Linear versus Nonlinear Coupling Effects in Single- and Multiphonon Atom-Surface Scattering

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We present a comparative assessment of the features of inelastic atom-surface scattering spectra that are produced by different forms of linear and nonlinear phonon coupling to the projectile atom. Starting from a simple theoretical model of atom-surface scattering and employing recently developed exact numerical and approximate analytical methods we calculate and compare the scattering probabilities ensuing from each form of interaction. This enables us to demonstrate that in the regime of thermal energy atom scattering from surfaces the dominant contributions to the zero-, one-, and multiphonon excitation probabilities arise from linear coupling treated to all orders in the interaction.

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Theoretical interpretations of inelastic atom-surface scattering experiments carried out in the past two decades to investigate vibrational properties of the various surfaces[1] have all been based on several assumptions concerning atom-surface interactions that have never been critically examined or discussed. The aim of the present Letter is to remedy this situation in one of its so far neglected aspects, viz., the lack of a detailed assessment of the effects that arise from different forms of atom coupling to quantized surface vibrations or phonons. We perform this task using a simple paradigmatic, yet realistic enough quantum model comprising all the essentials of single- and multiphonon atom-surface scattering.

The first assumption adopted by the majority of the authors in the development of inelastic atom-surface scattering theories reviewed in Refs. [2–8] has been the linear coupling of scattered atoms to vibrational displacements of surface atoms (i.e., linear coupling to the phonon field), and only few authors have resorted to descriptions based on nonlinear coupling [9,10]. The absence of a quantification of the effects originating from the different forms of coupling is rather surprising because they should manifest themselves in all the components of the scattering spectra, viz., in (a) elastic scattering probability given by the so-called Debye-Waller factor, (b) one-phonon scattering probability, and (c) multiphonon scattering probabilities.

The second assumption concerns the treatment of one-phonon excitation probabilities. Here, a rather general consensus prevailed that these should be calculated in the limit of linear atom-phonon coupling and in the Born approximation using distorted waves accounting for reflections of the atom from the surface to all orders in the static atom-surface potential [5,8]. However, as the distorted wave Born approximation (DWBA) yields nonunitary scattering amplitudes it can provide reliable estimates only for the relative magnitudes of single quantum excitation probabilities in the regime in which the multi-quantum excitations are negligible. In order to obtain accurate one-phonon excitation probabilities for comparison with the zero- and multiquantum ones (which are all sensitive to the form of atom-phonon coupling) and with the experimental data, the DWBA results should be unitarized to comply with the optical theorem.

The most striking differences arising from the assumptions of either linear or nonlinear atom-phonon coupling are expected in the calculated multiphonon scattering probabilities. Recent He atom scattering (HAS) experiments have successfully revealed and disentangled the one- and multiquantum features in the atom-surface scattering spectra for phonons with Einstein [11,12] and acoustic [13,14] types of dispersion. Hence, the resolution of the origin of multiquantum features in the measured spectra as being due either to (i) multiple single phonon scattering events describable in terms of linear coupling, or (ii) multiquantum excitations that arise from nonlinear coupling in each order of perturbation expansion, emerges as a task of utmost interpretative importance.

One of the important conditions for a conclusive testing of the roles that linear and nonlinear coupling may play in the various theoretical descriptions of atom scattering from surface phonons is that they all ought to be applicable to a model which realistically describes the essentials of a particular scattering system. Another condition is that a clear disentanglement of the single- and multi-quantum features is possible for comparison of the results of different theories with the available experimental evidence. Experimental systems that enable the easiest identification of and distinction between the various one- and multiphonon excitations in atom-surface collisions are those in which atoms are inelastically scattered by dispersionless or Einstein phonons. In this case the inelastic scattering spectra display a series of well-separated equidistant peaks at the multiples of Einstein phonon energy $\pm h\omega_0$ away from the elastic line. The weight of the $n$th peak measures the probability of excitation of $n$ phonons.
in the course of scattering. A prototype collision system of this kind is provided by HAS from monolayers of Xe atoms adsorbed on Cu(111) and Cu(001) surfaces which support vertically polarized Einstein modes [11]. Other systems with similar properties have also been reported in the literature [10,12]. The model Hamiltonians required for a full quantum mechanical description of these systems have been presented elsewhere [2,11]. However, for the present purpose all the relevant features of collision dynamics are included in the effective one-dimensional Hamiltonian \( H \) that describes the motion of a projectile nonlinearly coupled to a surface oscillator of frequency \( \omega_0 \). Denoting by \( z \) (\( Z \)), \( p \) (\( P \)), and \( m \) (\( M \)) the coordinate, momentum, and mass of the scattered particle (surface oscillator), respectively, we can write

\[
H = \frac{p^2}{2m} + \frac{p^2}{2M} + \frac{M\omega_0^2Z^2}{2} + De^{-a(z-Z)}
\]

\[
= \frac{p^2}{2m} + De^{-az} + \frac{p^2}{2M} + \frac{M\omega_0^2Z^2}{2} + De^{-az}(e^{az} - 1)
\]

\[
= H_0^p(p, z) + H_0^a(p, P, Z) + V(z, Z).
\] (1)

Here, the elastic particle motion in the model static surface potential of the Born-Mayer form, \( U(z) = De^{-az} \), is described by distorted waves [15] that are eigenstates of the particle Hamiltonian \( H_0^p(p, z) = p^2/2m + U(z) \). By introducing a purely repulsive \( U(z) \) we avoid the occurrence of resonant scattering effects associated with the bound states of the surface potential well [16–18] that are unimportant for the present study. The inelastic scattering is governed by the interaction potential,

\[
V(z, Z) = De^{-az}(e^{az} - 1)
\]

\[
= ZaDe^{-az} + \frac{Z^2a^2}{2}De^{-az} + \cdots
\]

\[
= ZV_1(z) + Z^2V_2(z) + \cdots,
\] (2)

that contains powers of oscillator displacements \( Z \) to all orders. The main merit of the thus defined model lies in its amenability to exact numerical [9,19] and approximate analytical treatments [2] in the calculations of single- and multiphonon scattering probabilities. This enables us to consistently investigate as to how the different forms of atom-phonon coupling affect the scattering spectra.

In this Letter the exact numerical treatments of elastic and inelastic atom scattering probabilities are carried out by employing the coupled channels (CC) method [19] to solve the Schrödinger equation of particle motion perturbed by three types of interactions embodied in expression (2): the linear coupling term \( ZV_1(z) \), the sum of linear and quadratic coupling terms \( ZV_1(z) + Z^2V_2(z) \), and the full potential \( V(z, Z) \). Tractable analytical solutions for the same model are obtained for the cases of linear coupling \( ZV_1(z) \) treated to all orders within the distorted wave exponentiated Born approximation (EBA) formalism [2] based on cumulant expansion, and for the full coupling \( V(z, Z) \) treated in the DWBA in regards to the particle motion. With the exception of the latter approximation, all other mentioned treatments yield unitary results in that the sum of all calculated scattering probabilities equals unity. Separate treatment of the sum of linear and quadratic coupling terms is particularly instructive because the quadratic term gives rise to both inelastic and elastic scattering processes, viz., the simultaneous two-phonon excitations and elastic scattering by the static potential \( V_2(z) \) renormalized by emission and reabsorption of a virtual phonon, an effect that is not present in linear coupling theories. These features are diagrammatically illustrated in Fig. 1 in which the virtual phonon excitation is represented by a closed phonon loop. Diagrammatic perturbation expansion in \( V(z, Z) \) shows that nonlinear coupling to all orders gives rise to the appearance of an arbitrary number of closed phonon loops in any single- or multiphonon vertex [20]. This leads to a Holstein type of renormalization [21] of inelastic particle scattering matrix elements by the factor \( \text{exp}[-(au_0)^2/2] \) where \( u_0 \) is the mean square displacement of the oscillator.

The calculations have been carried out for the elastic scattering probability \( P_0 \), the one-phonon scattering probability \( P_1 \), and the two-phonon scattering probability \( P_2 \) for the types of couplings and within the theoretical approaches described above by using the parameters representative of He and Ne atom scattering from adsorbed Xe atoms. Figure 2 compares the behavior of \( P_n (n = 0, 1, 2) \) calculated for linear, linear and quadratic, and full nonlinear couplings as the functions of scattered particle incoming energy \( E_i \), for He atom scattering from Xe atoms adsorbed on a cold Cu surface. The generalization
show the one-phonon scattering probability calculated in the DWBA applied to the full nonlinear coupling interaction \( V(z, Z) \). For very low incoming energies near the one-phonon excitation threshold \( E_i = \hbar \omega_0 = 2.7 \text{ meV} \), i.e., in the one-phonon scattering limit in which linear coupling yields the dominant contribution, the scattering probability calculated in the DWBA with full nonlinear coupling is in good agreement with the other ones. However, with the increase of \( E_i \), the deviations from the exact result soon become large and signify the breakdown of this approximation due to the nonunitary treatment of all the scattering events induced by \( V(z, Z) \).

Very similar trends are observed in the behavior of two-phonon scattering probabilities \( P_2 \) in Fig. 2. Again, the EBA results are in very good agreement with the exact ones and hence this formalism proves to be a very reliable approximate method for treating multi-phonon scattering in the quantum regime. This property allows us to use the analytical form of the EBA scattering probabilities [2] to demonstrate that the maxima of \( P_1(E_i) \) and \( P_2(E_i) \) appear approximately at the values of \( E_i \) for which \( P_1 = P_0 \) and \( P_2 = P_1 \), respectively, and that \( P_2(E_i) \) is largely given by \( P_2(E_i) = n(E_i) \exp[-n(E_i)] \), where \( n(E_i) = -\ln P_0(E_i) \) is the mean number of phonons excited in the scattering event [2].

Qualitatively very similar results are retrieved for Ne atom scattering treated in the same model (see Fig. 3). Likewise in the case of He scattering, all the unitary treatments yield quantitatively similar results which follow the general trends present in Fig. 2. The only strong discrepancy between exact and approximate results appears for the scattering probability calculated in the DWBA with nonlinear coupling that again completely fails to reproduce exact results. The center and lower panels also demonstrate how, due to the larger projectile mass, the maxima of all the unitary one-phonon and two-phonon scattering probabilities shift to lower \( E_i \) than in the case of lighter He atoms. This is readily explained by the scaling properties of \( n(E_i) \) which in the quasielastic limit of the EBA, here valid for \( E_i \lesssim 10 \text{ meV} \), is very accurately reproduced by the expression \( n(E_i) = 8 \alpha \omega_0 m E_i / \hbar^2 \) that is independent of both \( \alpha \) and \( D \). This causes exponentially faster attenuation of the Debye-Waller factor and all phonon excitation probabilities for larger projectile masses and fixed incoming energies.

The most striking feature of the results shown in Figs. 2 and 3 is a complete failure of the DWBA with full nonlinear coupling to describe the two-phonon scattering probabilities. In view of this and the earlier established excellent agreement between the measured and calculated EBA scattering probabilities for several prototype systems [2,11], the most important conclusion that can be drawn from Figs. 2 and 3 is that in inelastic low energy atom-surface scattering the main contribution to the two- and higher order phonon scattering probabilities comes from successive one-phonon scattering events and not
ent forms of linear and nonlinear atom-phonon couplings energy atom scattering from surface phonons [2].

EBA as a powerful tool for reliable interpretation of low dimensional scattering problems involving dispersive particularly important for the treatment of full three-dimensional treatments of nonlinear coupling by other methods that require. Hence, the finding that the EBA results are in immediate resort to the full nonlinear coupling in the model the CC computations of the scattering probabilities.

In the present case of a one-dimensional scattering regime of thermal energy atom scattering the linear coupling interaction treated to all orders gives a dominant contribution to the scattering probabilities.

In summary, we have investigated the effects of different forms of linear and nonlinear atom-phonon couplings on inelastic atom-surface scattering. By comparing the results of several exact numerical and approximate analytical treatments of a simple model of atom scattering from surface vibrations we have demonstrated that in the regime of thermal energy atom scattering the linear coupling interaction treated to all orders gives a dominant contribution to the scattering probabilities.

1. For recent reviews, see Refs. [2,3], and for the earlier ones, Refs. [4–8].