particularly in the case of multiphonon processes, unless some simplifying approximations regarding the particle dynamics are introduced.[8] Thus, without losing generality in the discussion of the essential properties of multiphonon reflection coefficients and scattering spectra, we shall resort to distorted waves corresponding to $U^0(z)$. The wave func-

tions of these states will be given by

$$\varphi_{\mathbf{k}}^{(+)}(\mathbf{r})=\frac{e^{i\mathbf{K}\cdot\boldsymbol{\rho}}\chi^{(+)}(k_z,z)}{\sqrt{L_s^2L_z}}\ ,$$
$$\varphi_{\mathbf{k}}^{(-)}(\mathbf{r})=\frac{e^{i\mathbf{K}\cdot\boldsymbol{\rho}}\chi^{(-)}(k_z,z)}{\sqrt{L_s^2L_z}}\ , \tag{7}$$

where $\mathbf{K}$ and $\boldsymbol{\rho}$ denote the momentum and radius vector of the particle in the direction parallel to the surface (lateral direction), $\chi^{(+)}$ and $\chi^{(-)}$ are the eigenstates of $H_0^z=(p_z^2/2M)+U^0(z)$ and denote the outgoing and incoming distorted waves describing particle motion perpendicular to the surface, respectively, $z$ is the coordinate of the particle in this direction taken positive outward the surface, and $k_z$ is the asymptotic value of the perpendicular component of the particle momentum far away from the surface where $U^0(z)$ is already negligible. For a flat surface the difference between $\chi^{(+)}$ and $\chi^{(-)}$ is only an irrelevant phase factor,[7] because the eigenstates $\chi(k_z,z)$ of $H_0^z$ are nondegenerate. Hence, again without any loss of generality, the stationary waves $\chi(k_z,z)$ may be taken to be real,[15] satisfying $\chi(k_z,z\rightarrow\infty)\rightarrow 2\cos(k_zz+\delta_{k_z})$. From now on we shall use these states in defining (7) unless stated otherwise, and hence omit the superscripts $(+)$ and $(-)$ in $\varphi_{\mathbf{k}}$ defined by Eq. (7). Also, we have assumed the box normalization, the quantization length parallel and perpendicular to the surface being $L_s$ and $L_z$, respectively. Taking into account all these premises we find that the distorted wave functions $\varphi_{\mathbf{k}}$ are normalized according to

$$\langle\varphi_{\mathbf{k}}|\varphi_{\mathbf{k}'}\rangle=\delta_{\mathbf{k},\mathbf{k}'}\ , \tag{8}$$

where $\mathbf{k}=(\mathbf{K},k_z)$, and the incident particle current (flux) perpendicular to the surface is then given by

$$|j_{zi}|=\frac{\hbar|k_{zi}|}{ML_z}=\frac{|v_{zi}|}{L_z}\ . \tag{9}$$

In the present box normalization this quantity has the dimension and meaning of the inverse of the collision time. Obviously, the optical theorem expressing the conservation of the particle flux in a scattering experiment[33] can also be formulated in terms of the particle states defined by (7) and (8).

The multitude of the phonon excitation energies in the final and initial state of the crystal will be denoted by $\varepsilon_f$ and $\varepsilon_i$, respectively, and the multitude of the excited phonon momenta by $\{\hbar\mathbf{Q}\}$. The distorted-wave particle energy will be denoted by $\epsilon_{\mathbf{k}}=\epsilon_{\mathbf{K},k_z}=\hbar^2(\mathbf{K}^2+k_z^2)/2M$. Thus $\epsilon_{\mathbf{k}_i}=\epsilon_i$ and $\epsilon_{\mathbf{k}_f}=\epsilon_f$. Recalling that for flat surfaces the total lateral momentum in the particle-surface interactions is conserved, i.e., $\mathbf{K}_f\pm\{\mathbf{Q}\}=\mathbf{K}_i$, where $\pm$ correspond to phonon emission/absorption, for the argument of the energy-conserving $\delta$ function in (1) we can write

$$E_f-E_i=\mp\frac{\hbar\mathbf{K}\{\hbar\mathbf{Q}\}}{M}+\frac{\{\hbar\mathbf{Q}\}^2}{2M}+\frac{\hbar^2k_{zf}^2}{2M}-\frac{\hbar^2k_{zi}^2}{2M}+\varepsilon_f-\varepsilon_i\ . \tag{10}$$

An extension to include reciprocal-lattice vectors into these equations was presented in Ref. 32.

Next, we make use of the formal identities

$$|2\pi\delta(E_f-E_i)|^2=\lim_{t\rightarrow\infty}\frac{2\pi}{\hbar}\delta(E_f-E_i)t=\frac{2\pi}{\hbar j_{zi}}\delta(E_f-E_i)=\frac{1}{\hbar^2j_{zi}j_{zf}}\delta_{k_{zf},k_{zi}}\Theta(\bar{k}_{z\pm}^2)\ , \tag{11}$$

where the first one is standard in the formal scattering theory,[34] and the other two follow from Eqs. (9) and (10) and by converting the $\delta$ function into a Kronecker symbol according to

$$\delta(E_f-E_i)=\frac{1}{\hbar v_{zf}}\delta(k_{zf}-\bar{k}_{z\pm})\Theta(\bar{k}_{z\pm}^2)=\frac{L_z}{2\pi\hbar v_{zf}}\delta_{k_{zf},\bar{k}_{z\pm}}\Theta(\bar{k}_{z\pm}^2)\ , \tag{12}$$

where again $+$ and $-$ stand for phonon emission and absorption processes, and

$$\bar{k}_{z\pm}^2=\frac{2M}{\hbar^2}\left[\frac{\pm\hbar\mathbf{K}\{\hbar\mathbf{Q}\}}{M}-\frac{\{\hbar\mathbf{Q}\}^2}{2M}+\frac{\hbar^2k_{zi}^2}{2M}-\varepsilon_f+\varepsilon_i\right]\ . \tag{13}$$

The step function $\Theta(\bar{k}_{z\pm}^2)$ appearing in (11) allows transitions only into channels in which the energy of motion in the $z$ direction is positive. This means that the processes leading to capture of the particle into the bound states of the surface potential well have been excluded from the present formulation of the reflection coefficient. The conversion $\delta(k_z-k_z')=(L_z/2\pi)\delta_{k_z,k_z'}$ made in (12) enables the $k$ summations in all expressions containing $\delta$ functions to be carried out without difficulties or ambiguities.[15] Substituting expressions (9), (10), and (12) into Eq. (1), we obtain

$$R_{\mathbf{k}_i}(\mathbf{k}_f)=\sum_{\{n_i\}}\rho_{\mathrm{ph}}(n_i)\sum_{\{n_f\}}\frac{1}{\hbar^2}|\tilde{T}_{f,i}^V\delta_{k_{zf},\bar{k}_{z\pm}}\Theta(\bar{k}_{z\pm}^2)|^2,\quad f\neq i\ , \tag{14}$$

where the matrix elements $\tilde{T}_{fi}^V$ are now calculated with the wave functions $\tilde{\varphi}$ normalized to the unit current in the $z$ direction:

$$\tilde{\varphi}_k(\mathbf{r})=\frac{e^{i\mathbf{K}\cdot\boldsymbol{\rho}}\chi(k_z,z)}{\sqrt{L_s^2v_z}}\ . \tag{15}$$

Here it should be observed that in this normalization the dimension of $\tilde{T}_{fi}^V$ is equal to the dimension of $\hbar$, and that for zero surface temperature only the term $\rho_{\mathrm{ph}}(n_i=0)=1$ contributes to the sum in (14). For the sake of clarity and simplicity, in the following we shall restrict our discussion to the case of zero initial temperature of the surface. The consequences of finite temperatures will be briefly outlined in Sec. III B.

We proceed by recalling that according to time-

dependent perturbation theory the matrix elements of the evolution operator $U(t,t_0)$ of the interacting system, calculated the wave functions (7) and taken in the limit $(t\to\infty, t_0\to-\infty)$ appropriate to the scattering boundary conditions, are given by

$$\langle f|U(\infty,-\infty)|i\rangle = S_{fi} = \langle f|i\rangle - 2\pi i\langle f|T^V|i\rangle\delta(E_f-E_i)\ . \tag{16}$$

The meaning of $S_{fi}$ is that within the normalization chosen it gives the amplitude of the $i\to f$ transition of the system in the course of the collision. By manipulating with the energy-conserving $\delta$ function as in Eq. (12), we find that the total probability of elastic scattering $|i\rangle\to|i\rangle$ or elastic reflection, usually termed the Debye-Waller factor and for later convenience denoted as $e^{-2W}$, is given by

$$|S_{ii}|^2 = R_{ii} = e^{-2W} = \left|1-\frac{i}{\hbar}\tilde{T}^V_{ii}\right|^2 = 1-\sum_{f(\neq i)}\left|\frac{\tilde{T}^V_{fi}\delta_{k_{zf},\bar{k}_{z\pm}}\Theta(\bar{k}^2_{z\pm})}{\hbar}\right|^2 . \tag{17}$$

The last term on the right-hand side of (17) follows from an optical theorem also valid in the Hilbert space spanned by the complete set of distorted waves (15).[33] Here the summation ranges over all open scattering channels differing from the incident one. For later convenience we shall call such a Debye-Waller factor "complete". Analogously, for the state-to-state inelastic-scattering probability or inelastic reflection $|i\rangle\to|f\rangle$, we find

$$R_{fi} = |S_{fi}|^2 = \left|\frac{\tilde{T}^V_{fi}\delta_{k_{zf},\bar{k}_{z\pm}}\Theta(\bar{k}^2_{z\pm})}{\hbar}\right|^2 , \quad f\neq i\ . \tag{18}$$

This expression will prove useful below in discussions of the properties of the scattering spectra. As is now seen from (17) and (18), the reflection coefficients obey the unitarity requirement

$$R_{ii}+\sum_{f(\neq i)}R_{fi}=1\ , \tag{19}$$

which is simply a consequence of the optical theorem which, in turn, derives from the unitarity of the $S$ matrix. The familiar expression for the inelastic differential reflection coefficient is then obtained by converting the summation over the particle final states in (19) into integration, and making use of the conversion formula (12) and definition (14):

$$\begin{aligned}\sum_{f(\neq i)}R_{fi} &= \sum_{\mathbf{k}_f}\frac{2\pi}{\hbar j_{zi}}\sum_{\{n_f\}}|T^V_{f,i}|^2\delta(E_f-E_i)\\ &= \int d\epsilon_f d\Omega_f\frac{L_zL_s^2}{(2\pi)^3}\frac{Mk_f}{\hbar^2}\sum_{\{n_f\}}\frac{2\pi}{\hbar j_{zi}}|T^V_{f,i}|^2\delta(E_f-E_i)\\ &= \int d\epsilon_f d\Omega_f\rho_{\text{part}}(\epsilon_f)R_{\mathbf{k}_i}(\mathbf{k}_f) = \int d\epsilon_f d\Omega_f\frac{dR_{\mathbf{k}_i}(\epsilon_f,\Omega_f)}{d\epsilon_f d\Omega_f}\ ,\end{aligned} \tag{20}$$

where, in going from the phase space of the final particle momenta to the phase space in which the final energy of the scattered particle lies in the interval $(\epsilon_f,\epsilon_f+d\epsilon_f)$ and the momentum in the solid angle $(\Omega_f,\Omega_f+d\Omega_f)$, we have used

$$\frac{L_zL_s^2}{(2\pi)^3}d^3\mathbf{k}_f = \frac{L_zL_s^2}{(2\pi)^3}\frac{Mk_f}{\hbar^2}d\epsilon_f d\Omega_f = \rho_{\text{part}}(\epsilon_f)d\epsilon_f d\Omega_f\ , \tag{21}$$

and denoted by $\rho_{\text{part}}(\epsilon_f)$ the density of the final particle states. Hence the inelastic differential reflection coefficient

$$\frac{dR_{\mathbf{k}_i}(\epsilon_f,\Omega_f)}{d\epsilon_f d\Omega_f} = \rho_{\text{part}}(\epsilon_f)R_{\mathbf{k}_i}(\mathbf{k}_f) = \rho_{\text{part}}(\epsilon_f)\sum_{\{n_f\}}\frac{2\pi}{\hbar j_{zi}}|T^V_{f,i}|^2\delta(E_f-E_i) \tag{22}$$

appearing as the integrand on the right-hand side of Eq. (20) is independent of the quantization lengths $L_s$ and $L_z$, as it should be. With these definitions we can establish the desired relation between the reflection coefficient and the scattering spectrum.

In defining the scattering spectrum we first observe that, due to the total-energy conservation in the collision, the energy lost by the particle will be transferred to the phonon system. This allows us to define the scattering spectrum either with respect to the particle energy loss (gain) or with respect to the energy gain (loss) of the phonon system. The latter alternative usually turns out to be more convenient, because it is much simpler to deal with the phonon (boson) operator algebra than with the algebra of particle operators. With this in mind and following Ref. 7, we define the scattering spectrum $N_{\mathbf{k}_i}(\varepsilon)$ which describes the probability of the energy transfer $\varepsilon$ from the scattering particle to phonon excitations in the course of the collision by

$$N_{\mathbf{k}_i}(\varepsilon)=\lim_{t\to\infty,t_0\to-\infty}\langle\Psi(t,t_0)|\delta[\varepsilon-(H_0^{\rm ph}-\varepsilon_i)]|\Psi(t,t_0)\rangle\ , \tag{23}$$

where $\varepsilon_i$ is the initial energy of the crystal phonon field described by the unperturbed phonon Hamiltonian $H_0^{\rm ph}$, and $|\Psi(t,t_0)\rangle$ is the wave function of the collision system obtained as the time-dependent solution of the Schrödinger equation

$$H|\Psi(t)\rangle=i\hbar(\partial/\partial t)|\Psi(t)\rangle\ , \tag{24}$$

where $H$ is the total Hamiltonian of the interacting system

$$H=H_0^p+H_0^{\rm ph}+gV=H_0+gV\ , \tag{25}$$

with $H_0^p=(\mathbf{p}^2/2M)+U(\mathbf{r})$ and $V=V(\mathbf{r})$ denoting the unperturbed particle Hamiltonian and the particle-phonon interaction, respectively. $g$ is the coupling constant which we have introduced for later convenience. In the case of the scattering boundary conditions in the interval $(t\to\infty,t_0\to-\infty)$, we assume the solution of (24) at instant $t_0\to-\infty$ in the form $|\Psi_0\rangle=|i\rangle=e^{-iE_it_0}|\mathbf{k}_i\rangle|0\rangle$. Here $\mathbf{k}_i$ denotes the incident particle quantum number (free-particle wave vector far away from the surface), and $|0\rangle$ is the initial ground state of the phonon system [the generalization of all the expressions to finite substrate temperature is straightforward, cf. Eq. (1) and Eq. (68) below]. Then

$$\lim_{t\to\infty,t_0\to-\infty}|\Psi(t,t_0)\rangle=\lim_{t\to\infty,t_0\to-\infty}U(t,t_0)|\Psi_0\rangle=S|\Psi_0\rangle=S|i\rangle\ , \tag{26}$$

and, consequently,

$$\begin{aligned}N_{\mathbf{k}_i}(\varepsilon)&=\langle i|S^\dagger\delta[\varepsilon-(H_0^{\rm ph}-\varepsilon_i)]S|i\rangle\\&=\sum_f|\langle f|S|i\rangle|^2\delta[\varepsilon-(\varepsilon_f-\varepsilon_i)]\\&=\sum_f R_{\mathbf{k}_i}(\mathbf{k}_f;n_f)\delta[\varepsilon-(\varepsilon_f-\varepsilon_i)]\\&=\sum_{\{n_f\}}R_{\mathbf{k}_i}(n_f)\delta[\varepsilon-(\varepsilon_f-\varepsilon_i)]=\sum_{\mathbf{k}_f}R_{\mathbf{k}_i}(\mathbf{k}_f)\delta(\varepsilon+\epsilon_f-\epsilon_i)\ ,\end{aligned} \tag{27}$$

where

$$\begin{aligned}R_{\mathbf{k}_i}(n_f)&=\sum_{\mathbf{k}_f}R_{\mathbf{k}_i}(\mathbf{k}_f;n_f)\ ,\\R_{\mathbf{k}_i}(\mathbf{k}_f)&=\sum_{\{n_f\}}R_{\mathbf{k}_i}(\mathbf{k}_f;n_f)\ ,\end{aligned} \tag{28}$$

and the cumulative index $f=\{\mathbf{k}_f,n_f\}$ now ranges over all open scattering channels, both elastic and inelastic. Here we have exploited the fact that in the collision $\epsilon_i-\epsilon_f=\varepsilon_f-\varepsilon_i$ [cf. Eqs. (10)–(12)]. The energy conservation also affects the summation over the final particle states, so as that it effectively ranges only over the lateral wave vector $\mathbf{K}_f$. The final expression on the right-hand side of (27) for the scattering spectrum (23) has the appearance of the probability density per unit energy interval and, hence, can be also identified with the total reflection spectrum $R_{\mathbf{k}_i}(\varepsilon)$ for the particle.

The lateral momentum-transfer-resolved scattering spectrum for a flat surface at zero temperature is then given by a generalization of Eq. (23):

$$N_{\mathbf{k}_i}(\varepsilon,\Delta\mathbf{K})=\lim_{t\to\infty,t_0\to-\infty}\langle\Psi(t,t_0)|\delta[\varepsilon-(H_0^{\rm ph}-\varepsilon_i)]\times\delta(\hbar\Delta\mathbf{K}-\hat{\mathbf{P}})|\Psi(t,t_0)\rangle\ , \tag{29}$$

where $\Delta\mathbf{K}=\mathbf{K}_i-\mathbf{K}_f$, and $\hat{\mathbf{P}}$ is the lateral momentum operator of the phonon field

$$\hat{\mathbf{P}}=\sum_{\mathbf{Q},j}\hbar\mathbf{Q}\hat{n}_{\mathbf{Q},j}\ , \tag{30}$$

with $\hat{n}_{\mathbf{Q},j}$ standing for the surface phonon number operator of the mode $(\mathbf{Q},j)$. For convenience we have again expressed the energy and lateral momentum transfer in terms of the phonon rather than particle operators for the reasons mentioned earlier, and because the quasiclassical limit of the particle motion is easier to retrieve in this representation. Now, since in terms of the operators $\hat{n}_{\mathbf{Q},j}$ the unperturbed Hamiltonian of the surface phonon field is written as

$$H_0^{\rm ph}=\sum_{\mathbf{Q},j}\hbar\omega_{\mathbf{Q},j}\hat{n}_{\mathbf{Q},j}\ , \tag{31}$$

where $\omega_{\mathbf{Q},j}$ is the frequency of the corresponding mode, the operators $H_0^{\rm ph}$ and $\hat{\mathbf{P}}$ commute, and, hence, the correctness of the definition (29) is guaranteed. It should also be noted that both scattering spectra (23) and (29) are inherently normalized to unity.

Making use of Eqs. (17), (18), and (29), the lateral momentum-resolved scattering spectrum can now be expressed in terms of the reflection coefficients:

$$N_{\mathbf{k}_i}(\varepsilon,\Delta\mathbf{K})=\sum_f R_{\mathbf{k}_i}(\mathbf{k}_f;n_f)\delta[\varepsilon-(\varepsilon_f-\varepsilon_i)]\times\delta(\hbar\Delta\mathbf{K}-\{\hbar\mathbf{Q}\})\ . \tag{32}$$

The weight of the elastic line in this spectrum is then given by Eq. (17), which justifies the identification of $R_{ii}$ with the Debye-Waller factor. Again, one may express the arguments of the $\delta$ functions in (32) in terms of the particle quantities and convert the $\delta$ functions into

Kronecker symbols following Eq. (12). Then, by multiplying each side of Eq. (32) by $Mk_f/\hbar^2$, we obtain

$$\hbar^2 k_f k_{zf} N_{\mathbf{k}_i}(\varepsilon,\Delta\mathbf{K}) = \frac{L_z L_s^2}{(2\pi)^3}\frac{Mk_f}{\hbar^2}\sum_{\{n_f\}} R_{\mathbf{k}_i}(\bar{k}_{z\pm},\mathbf{K}_i-\Delta\mathbf{K};n_f) = R_{\mathbf{k}_i}(\bar{k}_{z\pm},\mathbf{K}_i-\Delta\mathbf{K})\rho_{\rm part}(\epsilon_f) = \frac{dR_{\mathbf{k}_i}(\epsilon_f,\Omega_f)}{d\epsilon_f d\Omega_f} , \tag{33}$$

where $R_{\mathbf{k}_i}(\bar{k}_{z\pm},\mathbf{K}_i-\Delta\mathbf{K})$ is defined in accord with Eq. (28), including also the case $f=i$. An equivalent relationship has been quoted in Ref. 7. The generalization to the case of finite crystal temperatures, in which the phonon initial-state distribution is given by $\rho_{\rm ph}(n_i)$, is then straightforward. Note here that the reflection coefficient on the right-hand side of (33) should bear the same normalization as does the scattering spectrum. Now, as even perturbative approaches based on a partial summation of certain classes of contributions to the scattering amplitude produce unitary scattering spectra and the Debye-Waller factor in exponential form (see Sec. III), the same unitarity properties should also hold for the reflection coefficients obtained through Eq. (33). Moreover, as due to the normalization of $N_{\mathbf{k}_i}(\varepsilon,\Delta\mathbf{K})$ the right-hand side of Eq. (32) should also integrate to unity, one can retrieve the optical theorem (19) and thereby the unitarity of the reflection coefficients directly from the properties of the scattering spectrum. In Sec. III we shall demonstrate a very systematic and rigorous derivation of a general quantum-mechanical expression for the scattering spectrum of a particle interacting with phonons (generally bosons) which naturally lends itself to various approximate treatments which preserve the unitarity property. A passage to the corresponding approximate but still unitary reflection coefficients is then straightforward by means of Eqs. (32) and (33). These features cannot easily be retrieved in approaches based on standard approximate treatments of the $T$ matrix in Eq. (1), especially in the case of low-order perturbative solutions such as the DWBA, which may completely miss out the unitarity property.

## III. ANGULAR-RESOLVED SCATTERING SPECTRUM AND THE DEBYE-WALLER FACTOR

In this section we shall first present a formal derivation of a rigorously exact expression for the energy and lateral momentum-resolved scattering spectrum in terms of perturbation $V$, and demonstrate some of its general properties and features like the Debye-Waller factor, etc. Using the formulas obtained we shall then introduce the exponentiated Born approximation (EBA) expression for this spectrum and point out other approximations which naturally derive from it as the limiting cases. These are, for instance, the impulse or fast collision approximation (IA), the trajectory approximation (TA), and some others, all of which are commonly used in the theoretical descriptions of HAS.

### A. Formal derivation of the energy- and momentum-resolved scattering spectrum

A convenient expression for the scattering spectrum, which is also amenable to application of the various approximations popular in atom-surface scattering theory and which gives the ubiquitous Debye-Waller factor in an explicit form, can be obtained by making use of a trick similar to the one employed by van Hove[14] and Glauber[13] in their derivation of the inelastic scattering cross section in terms of phonon correlation functions. By expressing the energy- and momentum-conserving $\delta$ functions in (29) as Fourier transforms of exponentials of the operators $H_0^{\rm ph}$ and $\hat{\mathbf{P}}$ (cf. Refs. 13 and 14), we obtain

$$\begin{aligned} N_{\mathbf{k}_i}(\varepsilon,\Delta\mathbf{K}) &= \int_{-\infty}^{\infty}\frac{d\tau}{2\pi\hbar}\int\frac{d^2\mathbf{R}}{(2\pi\hbar)^2}e^{(i/\hbar)[\varepsilon\tau-\hbar(\Delta\mathbf{K})\mathbf{R}]}\langle\Psi(\infty)|e^{-(i/\hbar)(H_0^{\rm ph}\tau-\hat{\mathbf{P}}\mathbf{R})}|\Psi(\infty)\rangle \\ &= \int_{-\infty}^{\infty}\frac{d\tau}{2\pi\hbar}\int\frac{d^2\mathbf{R}}{(2\pi\hbar)^2}e^{(i/\hbar)[\varepsilon\tau-\hbar(\Delta\mathbf{K})\mathbf{R}]}\langle i|S_I^\dagger e^{-(i/\hbar)(H_0^{\rm ph}\tau-\hat{P}_x X-\hat{P}_y Y)}S_I|i\rangle \\ &= \int_{-\infty}^{\infty}\frac{d\tau}{2\pi\hbar}\int\frac{d^2\mathbf{R}}{(2\pi\hbar)^2}e^{(i/\hbar)[\varepsilon\tau-\hbar(\Delta\mathbf{K})\mathbf{R}]}\langle i|e^{-(i/\hbar)(\mathcal{H}_0^{\rm ph}\tau-\mathcal{P}_x X-\mathcal{P}_y Y)}|i\rangle . \end{aligned} \tag{34}$$

Here $\mathbf{R}=(X,Y)$ is a two-dimensional radius vector parallel to the surface plane, where the capital letters have been introduced to avoid confusion with the coordinates $(x,y)$ of the particle; $S_I$ is the $S$ operator in the interaction picture

$$S_I = \lim_{t\to\infty,t_0\to-\infty} U_I(t,t_0) , \tag{35}$$

where $U_I(t,t_0)=e^{(i/\hbar)H_0(t-t_0)}U(t,t_0)=e^{(i/\hbar)H_0 t}U(t,t_0)e^{-(i/\hbar)H_0 t_0}$, and the canonically transformed operators appearing in the last line of Eq. (34) are defined by

$$\mathcal{H}_0^{\rm ph} = S_I^\dagger H_0^{\rm ph} S_I , \tag{36}$$

$$\mathcal{P}_x = S_I^\dagger \hat{P}_x S_I , \tag{37}$$

$$\mathcal{P}_y = S_I^\dagger \hat{P}_y S_I . \tag{38}$$

Now, according to a general theorem[35] the operator $U_I(t,t_0)$, and thereby $S_I$, can be represented in an exponential

form:

$$U_I(t,t_0)=e^{-iG(t,t_0)}=\exp\left[-i\sum_{n=1}^{\infty}G_n(t,t_0)\right], \tag{39}$$

where $G(t,t_0)$ is a Hermitian operator which has a nested commutator expansion in powers of the coupling constant $g$:[35]

$$G_1(t,t_0)=\frac{g}{\hbar}\int_{t_0}^{t}dt_1 V_I(t_1), \tag{40}$$

$$G_2(t,t_0)=-\frac{i(g/\hbar)^2}{2}\int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2[V_I(t_1),V_I(t_2)], \tag{41}$$

$$G_3(t,t_0)=\frac{(g/\hbar)^3}{4}\int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2\int_{t_0}^{t_2}dt_3[V_I(t_1),[V_I(t_2),V_I(t_3)]] + \frac{(g/\hbar)^3}{12}\int_{t0}^{t}dt_1\int_{t_0}^{t_1}dt_2\int_{t_0}^{t_1}dt_3[[V_I(t_1),V_I(t_2)],V_I(t_3)], \tag{42}$$

etc., where all other higher-order terms in the coupling constant comprise higher-order commutators $[.,[..,[\ldots,]]]$ of the particle-boson interaction operators:

$$V_I(t_j)=e^{(i/\hbar)H_0t_j}Ve^{-(i/\hbar)H_0t_j}. \tag{43}$$

Thus the $S$ matrix in the interaction picture can be written in a general form:

$$S_I=\lim_{t\to\infty,t_0\to-\infty}e^{-iG(t,t_0)}=e^{-iG(\infty,-\infty)}=e^{-iG}. \tag{44}$$

From now on the formal solution of Eq. (34) can be presented much more clearly by introducing a unified vector notation for the variables and exponentiated operators:

$$(\tau,X,Y)\to(\xi_0,\xi_1,\xi_2)=\xi, \tag{45}$$

$$\left[\frac{\varepsilon}{\hbar},-\Delta K_x,-\Delta K_y\right]\to(\varepsilon_0,\varepsilon_1,\varepsilon_2)=\varepsilon, \tag{46}$$

$$(\omega_{Q,j},-Q_x,-Q_y)\to(\nu_0,\nu_1,\nu_2)=\nu, \tag{47}$$

$$\left[\frac{H_0^{\rm ph}}{\hbar},-\frac{\hat{P}_x}{\hbar},-\frac{\hat{P}_y}{\hbar}\right]\to(\mathcal{H}_0,\mathcal{H}_1,\mathcal{H}_2)=\mathcal{H}, \tag{48}$$

where, due to the property that $H_0^{\rm ph}$ and $\hat{\mathbf{P}}$ commute, the components of the operator $\mathcal{H}$ also commute with each other, i.e.,

$$[\mathcal{H}_l,\mathcal{H}_{l'}]=0. \tag{49}$$

Using the notation of Eqs. (45)–(48), we can write

$$\frac{\varepsilon}{\hbar}\tau-(\Delta\mathbf{K})\mathbf{R}=\sum_{l=0}^{2}\varepsilon_l\xi_l=\varepsilon\xi, \tag{50}$$

$$\frac{H_0^{\rm ph}}{\hbar}\tau-\frac{\hat{P}_x}{\hbar}X-\frac{\hat{P}_y}{\hbar}Y=\sum_{l=0}^{2}\mathcal{H}_l\xi_l=\mathcal{H}\xi, \tag{51}$$

$$\mathcal{L}=(\mathcal{L}_0,\mathcal{L}_1,\mathcal{L}_2)=S_I^{\dagger}\mathcal{H}S_I, \tag{52}$$

which enables us to express Eq. (34) in a compact form amenable to various approximate treatments:

$$N_{\mathbf{k}_i}(\varepsilon,\Delta\mathbf{K})=N_{\mathbf{k}_i}(\varepsilon)=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{d^3\xi}{(2\pi\hbar)^3}\exp(i\varepsilon\xi)\langle i|\exp(-i\mathcal{L}\xi)|i\rangle. \tag{53}$$

The standard energy-resolved spectrum $N_{\mathbf{k}_i}(\varepsilon)$ defined by Eq. (23) and elaborated in Refs. 9 and 10 is obtained by restricting the right-hand side of (53) to a single component $l=0$.

To obtain a perturbative solution to Eq. (53), we proceed by making use of the operator identity

$$\mathcal{L}=S_I^{\dagger}\mathcal{H}S_I=e^{iG}\mathcal{H}e^{-iG}=\sum_{n=0}^{\infty}\frac{i^n}{n!}G^n[\mathcal{H}], \tag{54}$$

where $G^n[\Lambda]=[G,[G,\ldots,[G,\Lambda]]$ is the $n$th-order repeated commutator of $G$ with arbitrary operator $\Lambda$. Using this we find

$$N_{\mathbf{k}_i}(\varepsilon,\Delta\mathbf{K})=N_{\mathbf{k}_i}(\varepsilon)=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{d^3\xi}{(2\pi\hbar)^3}\exp(i\varepsilon\xi)\langle i|\exp[-i(\mathcal{H}+\mathcal{W})\xi]|i\rangle, \tag{55}$$

where, according to Eq. (54),

$$\mathcal{W}=\sum_{n=1}^{\infty}\frac{i^n}{n!}G^n[\mathcal{H}]. \tag{56}$$

The diagonal matrix element of the exponential operator on the right-hand side of (53) and (55) can be evaluated on noticing that each of the exponentiated $l$th components of this operator has the appearance of an evolution operator in $\xi_l$ space:

$$e^{-i(\mathcal{H}_l+\mathcal{W}_l)\xi_l}=e^{-i\mathcal{H}_l\xi_l}\mathcal{T}_l\exp\left[-i\int_0^{\xi_l}\mathcal{W}_l^I(\xi_l')d\xi_l'\right], \tag{57}$$

where the symbols $\mathcal{T}_l$ stand for the ordering operators, each acting only in its own $\xi_l$ subspace (in $\tau$ space this is the usual time-ordering operator). Note also that $\mathcal{T}_l$'s commute with each other.

The averages (here diagonal values) of the exponential operators appearing in the above expressions can be obtained by a generalized cumulant expansion,[36] and in the present case this gives

$$N_{\mathbf{k}_i}(\varepsilon,\Delta\mathbf{K})=N_{\mathbf{k}_i}(\varepsilon)=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{d^3\xi}{(2\pi\hbar)^3}\exp(i\varepsilon\xi)\exp\left[\sum_{n=1}^{\infty}C_n(\xi)\right], \tag{58}$$

where $C_n(\xi)$ stands for the $n$th-order cumulant generated by the operators $\mathcal{W}_l^I(\xi_l)$, whose time dependence in the interaction picture in the $\xi_l$ space is governed by $\mathcal{H}_l$:

$$\mathcal{W}_l^I=e^{i\mathcal{H}\xi_l}\mathcal{W}_l e^{-i\mathcal{H}\xi_l}. \tag{59}$$

Explicitly, these cumulants read

$$C_n(\xi_0,\xi_1,\xi_2)=\frac{(-i)^n}{n!}\sum_{l,l',l''=0}^{2}\mathcal{T}_l\mathcal{T}_{l'}\mathcal{T}_{l''}\int_0^{\xi_l}d\xi_{l_1}\cdots\int_0^{\xi_l}d\xi_{l_m}\int_0^{\xi_{l'}}d\xi_{l'_1}\cdots\int_0^{\xi_{l'}}d\xi_{l'_p}\int_0^{\xi_{l''}}d\xi_{l''_1}$$
$$\cdots\int_0^{\xi_{l''}}d\xi_{l''_q}\langle i|\mathcal{W}_{l_1}^I(\xi_{l_1})\cdots\mathcal{W}_{l''_q}^I(\xi_{l''_q})|i\rangle_c,\quad m+p+q=n. \tag{60}$$

Here $\langle i|\ldots|i\rangle_c$ denotes the cumulant average[36] of the product of $n$ interaction operators $\mathcal{W}^I(\xi)$.

Equations (58) and (60) represent a formal closed-form solution for the required energy- and lateral-momentum-resolved scattering spectrum (34) of the particle-phonon collision system. *It is exact as no approximations regarding either the particle or the phonon dynamics have been employed yet.* Also, it exhibits the unitarity property, i.e., normalization to unity. The elastic line $\delta$-function component of the spectrum is weighted by the Debye-Waller factor which appears in the form of an exponentiated sum of all $\xi_i$-independent terms remaining in the cumulants after the integration over all dummy $\xi_l$ variables has been carried out. Hence it is the intrinsic property of the present method that it gives the DWF as an exponential of an infinite series in powers of the coupling constant $g$. This is in contrast to the right-hand side of Eq. (17), where the DWF has a formal appearance of an ordinary expansion in powers of $g$.

Another important characteristic of the so-derived DWF is its completeness or unitarity. That is, in the present formulation the Debye-Waller exponent $2W$ is obtained by carrying out a summation over all final scattering channels different from the incident one, which is in accord with the optical theorem and the quantum reflection coefficient derived from it [cf. the discussion following Eqs. (17) and (19)], but also with the semiclassical theories of particle scattering by surface phonons.[23,24,31,37] Such a DWF is conceptually somewhat different from the analogous quantity appearing in the standard van Hove–Glauber Born approximation descriptions of x-ray and neutron scattering by the vibrating crystal lattices, and their later extensions to surface scattering problems.[29] In these theories the attenuation of the scattered beams arises as a consequence of a disarray introduced into the system through the thermal motion of the crystal ions (i.e., the scattering centers) and nonlinear projectile-phonon coupling. The corresponding DWF plays a role in the normalization of the $(\mathbf{k}_f-\mathbf{k}_i)$ component of the exponentiated-lattice-atom-displacement correlation function, and originates from the noncommutativity of the crystal vibration operators at different instants. Obviously, such a DWF is independent of the matrix elements of the atom-surface interaction potential, and incomplete because it is associated only with phonon momentum and energy exchanged in a particular transition $\mathbf{k}_i\rightarrow\mathbf{k}_f$ of the particle. As the calculations of the inelastic reflection coefficient $R_{fi}$ based on either the BA or its improvements in treating the total scattering potential $U(\mathbf{r})$ leave out the true elastic line (17), they can yield only such an incomplete or single-channel DWF. Hence, to obtain unitarity of the reflection coefficient in this case, one has to sum up contributions over all final scattering channels $|f\rangle$, as pointed out here in connection with Eqs. (17) and (19) and also earlier in Refs. 7 and 24. On the other hand, in the formulation of the scattering spectrum through Eqs. (29), (34), and (58) the thus-obtained complete DWF gives the depletion of the particle flux in the specularly reflected beam due to inelastic scattering through real phonon emission or absorption, i.e., through transitions into all scattering channels different from the elastic one. Therefore, the corresponding Debye-Waller exponent involves matrix elements describing dissipative atom-surface interaction denoted by $V$ in Eq. (25) even in the simplest case of linear coupling of the atom to the boson field.

Despite the fact that the exponentiated cumulant series appearing on the right-hand side of (58) gives a compact

closed-form solution for the scattering spectrum, it still involves an infinite number of terms, each of which itself contains contributions to all orders in the coupling constant. Hence a tractable form of $N_{\mathbf{k}_i}(\varepsilon,\Delta\mathbf{K})$ can be obtained only in certain limiting cases. This will occur if the series can be truncated after a relatively small number of terms, or easily summed up by using some common functional properties of the cumulants arising from the specificities of the interaction studied. Here it should be observed that one of the major advantages of using the cumulant approach is that it produces the scattering spectrum (58) which retains the unitarity property and the corresponding Debye-Waller factor of the exponential form irrespective of the approximations employed in the derivation of $G$ or $\mathcal{W}(\xi)$. In the following we shall demonstrate how this procedure can be carried out in a particular case of a particle coupled linearly to phonons, as discussed in connection with the inelastic particle-surface interaction described by Eq. (4).

### B. Energy- and momentum-resolved scattering spectrum in the exponentiated Born approximation

To demonstrate the derivation of the exponentiated Born approximation (EBA) expression for the scattering spectrum (29) or (34), we must specify the unperturbed atom and phonon states and the dynamic atom-phonon interaction $V(\mathbf{r})$. Here we first make use of the hitherto assumed translational invariance of the static atom-surface potential $U^0(\mathbf{r})=U^0(z)$ which yields distorted particle waves $\varphi_{\mathbf{k}}(\mathbf{r})$ and the corresponding energies $\epsilon_{\mathbf{K},k_z}$ defined in Sec. II. The phonon excitations of the surface are characterized by their quantum numbers $(\mathbf{Q},j)$ defined earlier, and the dispersion relation reads $\omega=\omega_{\mathbf{Q},j}$. Inelastic atom-surface processes will be described by a harmonic interaction of the type given by Eq. (4). Then, in terms of these quantities, the Hamiltonian of the system acquires in second quantization a simple form,

$$H=H_0+gV=\sum_{\mathbf{K},k_z}\epsilon_{\mathbf{K},k_z}c^{\dagger}_{\mathbf{K},k_z}c_{\mathbf{K},k_z}+\sum_{\mathbf{Q},j}\hbar\omega_{\mathbf{Q},j}a^{\dagger}_{\mathbf{Q},j}a_{\mathbf{Q},j}$$
$$+g\sum_{\mathbf{K},\mathbf{K}',k_z,k_z'}\sum_{\mathbf{Q},j}V^{\mathbf{K}',\mathbf{K},\mathbf{Q}}_{k_z',k_z,j}\delta_{\mathbf{K}',\mathbf{K}+\mathbf{Q}}c^{\dagger}_{\mathbf{K}',k_z'}c_{\mathbf{K},k_z}a_{\mathbf{Q},j}+\text{H.c.}\ , \tag{61}$$

where $c^{\dagger}_{\mathbf{K},k_z}$, $c_{\mathbf{K},k_z}$ and $a^{\dagger}_{\mathbf{Q},j}$, $a_{\mathbf{Q},j}$ are the particle and phonon creation and annihilation operators, respectively, and the appearance of the Kronecker $\delta$ is a consequence of the translational invariance of the surface. The phonon operators satisfy the ordinary boson commutation relations, whereas the particle operators may obey either bosonic or fermionic commutation rules. The explicit expression for the interaction matrix element $V^{\mathbf{K}',\mathbf{K},\mathbf{Q}}_{k_z',k_z,j}$ will be given and discussed in Sec. IV within the context of HAS from some specific surfaces.

With the interaction Hamiltonian defined, the EBA expression for the scattering spectrum is obtained by retaining in the operator series for $G$ [Eq. (39)] the full $G_1$ (proportional to $g$) and only the diagonal components of $G_2$ (proportional to $g^2$). Physically, this means the neglect of the correlated multiphonon processes in the spectrum relative to the effects brought about by the multiple excitation or absorption of uncorrelated phonons. The justification of this approximation in the case of HAS will be given in Sec. IV. The various aspects of this approximation have been discussed in Refs. 9 and 10. With such an approximate $G$ substituted into Eq. (56), we obtain an approximate $\mathcal{W}_l$,

$$\mathcal{W}_l=\mathcal{W}_l^{(1)}+\mathcal{W}_l^{(2)}\ , \tag{62}$$

in which

$$\mathcal{W}_l^{(1)}=i[G_1,\mathcal{H}_l]=\sum_{\mathbf{K},\mathbf{Q},k_z,k_z',j}[i\hbar\nu_l\mathcal{V}^{\mathbf{K},\mathbf{Q}}_{k_z,k_z',j}(-)c^{\dagger}_{\mathbf{K}+\mathbf{Q},k_z'}c_{\mathbf{K},k_z}a_{\mathbf{Q},j}+\text{H.c.}]\ \propto g\ , \tag{63}$$

$$\mathcal{W}_l^{(2)}=-\tfrac{1}{2}[G_1,[G_1,\mathcal{H}_l]]\approx\sum_{\mathbf{K},k_z,k_z'}c^{\dagger}_{\mathbf{K},k_z}c_{\mathbf{K},k_z'}\sum_{\mathbf{Q},k_z'',j}\hbar\nu_l[\mathcal{V}^{\mathbf{K},\mathbf{Q}}_{k_z,k_z'',j}(+)]^*\mathcal{V}^{\mathbf{K},\mathbf{Q}}_{k_z'',k_z',j}(+)\propto g^2\ , \tag{64}$$

and other terms in (64) containing phonon operators are small.[10] The next term

$$\mathcal{W}_l^{(3)}=i[G_2,\mathcal{H}_l]\propto g^2\ , \tag{65}$$

and higher-order ones in powers of $g$ in Eq. (56), which give rise to correlated phonon processes, are neglected within the EBA. Thus, in contrast to standard perturbational treatments in powers of the coupling constant $g$, the EBA expansion is based on a tradeoff between the magnitude of $g$ and the small overall contribution of correlated phonon processes described by the terms $\mathcal{W}_l^{(n)}$ for $n>2$.

The off-diagonal matrix elements of $G_1$ giving the probability amplitude of one-phonon absorption and emission processes, viz.,

$$\mathcal{V}^{\mathbf{K},\mathbf{Q}}_{k_z,k_z',j}(\mp)=\frac{gV^{\mathbf{K},\mathbf{K}',\mathbf{Q}}_{k_z,k_z',j}\delta_{\mathbf{K}',\mathbf{K}\pm\mathbf{Q}}}{\hbar}\int_{-\infty}^{\infty}dt_1 e^{\pm(i/\hbar)(\epsilon_{\mathbf{K}',k_z'}-\epsilon_{\mathbf{K},k_z}\mp\hbar\omega_{\mathbf{Q},j})t_1}=\frac{\tilde{V}^{\mathbf{K},\mathbf{K}\pm\mathbf{Q}}_{k_z,k_z',j}\delta_{k_z',k_{z\pm}}\Theta(\bar{k}^2_{z\pm})}{\hbar}\ , \tag{66}$$

which appear in the operators $\mathcal{W}_l^{(1)}$ and $\mathcal{W}_l^{(2)}$ are, following the arguments of Sec. II, first-order DWBA probability amplitudes for the on-the-energy-shell state-to-state transition $|\mathbf{K},k_z\rangle \rightarrow |\mathbf{K}',k_z'\rangle$ of the particle. Here the tilde denotes matrix elements calculated in accord with the normalization of Eq. (15), and $\bar{k}_{z\pm}$ is defined by Eq. (13). Now, according to (18), the absolute square of the expression on the right-hand side of (66) gives the particle inelastic reflection probability from the state $|\mathbf{K},k_z\rangle$ to the state $|\mathbf{K}\pm\mathbf{Q},k_z'\rangle$ in the DWBA.

To obtain $N_{\mathbf{k}_i}^{\mathrm{EBA}}(\varepsilon,\Delta\mathbf{K})$ for zero substrate temperature, we substitute (62) into Eqs. (58) and (60). Then, on noticing that $\mathcal{W}_l^{(2)}$ is to a good approximation proportional to the particle number operator which commutes with $\mathcal{W}_l^{(1)}$, we find that $\mathcal{W}_l^{(2)}$ makes a contribution only to the first cumulant in (58) which is linear in $\xi_l$, and which is canceled by an identical expression arising from $\mathcal{W}_l^{(1)}$ in the second cumulant.[10] Thus there are no terms linear in $\xi_l$ (so-called relaxation shifts) in the final expression for the EBA scattering spectrum. Taking all this into account and reverting back to the original variables $(\tau,X,Y)$, we obtain the result alluded to in Ref. 9:

$$N_{\mathbf{k}_i}^{\mathrm{EBA}}(\varepsilon,\Delta\mathbf{K})=\int_{-\infty}^{\infty}\frac{d\tau\,d^2\mathbf{R}}{(2\pi\hbar)^3}e^{(i/\hbar)[\varepsilon\tau-\hbar(\Delta\mathbf{K})R]}\exp\left\{-\sum_{\mathbf{Q},j,k_z}|\mathcal{V}_{k_z,k_{zi},j}^{\mathbf{K}_i,\mathbf{Q}}(+)|^2[1-e^{-i(\omega_{\mathbf{Q},j}\tau-\mathbf{QR})}]\right\}, \tag{67}$$

where $(\mathbf{K}_i,k_{zi})$ denotes the incident particle quantum numbers.

Generalizing the same procedure to the case of finite substrate temperatures $T_s$ (i.e., both phonon emission and absorption processes), we find

$$N_{\mathbf{k}_i,T_s}^{\mathrm{EBA}}(\varepsilon,\Delta\mathbf{K})=\int_{-\infty}^{\infty}\frac{d\tau\,d^2\mathbf{R}}{(2\pi\hbar)^3}e^{(i/\hbar)[\varepsilon\tau-\hbar(\Delta\mathbf{K})R]}\exp[2W^{\mathrm{EBA}}(\mathbf{R},\tau)-2W^{\mathrm{EBA}}(0,0)], \tag{68}$$

where

$$2W^{\mathrm{EBA}}(\mathbf{R},\tau)=\sum_{\mathbf{Q},j,k_z}[|\mathcal{V}_{k_z,k_{zi},j}^{\mathbf{K}_i,\mathbf{Q}}(+)|^2[\bar{n}(\hbar\omega_{\mathbf{Q},j})+1]e^{-i(\omega_{\mathbf{Q},j}\tau-\mathbf{QR})}+|\mathcal{V}_{k_z,k_{zi},j}^{\mathbf{K}_i,\mathbf{Q}}(-)|^2\bar{n}(\hbar\omega_{\mathbf{Q},j})e^{i(\omega_{\mathbf{Q},j}\tau-\mathbf{QR})}] \tag{69}$$

is the so-called driving function which is generally complex and whose zero-point value $2W^{\mathrm{EBA}}(0,0)=2W_{T_s}^{\mathrm{EBA}}$ gives the DWF exponent in the EBA. Here $\omega_{\mathbf{Q},j}$ is again restricted only to positive values and $\bar{n}_{\mathrm{ph}}(\varepsilon)$ is the Bose function describing the initial distribution of phonons thermally excited in the substrate kept at finite temperature $T_s$. Equations (67) and (68) describe the scattering spectrum containing all uncorrelated real multiphonon processes, and this will be a good approximation of the exact spectrum (58) (which comprises both all uncorrelated and correlated multiphonon processes) under the conditions discussed in Sec. IV (cf. also discussions in Refs. 9, 10, and 11).

The EBA expression for the Debye-Waller factor which describes specular elastic scattering and corresponds to Eq. (17) is then given by the $\delta(\varepsilon)\delta(\Delta\mathbf{K})$ component of the scattering spectrum. For substrates at finite temperatures, this reads

$$\begin{aligned}e^{-2W^{\mathrm{EBA}}}&=\exp\left\{-\sum_{\mathbf{Q},j,k_z}[|\mathcal{V}_{k_z,k_{zi},j}^{\mathbf{K}_i,\mathbf{Q}}(+)|^2[\bar{n}_{\mathrm{ph}}(\hbar\omega_{\mathbf{Q},j})+1]+|\mathcal{V}_{k_z,k_{zi},j}^{\mathbf{K}_i,\mathbf{Q}}(-)|^2\bar{n}_{\mathrm{ph}}(\hbar\omega_{\mathbf{Q},j})]\right\}\\&=e^{-\sum_{f(\neq i)}R_{f_i}^{\mathrm{DWBA}}},\end{aligned} \tag{70}$$

where $f$ is now short for the set of quantum numbers $\{k_z,\mathbf{Q},j\}$. This important relationship gives the expression for the DWF in the EBA as a function of the total inelastic reflection coefficient obtained in the DWBA. As has been shown earlier,[10] the physical meaning of on-the-energy-shell quantity $2W^{\mathrm{EBA}}$ can be identified with the mean number of uncorrelated real phonons exchanged during the collision event.

Although it is presently not clear whether a generalization of Eq. (70) beyond the EBA would be a prohibitive task, it is already obvious at this stage that in both representations of the Debye-Waller factor, viz., the one deriving from the optical theorem (17) and the other following from the cumulant expansion (58), the probability of elastic scattering is obtained from expressions involving summations over all final states in all open scattering channels differing from the incident one. However, it is only in the latter representation that this quantity also appears as a common multiplicative factor for all other inelastic peaks in the spectrum characterized either by finite energy or momentum transfer. This property can easily be verified by factorizing out of the triple integral in (58) all $(\xi_1,\xi_2,\xi_3)=(\tau,\mathbf{R})$-independent terms appearing in the exponentiated cumulants and expanding the remaining $(\tau,\mathbf{R})$-dependent exponential into a series in powers of $e^{-i\omega_{\mathbf{Q},j}\tau}$ and $e^{i\mathbf{QR}}$. On the other hand, that such a common exponential factor would always exist is much less obvious in the standard $T^V$-matrix approach, where it could emerge only after a tedious resummation of *infinite*

sequences of various higher-order perturbation contributions to the scattering amplitude. For this reason the present approach via Eqs. (34)–(60) is far more advantageous and elegant regarding the explicit form of the DWF.

Now, it is straightforward to see that, in the weak-coupling limit $g \ll 1$, the EBA expression for the scattering spectrum turns into the DWBA formula upon expanding the exponential in the integrands on the right-hand side of Eqs. (67) and (68) into a power series and retaining only the zeroth- and first-order terms in $|\mathcal{V}^{\mathbf{K}_i,\mathbf{Q}}_{k_z,k_{zi},j}(\pm)|^2$.

The TA limit of scattering spectrum (67) or (68) is obtained upon replacing the DWBA scattering probability amplitude by its classical limit[38,37,9]

$$\mathcal{V}^{\mathbf{K}_i,\mathbf{Q}}_{k_z,k_{zi},j}(\mp)=2\pi V^{\mathbf{K},\mathbf{K}\pm\mathbf{Q}}_{k_z',k_z,j}\delta(\epsilon_{\mathbf{K}\pm\mathbf{Q},k_z'}-\epsilon_{\mathbf{K},k_z}\mp\hbar\omega_{\mathbf{Q},j})$$

$$\rightarrow V^{\mathrm{TA}}_{\pm\mathbf{Q}}(\mp\hbar\omega_{\mathbf{Q},j}) , \tag{71}$$

where the correspondence is achieved if the $\delta$ function on the left-hand side of the arrow is handled as outlined in Eqs. (10)–(13) and $V^{\mathrm{TA}}_{\pm\mathbf{Q}}(\mp\hbar\omega)=V^{\mathrm{TA}}_{\mp\mathbf{Q}}(\pm\hbar\omega)^*$ is taken to be the $\pm\mathbf{Q}$th component of the time Fourier transform of $V(\mathbf{r}(t))$ taken along the classical trajectory $\mathbf{r}(t)$.[38,37] The expression thus obtained is then in full correspondence with those obtained earlier which were derived by using the classical trajectory assumption in (29) and (67) from the very outset.[24,31,37]

The impulse or fast collision approximation (IA) for the scattering spectrum is derived upon replacing the true matrix elements in (66) by their limiting values reached in the fast collision regime. This approximation will be justified if the momentum recoil of the particle in the perpendicular and lateral directions is small relative to the inverse range $d^{-1}$ of the inelastic atom-surface interaction potential in the normal direction and to the incident lateral momentum, respectively. For flat surfaces, one finds in this case from conservation laws that the only important $z$ components of the matrix elements of force (5) appearing in $V(\mathbf{r})$ are given asymptotically by

$$\lim_{(k_z-k_z')d\rightarrow 0,\,Q\ll K_i} F^{\mathbf{K}_i+\mathbf{Q},\mathbf{K}_i}_{k_z',k_z}=\hbar(k_z+k_z')f(\mathbf{Q}) , \tag{72}$$

where $f(\mathbf{Q}\rightarrow 0)=1$. Substitution of such expression into (66) and this into (67) and (68) would yield the impulse approximation expression for the scattering spectrum.

The EBA spectrum (68) reduces to a particularly simple Gaussian or classical form in the extreme multiphonon limit in which the quantity $|\mathcal{V}^{\mathbf{K}_i,\mathbf{Q}}_{k_z',k_z,j}(\pm)|^2$ can be considered invariant with respect to the change $(\mathbf{Q}\rightarrow-\mathbf{Q},\hbar\omega_{\mathbf{Q},j}\rightarrow-\hbar\omega_{\mathbf{Q},j})$ and $2W^{\mathrm{EBA}}\gg 1$. In this case,

$$N^{\mathrm{EBA}}_{\mathbf{k}_i,T_s}(\epsilon,\Delta\mathbf{K})=\frac{\exp\left[-\frac{(\epsilon-\overline{\Delta\epsilon})^2}{2\sigma_0^2(T_s)}-\frac{(\hbar\Delta K_x)^2}{2\sigma_x^2(T_s)}-\frac{(\hbar\Delta K_y)^2}{2\sigma_y^2(T_s)}\right]}{(2\pi)^{3/2}\sigma_0(T_s)\sigma_x(T_s)\sigma_y(T_s)} , \tag{73}$$

where the mean energy transfer is defined as

$$\overline{\Delta\epsilon}=\hbar\sum_{\mathbf{Q},j,k_z}|\mathcal{V}^{\mathbf{K}_i,\mathbf{Q}}_{k_z,k_{zi},j}(+)|^2\omega_{\mathbf{Q},j} , \tag{74}$$

and the mean square deviation as

$$\sigma_l^2(T_s)=\hbar^2\sum_{\mathbf{Q},j,k_z}|\mathcal{V}^{\mathbf{K}_i,\mathbf{Q}}_{k_z,k_{zi},j}(+)|^2[2\bar{n}_{\mathrm{ph}}(\omega_{\mathbf{Q},j})+1]\lambda_l^2, \quad l=0,x,y , \tag{75}$$

where $\lambda_0=\omega_{\mathbf{Q},j}$, $\lambda_x=-Q_x$, and $\lambda_y=-Q_y$, in accord with (47). Hence in the high-temperature limit, in which $[2\bar{n}_{\mathrm{ph}}(\omega_{\mathbf{Q},j})+1]\propto T_s$, the angular-resolved EBA spectrum bears a normalization prefactor proportional to $T_s^{-3/2}$.

## IV. VALIDITY OF THE EBA AND QUASICLASSICAL APPROXIMATIONS IN HAS

The basic approximation leading to the EBA expression for scattering spectrum (68) has meant the neglect of the off-diagonal components of the operator $G_2$ and all higher operators $G_n$ relative to the diagonal components of $G_2$ and the complete $G_1$ in all manipulations with the exponential form of the evolution operator (39). A mere inspection of Eqs. (40) and (41) shows that, in the case of atom-phonon coupling (61), the quantity

$$P_1^{f,i}=|\langle f|G_1|i\rangle|^2, \quad f\neq i \tag{76}$$

gives the probability of one-phonon emission in the state-to-state transition $|i\rangle\rightarrow|f\rangle$. This probability is, by the definition of $G_1$, uncorrelated. On the other hand, the quantity

$$P_2^{f',i}=|\langle f'|G_2|i\rangle|^2, \quad f'\neq i \tag{77}$$

gives the probability of a correlated two-phonon emission event in the state-to-state transition $|i\rangle\rightarrow|f'\rangle$. The latter is correlated because $G_2$ involves a commutator of the interaction potentials in which neither the phonon nor the particle operators commute at different instants. A manifestation of this correlation is the particle propagation in the intermediate states between two successive phonon emission events.

Thus, for an angular integrated EBA spectrum, we can introduce a measure of the probability of uncorrelated one-phonon emissions by

$$P_1=\sum_{f\neq i}P_1^{f,i}=\langle i|G_1^\dagger G_1|i\rangle-|\langle i|G_1|i\rangle|^2 , \tag{78}$$

where we have made use of the completeness of the set of the scattering states $\{|j\rangle\}$ of the system. Analogously, the same measure of the probability of the correlated two-phonon excitation events would be given by

$$P_2=\sum_{f'\neq i}P_2^{f',i}=\langle i|G_2^{\dagger}G_2|i\rangle-|\langle i|G_2|i\rangle^2| \ . \tag{79}$$

The significance of $P_2$ is that in the absence of any correlated motion of the particle between two successive phonon emission events (as, e.g., in the TA) one has $P_2=0$. Thus $P_1$ and $P_2$ have the appearance of the mean-square deviation or the autodistribution function of the operators $G_1$ and $G_2$, respectively, where the mean is defined with respect to the initial state $|i\rangle$. Then, if

$$\frac{P_2}{P_1}\ll 1 \ , \tag{80}$$

the angular-integrated EBA spectrum is expected to provide a fairly accurate description of the scattering event. A similar criterion has been introduced in Ref. 9.

For an angular-resolved EBA spectrum, one can establish a completely analogous condition

$$\frac{P_2(\mathbf{k}_f,\mathbf{k}_i)}{P_1(\mathbf{k}_f,\mathbf{k}_i)}\ll 1 \ , \tag{81}$$

in which the summation in each $P(\mathbf{k}_f,\mathbf{k}_i)$ has been carried out over all final momenta of excited phonons which comply with the total energy and momentum conservation.

Obviously, the magnitudes of $P_1$ and $P_2$, as well as of $P_1(\mathbf{k}_f,\mathbf{k}_i)$ and $P_2(\mathbf{k}_f,\mathbf{k}_i)$, depend on very many factors, e.g., impact parameters of the collision, including the mass of the scattered particle, phonon densities of states, distorting and inelastic potentials $U^0(\mathbf{r})$ and $V(\mathbf{r})$, respectively, etc. Thus conditions for the validity of the EBA [(80) and (81)] should be investigated for each particular collision system and for a whole range of impact parameters of interest. Once the EBA is established to provide a satisfactorily accurate description of the scattering spectra (23) and (29) in the sense of Eqs. (80) and (81), respectively, the validity of other quantal and semiclassical approximations deriving from the EBA can then be estimated by comparing the results they predict with the exact ones obtained in the EBA. This procedure will be followed in Secs. IV A and IV B.

In the case of He-atom scattering from surface phonons, the values of the particle incident energies $\epsilon_i$ lie in the interval (10 meV $<\epsilon_i<100$ meV), as this spans the range of nozzle beam energies commonly utilized in HAS experiments. In order to make a semiquantitative estimate of $P_1$ and $P_2$ in the multiphonon regime for which, say, $\epsilon_i\geq 30$ meV, it would suffice to approximate the He-atom-surface interaction $U^0(z)$ by an electronic overlap-induced exponential repulsion $U^0_{\rm rep}(z)=U^0_{\rm rep}e^{-z/d}$, as this should make the dominant contribution to the total interaction energy if $\epsilon_i\gg D_0$, where $D_0\sim 5$–$7$ meV is a typical value of the surface potential well depth.[39] In this case the particle wave functions (7) and the interaction matrix elements (66) are known in analytic form.[40] The last problem of the surface-projected phonon densities of states cannot be circumvented so easily, because they are extremely substrate specific. However, a general estimate of the validity of the EBA and related approximations can be obtained on noticing that in many systems which have been investigated by HAS the various surface phonon and adsorbate vibrational modes can be roughly characterized as giving rise to either Debye- or Einstein-like phonon densities of states. Such surface phonons giving rise to a nearly Debye-like phonon density of states are the high intensity longitudinal resonance modes on surfaces of $d$-band metals,[17] of which Cu(001),[26,27] Ag(001),[41] and Pt(111) (Ref. 2) are typical examples. On the other hand, almost dispersionless Einstein-like phonon modes of various origins ($\hbar\omega_0\sim 4$–$6$ meV) have been detected in adlayers of rare-gas atoms on Ag(111) (Ref. 42) and graphite,[43] alkali atoms on graphite,[44] and CO on Pt(111),[45] Ni(001),[46] Fe(110),[47] Cu(001),[48] and Rb(111).[5] Thus, by demonstrating that the EBA is valid for the phonon densities of states corresponding to these two limiting cases which are canonical or textbook examples of the phonon spectra, one may envisage that it should also be valid in other cases interpolating between these two extremes. Hence, to demonstrate the general applicability of our formalism developed in Secs. II and III and to illustrate the method on the systems for which multiphonon features have been unambiguously detected, we shall investigate the validity of the EBA and related approximations in describing He scattering from Einstein-like frustrated translation mode of CO molecules adsorbed on Rh(111) (Ref. 5) and from the Debye-like longitudinal resonance mode and Rayleigh wave typical of the Cu(001) surface.[6,26,27] An additional estimate of the validity of the EBA in HAS from metal surfaces for which computed phonon densities of states are available will be postponed for future publications.

### A. Validity of EBA and quasiclassical approximations in HAS from Einstein-like phonons

CO molecules adsorbed on Rh(111) surfaces exhibit two ordered phases at submonolayer coverage. The first one is a CO $(\sqrt{3}\times\sqrt{3})R30°$ structure corresponding to $\Theta_{\rm CO}=\frac{1}{3}$, in which the CO molecules occupy only on-top sites.[49] The other one corresponds to $\Theta_{\rm CO}=\frac{3}{4}$, in which CO molecules occupy both on-top and bridge sites to form a CO(2×2)-ordered structure.[50]. In both phases the CO molecules may exhibit frustrated (hindered) translations in directions parallel to the surface for which the corresponding restoring force is relatively very weak, giving rise to vibrational frequencies (energies) of the order 5–6 meV. In particular, for the structure at $\Theta_{\rm CO}=\frac{1}{3}$ the next-nearest-neighbor interactions between the CO molecules are extremely weak and the frequency of the hindered translation mode shows no observable dispersion, making this phonon almost truly Einstein-like with $\hbar\omega_0=5.75$ meV.[5] Due to their low excitation energy these modes are already thermally activated at low substrate temperatures.

The angular-resolved HAS experiments carried out on the CO$(\sqrt{3}\times\sqrt{3})R30°$/Rh(111) adsorption system, for incident He energies $\epsilon_i$ around and above 50 meV, produce the TOF spectra which, when converted to energy loss, exhibit pronounced multiphonon peaks in both loss and gain regions. Thus, for instance, for substrate tem-

perature $T_s=128$ K, $\epsilon_i=57.16$ meV, incident angle $\theta_i=50°$, and scattering angle $\Theta_f=40.5°$, and up to seven loss peaks and two gain peaks are visible in the angular resolved scattering spectrum (cf. Fig. 2). This signifies that a true multiphonon-scattering regime has already been reached at these moderately high incident energies. Higher-order phonon excitations have also been detected for the CO(2×2)/Rh(111) structure at $\Theta_{CO}=\frac{3}{4}$, albeit with a smaller number of clearly detectable peaks and with an additional superposition of the substrate phonons.[5] All this is surprising at first sight, and calls for a careful examination and interpretation of the experimental data.

In order to interpret the high multiphonon intensity in the HAS spectra of the CO/Rh(111) system, and in particular the higher intensities for the ordered phase at lower CO coverage, we make the following observation. At $\Theta_{CO}=\frac{1}{3}$ the He beam atom wave functions $\chi(k_z,z)$ describing motion perpendicular to the surface will be reflected dominantly at turning points corresponding to the He-Rh(111) static surface potential. Hence the CO molecules which stick out as bumps from the surface will in this case strongly overlap with such wave functions, i.e., will be embedded in $\chi(k_z,z)$. On the other hand, by increasing the CO coverage the turning points of $\chi(k_z,z)$ will be squeezed out into the region of the outer part of the electronic density of adsorbed CO molecules, giving rise to a smaller overlap between the whole body of the CO molecule and such shifted wave functions through which the interaction matrix elements $V_{k_z',k_z,j}^{\mathbf{K}',\mathbf{K},\mathbf{Q}}$ in (61) are calculated. This effect should be most pronounced for the superstructure closest to the saturation coverage, which in the present case corresponds to $\Theta_{CO}=\frac{3}{4}$. For this reason the magnitude of such matrix elements can be expected to be weaker for the case $\Theta_{CO}=\frac{3}{4}$ than for $\Theta_{CO}=\frac{1}{3}$. A similar effect, usually termed the Armand effect,[7,51,52] is known to give rise to a reduction of the Debye-Waller exponent in atom-surface scattering because of the simultaneous collision of the projectile atom with several target atoms.

Thus, in the description of the strength of the coupling of He atoms to the dissipative component of the surface potential for the case of the CO($\sqrt{3}\times\sqrt{3}$)$R30°$/Rh(111) system, we shall assume that $\chi(k_z',z)$ and $\chi(k_z,z)$ appearing in the interaction matrix elements of the perturbation $V$ on the right-hand side of (61) are those corresponding to the laterally averaged He-Rh(111) static surface potential $U^0(z)$. To model the embedding effect we shall first take the inelastic potential $V(\mathbf{r})$ between the He atom and the CO molecule as centered on the molecule, i.e., shifted by some effective coverage-dependent distance $z_{\text{eff}}$ away from the surface defined by $z=0$ in $U^0(z)$, and then laterally average it. As a function of $\Theta_{CO}$ the embedding depth $z_{\text{eff}}$ should vary between the maximum value attained in the low-coverage limit (which should be of the order of the size of the CO molecule[53] but less than the height of CO islands detected on flat surfaces of some metals[54]), and the minimum value in the opposite limit of saturation coverage when the turning points of He atoms are shifted toward the oxygen end of the densely packed CO overlayer. However, $z_{\text{eff}}$ may also depend on $\epsilon_i$ and the angle of incidence $\theta_i$.

In the present discussion of multiphonon features in the HAS spectra of the CO/Rh adsorption system, we shall disregard the effects of diffuse elastic scattering of He atoms from adsorbates, first because they are not going to affect significantly the multiphonon processes which are the primary object of our investigations, and, second, because a proper account of diffuse scattering would require the introduction of an additional static perturbation into the total Hamiltonian (61).[55,56] A simultaneous perturbational treatment of both elastic and inelastic perturbing potentials proves almost formidable unless certain simplifying but usually heuristic approximations regarding the structure of the $T$ matrix are invoked.[57] However, as such a more complicated two-potential approach would go beyond the purpose of our analyses of inelastic multiphonon scattering events, we shall not pursue it in our estimates of the validity of the EBA. Neither shall we resort to the description based from the very outset on the trajectory or similar approximations, since their validity is going to be investigated in connection with the EBA. Hence we shall adopt an approach which includes the following.

(i) The scattering matrix elements $V_{k_z',k_z,j}^{\mathbf{K}',\mathbf{K},\mathbf{Q}}$ are calculated from the inelastic component of the potential $V(\mathbf{r})$ first obtained from the pairwise summation of the He-CO pair potentials and then averaged over the unit cell of the CO($\sqrt{3}\times\sqrt{3}$)$R30°$ superstructure. As a result of this the obtained matrix elements are periodic functions of the momentum transfer within the first Brillouin zone of the superstructure. Hence the phonon momenta are now restricted to the first Brillouin zone and the total lateral momentum conservation is satisfied up to values of the reciprocal-lattice vectors corresponding to the mesh of the superstructure, viz. $\mathbf{K}_i-\mathbf{K}_f=\mathbf{Q}+\mathbf{G}$.[15]

(ii) The elastic component of $V(\mathbf{r})$ giving rise to diffuse scattering at low coverage is altogether neglected. At higher coverages, however, it is precisely this elastic component of the potential which after averaging causes shifting of the He-atom wave functions outwards. Hence in such a situation the neglect of its overall effect on $\chi(k_z,z)$ would not be justified.

The situation encompassing (i) and (ii) can then be modeled by the Hamiltonian of Eq. (61), with the interaction matrix elements given by Eq. (82) below.

The form and parameters of the He-CO pair potential will be taken from Ref. 56. On the other hand, since the exact form of the He-Rh(111) potential is presently not available, we shall replace it by a plausibly similar He-Cu(111) potential calculated earlier[39] for which the best fit for the range $d$ of the laterally averaged repulsive component $U_{\text{rep}}^0(z)=U_{\text{rep}}^0 e^{-z/d}$ around the turning point $z_0$ for $\epsilon_i=50$ meV gives $d=0.8a_B$. The standard evaluation of $V_{k_z,k_z',j}^{\mathbf{K},\mathbf{K}',\mathbf{Q}}$ corresponding to the laterally averaged inelastic He-surface interaction then proceeds by taking the matrix elements of the gradient of the static He-adsorbate interaction suitably averaged over the unit cell of the CO

superstructure, following the procedure outlined in Ref. 58. For the matrix elements of the force the CO overlayer exerts on the He atoms, this yields

$$\mathbf{F}_{\mathbf{Q}}(k_z',k_z)=\frac{2\pi}{Q_c^2 A_c} \times e^{-Q^2/2Q_c^2}\langle \chi_{k_z'}|\left[i\mathbf{Q},\frac{\partial}{\partial z}\right]V^0_{\mathrm{rep}}(z)|\chi_{k_z}\rangle \ . \tag{82}$$

Here $Q_c$ is the Armand cutoff wave vector obtained after averaging the pairwise He-CO interaction over the surface, $A_c$ is the area of the surface unit cell of the CO superstructure, and $V^0_{\mathrm{rep}}(z)=V^0\exp(-z/\delta)$ is the repulsive $z$ component of the laterally averaged static He-adsorbate potential of strength $V^0$ and range $\delta$. This gives

$$V^{\mathbf{K},\mathbf{K}',\mathbf{Q}}_{k_z,k_z',j}=\mathbf{u}_{\mathbf{Q},j}\sum_{G}\mathbf{F}_{\mathbf{K}-\mathbf{K}'}(k_{z'},k_z)\delta_{\mathbf{K}-\mathbf{K}',\mathbf{Q}+\mathbf{G}} \ , \tag{83}$$

where the vector $\mathbf{u}_{\mathbf{Q},j}$ is a two-dimensional Fourier transform of the quantized displacement $\mathbf{u}_{l,m}$ of the vibrating adsorbate from its equilibrium position at $\mathbf{R}_l+\mathbf{R}_m$ at the surface.[15,17] Explicitly, $\mathbf{u}_{l,m}$ is expanded in terms of $\mathbf{u}_{\mathbf{Q},j}$ as

$$\mathbf{u}_{l,m}=\sum_{\mathbf{Q},j}\exp(i\mathbf{Q}\mathbf{R}_l)\mathbf{u}_{\mathbf{Q},j} =\sum_{\mathbf{Q},j}\exp(i\mathbf{Q}\mathbf{R}_l)\left[\frac{\hbar}{2M_{\mathrm{CO}}N_s\omega_{\mathbf{Q},j}}\right]^{1/2} \times\mathbf{e}_m(\mathbf{Q},j)(a_{\mathbf{Q},j}+a^{\dagger}_{-\mathbf{Q},j}) \ , \tag{84}$$

where $\mathbf{e}_m(\mathbf{Q},j)$ is the polarization vector of the mode $(\mathbf{Q},j)$, and $N_s$ is the number of surface cells in the surface area of the quantization box.

Now we are in a position to make explicit use of our assumption of the wave-function shifting in the quantitative estimate of the expression on the right-hand side of (82). That is, on noticing that the strengths $U^0_{\mathrm{rep}}$ and $V^0_{\mathrm{rep}}$ and ranges in the $z$ direction $d$ and $\delta$ of $U^0(z)$ and $V(\mathbf{r})$, respectively, are very similar for the present scattering system, we may obtain a good representation of (82) by replacing $V^0_{\mathrm{rep}}(z)$ by the $z_{\mathrm{eff}}$-shifted $U^0_{\mathrm{rep}}(z)$. This yields

$$\mathbf{F}_{Q}(k_z',k_z)\simeq\frac{2\pi}{Q_c^2 A_c} \times e^{z_{\mathrm{eff}}/d}e^{-Q^2/2Q_c^2}\langle \chi_{k_z'}|\left[i\mathbf{Q},\frac{\partial}{\partial z}\right]U^0_{\mathrm{rep}}(z)|\chi_{k_z}\rangle \ , \tag{85}$$

which can be expressed in analytic form as the remaining matrix element on the right-hand side of (85) is obtained as a three-dimensional analog of the one-dimensional Jackson-Mott formula[40] given explicitly in Refs. 9–11.

The exact value of $z_{\mathrm{eff}}$ is not known *a priori*, and should be determined independently. However, by increasing $\Theta_{\mathrm{CO}}$ the value of $z_{\mathrm{eff}}$ should diminish and eventually reach zero in the limit of a most closely packed CO monolayer, i.e., in the case in which $Q_c$ and $A_c$ reach their maximum and minimum values, respectively. Hence the factor $\exp(z_{\mathrm{eff}}/d)$ in (85) indeed plays a role of an Armand-like factor in the perpendicular direction, in contrast to the ordinary one $\exp(-Q^2/2Q_c^2)$ which introduces a cutoff in the lateral momentum exchange.

To proceed in estimating the validity of the EBA for the present scattering system [i.e., to find the appropriate ratio $P_2(\mathbf{k}_f,\mathbf{k}_i)/P_1(\mathbf{k}_f,\mathbf{k}_i)$ as a function of impact parameters], we need to select particular values of $Q_c$ and $z_{\mathrm{eff}}$. The former will be calculated following Ref. 58, and for the latter we shall first take a plausible value which will be then justified *a posteriori* as the optimum one in the calculation of the angular-resolved EBA scattering spectrum which compares best with experiments. Thus we tentatively set $z_{\mathrm{eff}}=2.29a_B$, which is the distance between the centers of the electronic charge accumulated in the outermost $\pi_{x,y}$ backbonding orbitals around the C and O atoms in the $COCu_5$ cluster which simulates chemical aspects of CO adsorption on Cu (cf. Fig. 3 of Ref. 59). This distance is very close to the intramolecular C-O separation $d_{\mathrm{C\text{-}O}}=2.17a_B$. We determine $Q_c=0.45a_B^{-1}$ by using the prescription of Ref. 58, take the lattice constant of Rh from tables ($a=7.18a_B$) and identify the lattice constant of the CO superstructure as roughly given by $a/\sqrt{2}$. By making use of the matrix elements (85) and the impact parameters corresponding to Fig. 2, we find the energy dependence of angular-resolved one-phonon uncorrelated emission probabilities and two-phonon correlated emission probabilities shown in Fig. 3.

It is seen in Fig. 3 that condition (81) for the validity of the EBA is satisfied in the entire interval of experimental energies of interest for given angles of incidence and scattering. Although $P_2(\mathbf{k}_f,\mathbf{k}_i)$ and $P_1(\mathbf{k}_f,\mathbf{k}_i)$ may depend significantly on the angles of incidence and scattering, the main trend regarding the magnitude of their ratio persists for all other angles we have investigated. This enables us to approximate with a high degree of accuracy

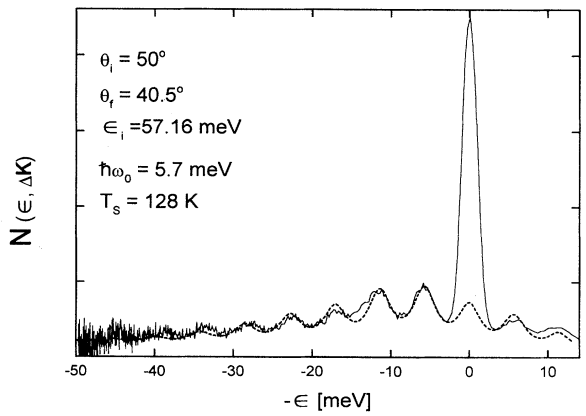


FIG. 2. Angular-resolved scattering spectrum corresponding to the He→CO($\sqrt{3}\times\sqrt{3}$)$R$30°/Rh(111) collision system. The experimental spectrum (Ref. 5) is given by the full line. The dashed line denotes the theoretical spectrum calculated in the exponentiated Born approximation (EBA) and expressed as a function of He-atom energy loss $\epsilon=-\varepsilon$.

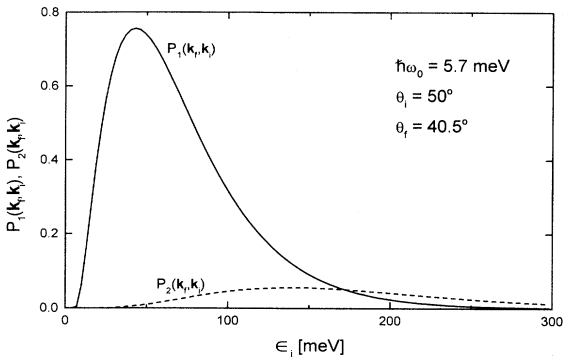


FIG. 3. Angular-resolved probabilities of uncorrelated one-phonon and correlated two-phonon emission events, $P_1(\mathbf{k}_f,\mathbf{k}_i)$ (full line) and $P_2(\mathbf{k}_f,\mathbf{k}_i)$ (dashed line), respectively, for the system He→CO($\sqrt{3}\times\sqrt{3}$)$R$30°/Rh(111) plotted as functions of the He-atom incident energy. $P_1(\mathbf{k}_f,\mathbf{k}_i)$ and $P_2(\mathbf{k}_f,\mathbf{k}_i)$ are defined through Eqs. (76), (77), and (81).

the full, exact DWF by its EBA counterpart given by Eq. (70), and the full spectrum by the EBA expressions (68) and (69). In doing so we also observe that with the present input parameters the imaginary part of driving function (69), which is a fastly oscillating odd function, makes an insignificant contribution to the final spectrum and, hence, can be neglected.

Having now all the prerequisites for the description of the HAS from the CO/Rh(111) adsorption system studied, we may calculate the angular-resolved scattering spectrum in the EBA by using the tentative value of $z_{\text{eff}}$ quoted earlier and then check if the experimental intensity ratios of, for instance, the first and second loss peaks are correctly reproduced. Note that here we are using a true multiphonon spectral feature to quantify the extent of shifting or squeezing out of the particle wave function, and that this information could not be extracted by considering only the characteristics of the first-order peaks which all scale linearly with this effect. Now it turns out that by taking $z_{\text{eff}}$ and other parameters as quoted above we can perfectly reproduce the required experimental peak intensity ratios from the spectrum depicted in Fig. 2. Moreover, an excellent overall agreement between the shapes of the calculated EBA spectrum and the experimental one is achieved (see Fig. 2) after a correction is made for the finite width of the loss and gain peaks which may arise due to various effects, including the instrumental[5] and phonon lifetime[60] broadening. This also provides an *a posteriori* justification of the consistency of our assumptions regarding the wave-function-shifting effect in the estimate of the validity of the EBA.

The mean energy loss of the atom or average energy transfer $\overline{\Delta\epsilon}(\epsilon_i,\theta_i,\theta_f)$ to the phonon heat bath in the course of a particular scattering event defined by the collision parameters $\epsilon_i$, $\theta_i$, and $\theta_f$ is obtained by computing the first moment of the corresponding angular-resolved scattering spectrum. In the case of the spectrum shown in Fig. 2, we find $\overline{\Delta\epsilon}(\epsilon_i,\theta_i,\theta_f)=14.4$ meV.

Neglecting phonon and experimental broadening of the loss and gain lines, one may obtain the angular-integrated spectrum for the present system in a closed form by integrating (69) over all the exchanged momenta $\Delta\mathbf{K}$. For finite substrate temperature $T_s$ a relatively simple result is obtained only in the limit of negligible effect of particle recoil on the interaction matrix elements, i.e., in the recoilless approximation (RA) in which

$$\sum_{\mathbf{Q},j,k_z}|\mathcal{V}^{\mathbf{K}_i,\mathbf{Q}}_{k_z,k_{zi},j}(-)|^2\approx\sum_{\mathbf{Q},j,k_z}|\mathcal{V}^{\mathbf{K}_i,\mathbf{Q}}_{k_z,k_{zi},j}(+)|^2=2W_0^{\text{RA}}\ .$$

Following standard procedures,[61] this yields[11]

$$N^{\text{RA}}_{\mathbf{k}_i,T_s}(\varepsilon)=e^{-2W_0^{\text{RA}}[2\bar{n}_{\text{ph}}(\hbar\omega_0)+1]}\sum_{l=-\infty}^{\infty}I_l(4W_0^{\text{RA}}\sqrt{\bar{n}_{\text{ph}}(\hbar\omega_0)[\bar{n}_{\text{ph}}(\hbar\omega_0)+1]})e^{l(\hbar\omega_0/2k_BT)}\delta(\varepsilon-l\hbar\omega_0)\ , \tag{86}$$

where $k_B$ is the Boltzmann constant and $I_l(z)$ is the Bessel function of the imaginary argument. This spectrum is correctly normalized, i.e., integrates to unity, which once again demonstrates the consistency of the formalism based on Eqs. (58) and (60) and the approximations introduced in obtaining tractable solutions for the scattering spectrum. It should be noted that such consistency and unitarity requirements would be much more complicated to satisfy by resorting to a more standard $T$-matrix approach in the description of the present multiphonon-scattering regime.

Now, since the criteria for the validity of the EBA for the present collision system are satisfied, we are in a position to estimate the validity of other approximations by comparing the results they predict with the exact ones obtained in the EBA. Here we shall make such comparisons for the trajectory (TA) and impulse or fast collision (IA) approximations as they both naturally arise as the limiting cases of the EBA (cf. Sec. III B). The physical quantity which we find most relevant for comparison is the Debye-Waller exponent or, according to Eq. (70), the total one-phonon inelastic reflection coefficient calculated in the respective approximations. Figure 4 shows the dependence of such normalized Debye-Waller exponents $2W_0/\epsilon_i$ as a function of the He-atom incident energy $\epsilon_i$ for incident angle fixed by the experiment[5] and zero substrate temperature. The normalization, i.e., the division by the incident energy, has been introduced for pictorial convenience to illustrate the transition from quasiadiabatic to nonadiabatic behavior of the Debye-Waller exponent around $\epsilon_i=20$ meV.[37] The temperature factor $\bar{n}_{\text{ph}}(\hbar\omega_{\mathbf{Q},j})\gg1$ is irrelevant here because for a single Einstein frequency $\hbar\omega_0\ll kT_s$ it factorizes as an overall multiplicative factor. As is clear from Fig. 4, in the scattering regime defined by the parameters given, both the TA and IA can overestimate the magnitude of the exact EBA values of $2W_0$ by a significant amount, reducing in some cases the weight of the elastic line by almost an order of

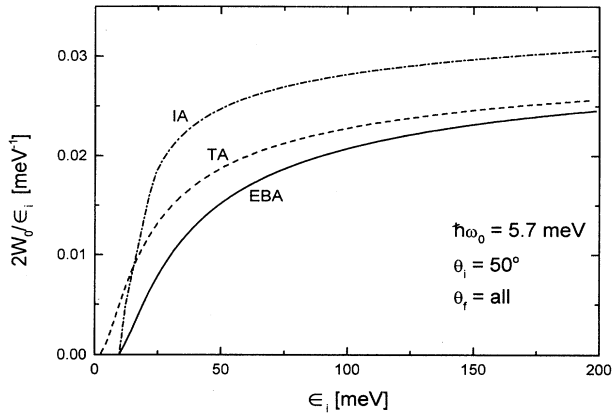


FIG. 4. Debye-Waller exponent or the total inelastic reflection coefficient for the system He→CO($\sqrt{3}\times\sqrt{3}$)$R$30°/Rh(111) calculated in the exponentiated Born approximation (EBA), trajectory approximation (TA), and impulse scattering (IA) approximations, denoted by full, dashed, and dashed-dotted lines, respectively. The plots show its behavior as a function of and as scaled (divided) by the He-atom incoming energy $\epsilon_i$ for a fixed incoming angle $\theta_i = 50°$.

magnitude. In all this the TA turns out to be a much better approximation than the IA, except for very low incoming energies below the excitation threshold where the former is bound to fail anyhow. This is an important finding, as quite often the IA has been considered superior to the TA, in particular for higher incoming energies of the scattered atom.

In summary of this subsection, we may state that the EBA can be used with confidence in model calculations of the multiphonon features appearing in the angular-resolved scattering spectrum and the differential reflection coefficient pertaining to the HAS from the CO($\sqrt{3}\times\sqrt{3}$)$R$30°/Rh(111) adsorption system. Moreover, the EBA provides a far more general and thereby superior description of the scattering event in the multiphonon regime, and is not more complicated to implement than any of the other two popular and frequently employed approximations, viz. the TA and IA, which appear just as its special limiting cases.

### B. Validity of the EBA and quasiclassical approximations in HAS from Debye-like phonons

Investigations of the dynamics of the Cu(001) surface by HAS have provided detailed information about the characteristics of the various phonon modes which the He atoms can interact with in the course of the collision.[6,26,27] Careful analyses of HAS time-of-flight intensities have revealed that at moderately high nozzle beam energies the scattering spectra already exhibit both single-phonon and multiphonon structures.[12] The study of the former indicate the existence of three distinct surface-localized vibrational modes which have been ascribed to the Rayleigh wave (RW), the longitudinal bulk resonance (LR), and a further acoustic bulk resonance at somewhat higher-energy transfers. The LR was found to couple strongly to the scattering He atoms, producing peaks which are more intense than those corresponding to the RW for a wide range of impact parameters. In particular, in the ⟨110⟩ symmetry direction the LR peak in the HAS spectrum was found to be four times more intense than the RW. The phonon density of states (DOS) corresponding to the LR mode can be assumed as almost Debye-like, with the Debye temperature $\Theta_D^{\mathrm{LR}} = 267$ K.[6,62] The estimates for the Debye temperature of the RW for the same surface varied in the interval 230 K $\leq \Theta_D^{\mathrm{RW}} \leq 280$ K (cf. Table 2 in Ref. 6). The third detectable single-phonon peak in the spectrum has been designated as mode 2 and attributed to a maximum in the transverse vertical polarized density of bulk phonon states. Its intensity, however, was found to be much smaller than those of the LR and RW.

Fitting of the HAS TOF spectra for the Cu(001) surface by Gaussians shows that already at 30-meV He beam incident energy the multiphonon component makes a significant contribution to the overall spectral weight.[12] Given the fact that the single-phonon components of the spectra are dominated by modes whose DOS may be considered Debye-like, one can envisage that the major contribution to the multiphonon features will also come from the same type of modes. Thus in our estimates of the validity of the EBA in the case of the He→Cu(001) scattering system, we shall investigate the behavior of the single- and correlated two-phonon emission probabilities for the phonon DOS modeled by the Debye spectrum, and the impact parameters characteristic of the multiphonon regime reached in experiments.[6]

The estimate of the magnitude of $P_1(\mathbf{k}_f,\mathbf{k}_i)$ is carried out for fixed impact parameters and momentum transfer to yield an energy loss typically of the order of the mean energy loss $\Delta\epsilon$ observed in the multiphonon-scattering regime. This is somewhat in contrast with the situation encountered in the case of Einstein-like modes for which the single-phonon energy loss was independent of the impact parameters and the momentum transfer. The same type of arbitrariness appears in the definition and estimate of $P_2(\mathbf{k}_f,\mathbf{k}_i)$, since here the angular-resolved final state may be characterized by the final energy varying in the interval $(\epsilon_i,\epsilon_i-2\Theta_D)$. For the purpose of our estimate we again fix the final energy at the value $\epsilon_f=\epsilon_i-\Delta\epsilon$ and allow the intermediate energies to vary continuously and integrate over all phonon wave vectors which comply with total energy and momentum conservation. The actual calculation of $P_1(\mathbf{k}_f,\mathbf{k}_i)$ and $P_2(\mathbf{k}_f,\mathbf{k}_i)$ is performed by using the interaction Hamiltonian (61) and the interaction matrix elements given by (82) in which $\mathbf{u}_{l,m}$ and $\mathbf{F}_{\mathbf{K}-\mathbf{K}'}(k_z',k_z)$ now correspond to the atoms of the Cu(100) surface. Thus $\mathbf{u}_{l,m}$ will be obtained from Eq. (84) upon replacing $M_{\mathrm{CO}}$ by $M_{\mathrm{Cu}}$ and $\mathbf{F}_{\mathbf{K}-\mathbf{K}'}(k_z',k_z)$ from Eq. (82) with unshifted $U_{\mathrm{rep}}^0(z)$, i.e., the one in which we set $z_{\mathrm{eff}}=0$ and change the range to $d=0.45a_B$, which is obtained from the best fit around the turning point corresponding to $\epsilon_i=82$ meV.[39] The total phonon density of states is taken to be Debye-like, with $\Theta_D=267$ K. We have adopted such a relatively simple approach because the present analysis of the validity of the EBA requires

neither introducing refinements into the expressions for the force matrix elements nor using an exact computed phonon DOS corresponding to the Cu(001) surface,[26,27] since details of the single-phonon features are washed away by very small Debye-Waller factors under extreme multiphonon conditions.

Figure 5 shows the behavior of $P_1(\mathbf{k}_f,\mathbf{k}_i)$ and $P_2(\mathbf{k}_f,\mathbf{k}_i)$ defined by Eqs. (76), (77), and (81), as functions of incident He-atom energy $\epsilon_i$ and impact parameters of the experiment described in Ref. 6. Here we have set $\epsilon_f=\epsilon_{f'}=\epsilon_i-\Delta\epsilon$ with $\Delta\epsilon=12$ meV, which is slightly above the value of the mean energy loss of 9 meV detected under extreme multiphonon scattering conditions at $T_s=800$ K.[6] These results demonstrate that in the energy interval $\epsilon_i<100$ meV and for other parameters and interactions fixed as above, the EBA may be considered as providing an almost exact description of the scattering of He atoms by Debye-like surface phonons. In particular, typical quantities which characterize the scattering spectrum, such as the DWF and the mean energy transfer $\Delta\varepsilon$ to the phonon heat bath, will be given by the corresponding EBA expressions of Eq. (70) above and Eq. (63) of Ref. 10, respectively. Hence their values can then be used as the reference ones in an estimate of the accuracy of other approximations employed in the description of the same scattering event.

Figure 6 shows the magnitude of the normalized DW exponent $2W_{T_s}/\epsilon_i$ as calculated in the EBA, TA, and IA, for substrate temperatures $T_s=0$ and 800 K. The qualitative behavior of all three curves is very similar to those found for the CO/Rh(111) surface discussed in Sec. IV A. On account of the exactness of the EBA in the scattering regime for which $\epsilon_i\leq 100$ meV (cf. Fig. 5), we again find that the TA turns out to be a much better approximation than the IA in the interval 50 meV $\leq\epsilon_i\leq 100$ meV over which the intensity of the multiphonon component in the He→Cu(001) scattering spectrum exhibits a significant increase.[6,62] Another clear message deducible from Fig. 6 is that within the present description the multiphonon conditions reached in the experiment for $T_s=800$ K and $\epsilon_i=82$ meV cannot be explained as being due to the strong projectile-phonon coupling but rather to the effect of high substrate temperature. For $T_s=0$ and $\epsilon_i=82$ meV the mean number of phonons $\bar{n}_{\rm ph}$ excited in the collision (as given by the value of the DW exponent[10]) is still low, namely $\bar{n}_{\rm ph}=0.66$ which would favor the single-phonon scattering regime, whereas for $T_s=800$ K it rises dramatically to $\bar{n}_{\rm ph}=12$.

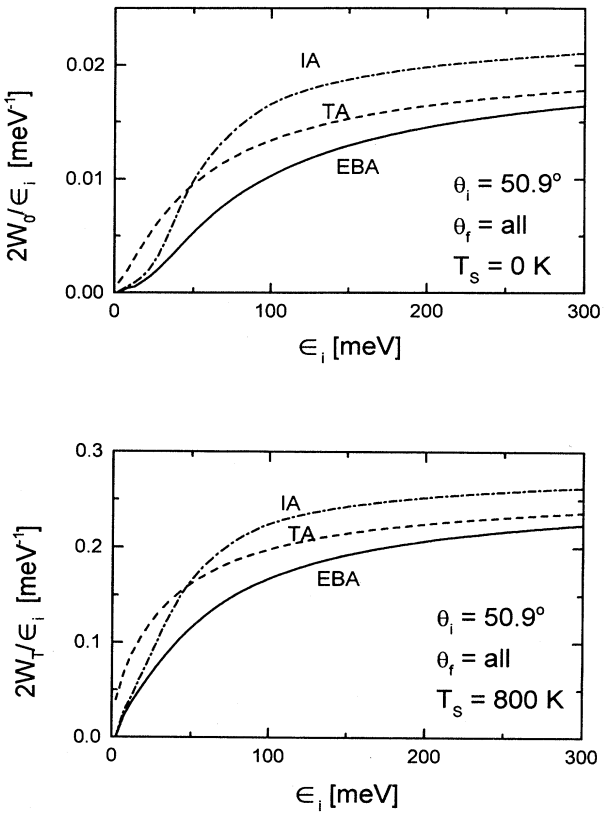


FIG. 6. Upper panel: Debye-Waller exponent or the total inelastic reflection coefficient for the system He→Cu(001) for zero substrate temperature and normalized to the incident He energy $\epsilon_i$. Values calculated in the exponentiated Born approximation (EBA), trajectory approximation (TA), and impulse scattering (IA) approximations are denoted by full, dashed, and dashed-dotted lines, respectively. Lower panel: Same as above but for substrate temperature $T_s=800$ K.

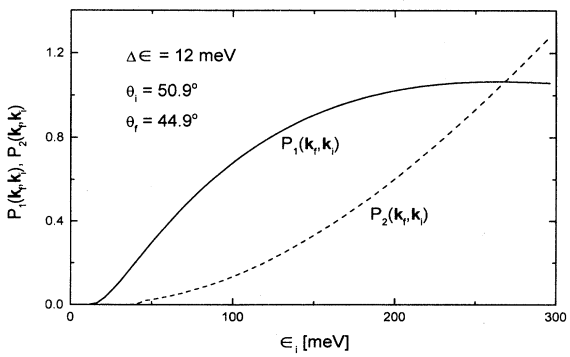


FIG. 5. Plots of the uncorrelated and correlated transition probabilities $P_1(\mathbf{k}_f,\mathbf{k}_i)$ (full line) and $P_2(\mathbf{k}_f,\mathbf{k}_i)$ (dashed line), defined by Eqs. (76), (77), and (81), for the He→Cu(001) system in the case of the total He-atom energy loss $\Delta\epsilon=12$ meV. The kinematic parameters are fixed at $\epsilon_i=82$ meV, $\theta_i=50.9°$, and $\theta_f=44.9°$. For parameters of the interaction potential, see main text.

In Fig. 7 we show a comparison between the experimental scattering spectrum for the system He→Cu(001) (Refs. 6 and 62) and the corresponding angular-resolved EBA spectrum for He-atom scattering by Debye phonons under extreme multiphonon conditions reached in the experiment. The mean energy transfer to the phonon heat bath computed from this EBA spectrum is $\overline{\Delta\epsilon}(\epsilon_i,\theta_i,\theta_f)=9.3$ meV. Given the fact that we have used a very simple model of the phonon DOS and have not introduced any adjustable parameters in our calculations, the agreement between the two spectra is remarkably good and indicates two mutually interdependent

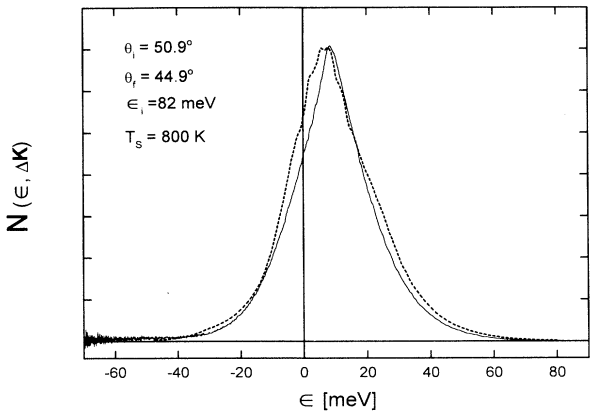


FIG. 7. Comparison of experimental (full line) and theoretical angular-resolved (dashed line) scattering spectra for the collision system He→Cu(001) under extreme multiphonon conditions ($\epsilon_i = 82$ meV, $T_s = 800$ K). The experimental spectrum is taken from Ref. 6, and the theoretical spectrum is calculated in the exponentiated Born approximation (EBA) and expressed as a function of He-atom energy loss $\epsilon = -\varepsilon$. All parameters are the same as in Figs. 5 and 6.

characteristics of the present model of multiphonon HAS from surfaces: (i) If the gross features of the densities of states of the multitude of surface and surface-projected phonon modes characteristic of the Cu(001) surface can be well modeled by a Debye spectrum, then (ii) the EBA provides a fairly accurate description of multiphonon scattering of He atoms from the Cu(001) surface in accessible collision regimes already investigated experimentally. This is not the case with the results of the TA and IA, which may deviate most strongly from the exact ones just in the intermediate-energy regime where the EBA description of multiphonon scattering is valid.

## V. CONCLUSIONS

In this work we have studied the effects of multiphonon processes in inelastic He-atom-surface scattering which have recently emerged as an interesting object of experimental investigation in their own right. The information which can be deduced from the multiphonon-scattering spectra is of notably different character than in the regime of single-phonon excitations which have been studied primarily to extract the phonon-dispersion curves and one-phonon densities of states for comparison with theoretical predictions. These differences arise, first, due to the fact that the total energy and momentum conservation applies in this case to the whole multitude of phonons exchanged between the particle and the surface. Hence the multiphonon-scattering spectra will be characterized by integrated quantities such as the Debye-Waller factor, mean energy transfer, etc. In our derivation of the scattering spectra which is based on a special cumulant expansion for the scattering amplitude, we have shown that a proper account of these quantities guarantees a consistent and unitary treatment of the scattering event. This is otherwise difficult to achieve in low-order perturbative treatments such as the DWBA which proved so useful in establishing the connection between the inelastic reflection coefficients and the one-phonon densities of states. Using the cumulant approach we have demonstrated that a proper unitary treatment of multiphonon scattering yields a *complete* Debye-Waller factor describing the total probability of elastic scattering in the form $e^{-2W}$ in which the Debye-Waller exponent $2W$ encompasses the probabilities of uncorrelated and correlated phonon excitations in all inelastic-scattering channels. We have also shown that in regimes in which the contributions of correlated phonon excitation processes can be neglected relative to those of the uncorrelated ones, the overall multiphonon-scattering spectrum acquires a particularly simple form which has the appearance of the exponentiated Born approximation (EBA), and that the corresponding DWF is expressed as an exponential function of the total inelastic reflection coefficient as obtained in the DWBA [cf. Eq. (70)]. This still fully quantal expression can then be used as a point of departure for deriving several other semiclassical limits of the scattering spectra, including ones obtainable in the trajectory approximation for a description of the scattered particle dynamics. A second important difference with respect to single-phonon-scattering regime also arises from the unitary property of the multiphonon spectra, and removes the arbitrariness related to the absolute strength of the DWBA inelastic reflection coefficients which otherwise violate unitarity unless heuristic corrections are introduced. This further implies that various moments of the scattering spectra can be used to estimate the magnitude of inelastic atom-surface coupling,[63] and this should represent an additional motivation for studying multiphonon scattering.

By exploiting the advantages of the developed formalism we were able to introduce and define general quantitative criteria for the validity of the EBA in HAS. This is based on the estimate of relative weights of the contributions of uncorrelated and correlated phonon emission processes to the scattering amplitudes. We have found that for scattering systems in which phonons can be typified by Einstein- and Debye-like densities of states, such estimates are relatively easy to carry out numerically. This has enabled us to apply these criteria to estimate the validity of the EBA in studies of the collision systems He→CO/Rh(111) and He→Cu(001), whose multiphonon-scattering spectra were found to be dominated by excitation of Einstein- and Debye-like modes, respectively. We have shown on examples of these two representative collision systems that the EBA can be considered almost exact for treating multiphonon excitation dynamics in a wide range of impact energies of interest in HAS. Using this and the available parameters characterizing He-surface interactions, we have computed the EBA spectra for both collision systems and obtained explicitly the characteristic spectral quantities such as the DWF, mean energy transfer, etc. A good agreement between experimental data and theoretical predictions has been found which has also enabled us to estimate and compare the validity of other semiclassical approxima-

tions in the description of the same collision systems under the same scattering conditions. Here we have found that in the multiphonon-scattering regime the TA and IA give results which may deviate substantially from the nearly exact ones obtained in the EBA. Interestingly enough, the TA proved to be a better approximation than the IA in a wide range of impact energies and substrate temperatures defining multiphonon-scattering conditions in HAS. Together with some earlier findings,[64,9] this sheds additional light on the general applicability of various approximations for treating inelastic HAS from surfaces in the regimes in which they have hitherto been used only heuristically. Of course, further refinements of the model, both in introducing a more detailed form of the interaction matrix elements[26,27] and using realistic computed phonon densities of states, could only additionally test our conclusions. However, although rigorously substantiated only for Einstein- and Debye-like surface phonon densities of states, these conclusions should prove of more general significance due to the universality of the criteria employed in analyses of the validity of the EBA in HAS.

## ACKNOWLEDGMENTS

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