Inelastic gas-surface scattering. I. Formalism

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We present a method for calculating elastic and inelastic scattering probabilities for light particles, such as helium and molecular hydrogen, scattering from surfaces with which they weakly interact. The method is a unitary one-phonon approximation in which the scattering probabilities are calculated from thermally averaged amplitudes which are generated numerically. The thermal averaging procedure is more general than this application and could be applied to other systems with weak inelastic scattering. We also discuss an approximation for the gas-surface interaction potential that can greatly simplify calculations where it is applicable. Finally we present some preliminary results using this method to study rotationally mediated selective adsorption resonances in HD scattering from copper.

I. INTRODUCTION

In all experiments in which helium or molecular hydrogen are scattered from single-crystal surfaces both inelastic scattering and selective adsorption resonances are present and can have an important effect on the elastic scattering. As the resolution of these experiments has improved not only is it possible to extract, from the elastic scattering, kinematical information like diffraction peak positions and selective adsorption energies but it has become possible to extract dynamic information like the diffraction peak intensities and the resonance lineshapes. It also has become possible to investigate inelastic scattering processes leading to an understanding of the full gas-surface interaction. To interpret these experiments and to compare the results with calculated potential energies it is necessary to be able to accurately describe the dynamics of the scattering process. In this paper we present a method for calculating scattering probabilities that can treat both inelastic scattering and selective adsorption resonances in the presence of the other. By studying inelastic molecular hydrogen scattering, in particular the effects of the rotational degrees of freedom on the scattering process, we hope to both describe these scattering experiments and discuss qualitatively how selective adsorption resonances and inelastic scattering affect each other in more general scattering situations.

This method is a unitary one-phonon approximation. Unitarity, i.e., that the sum of all the calculated scattering probabilities is one, is necessary for studying the thermal attenuation of the elastic scattering probability and for studying the coupling of selective adsorption resonances and inelastic scattering. As we showed in a previous paper[1] inelastic scattering is greatly enhanced by selective adsorption resonances, so much so that the distorted wave Born approximation breaks down. This breakdown is caused by the overcounting of scattering events that is inherent in the Born approximation, and is corrected for in

this new approximation by removing the overcounting. In spite of the breakdown of the distorted wave Born approximation at selective adsorption resonances a one-phonon approximation is still the appropriate approach for studying helium and molecular hydrogen scattering because away from resonance the inelastic scattering probability is still weak, so that once a resonant particle scatters inelastically its subsequent scattering probability is low.

In the experiments[2] we wish to describe, the scattering of H_2,[3] HD,[4] and He,[5] the low masses and moments of inertia of these particles cause those particles that diffract or undergo rotational transitions to leave the surface in well separated directions. This angular separation allows the detection of these effects simply by changing the relative angle of the detector with respect to the substrate and source. Furthermore, since the physisorption potentials wells are shallow, the bound states for these particles are well separated in energy and can be observed in these experiments through selective adsorption resonances. Selective adsorption resonances are observed in the intensity of outgoing scattering peaks as a function of the incidence conditions. They are due to virtual diffractive or rotational transitions into bound states and are caused by either the corrugation of the surface or its translational-rotational coupling.

While the inelastic scattering for these systems is weak enough to allow the observation of coherent elastic scattering effects, it is not negligible nor unobservable. The kinematical constraints of the scattering process permit single Rayleigh phonon creation and absorption events to be seen in the time of flight spectra of helium atoms.[5] Rayleigh phonons are normal modes of a semi-infinite surface that are localized to the surface; for a given wave vector parallel to the surface they have an energy that is lower than all the bulk phonon energies. The dispersion relation of the Rayleigh mode with respect to the parallel momentum allows the identification of various time-of-flight peaks as single Rayleigh phonon transi-

tions. In the case of molecular hydrogen scattering the decreased energy resolution and the increased inelastic scattering probability make it more difficult to observe single-phonon peaks experimentally. The stronger van der Waals attraction felt by the hydrogen molecule, compared to the helium atom, causes the molecule to scatter from a steeper part of the repulsive potential,[6] which increases the inelastic scattering. Increased multiphonon scattering masks single-phonon peaks in the time of flight distributions. Another aspect of inelastic scattering of current experimental interest is the degree to which the rotational degrees of freedom of molecular hydrogen affect the rate of sticking in either physisorption[7] or chemisorption[8] states. One-phonon calculations can describe the initial trapping step, when the sticking proceeds through such a step. But to completely describe the sticking process it is necessary to describe the transition of a trapped particle into a stuck particle,[9] and that is beyond the scope of the current method.

The simple scattering behavior of helium and molecular hydrogen allow straightforward calculation of the scattering rates. The small observed number of elastic and internally inelastic channels makes coupled channels calculations practical while the low inelastic scattering probabilities mean one-phonon-change calculations are relevant to the description of the scattering process. For heavier atoms and molecules both the number of elastic channels, which are not well separated experimentally, that have to be included and the increased inelastic scattering make both the observation and the calculation of elastic and inelastic scattering more difficult.

In many ways the present calculation is related to a long line of previous calculations but it has some new features. To describe the translational-rotational coupling we use a coupled channels approach in which the wave function is expanded in the spherical harmonics so that the rotational behavior is calculated using a discrete set of states instead of a continuum. The coupled channels description of scattering from a static substrate has been used to very accurately describe both helium[10] and molecular hydrogen[11] experiments. The main point of such calculations has been to extract the particle-surface potential from the experimental scattering intensities. Since direct inversion of experimental data to generate the potential is impossible, it is necessary to search through possible potentials to find the one for which the calculated scattering probabilities best match those observed experimentally. Alternatively the bound state energies, extracted from selective adsorption resonances, can be used to determine the potential. Provided both that the coupling that leads to the resonances is weak and the resonances are well separated from each other, the bound-state energies can be extracted from the energies of the resonances using the kinematics of the scattering process. If these conditions are not satisfied then either a full coupled channels calculation or its equivalent is required to match the experimental and calculated resonances.

Inelastic gas-surface scattering probabilities have been calculated in many ways ranging from classical[12] to fully quantum mechanical. Between these two extremes, the latter of which is discussed in more detail below, calcula-

tional approaches have included wave packet calculations[13] (both for elastic and inelastic scattering), and various semiclassical calculations[14] in which the motion of the scattering particle is treated classically and the phonons are treated quantum mechanically.

For helium and molecular hydrogen, quantum-mechanical calculations are the most valid approaches due to both the quantum-mechanical nature of the elastic scattering process and the discrete nature of the one-phonon-change scattering process. The simplest quantum mechanical approach is the distorted wave Born approximation,[15] which is a Fermi's golden rule approach. The rate for transitions caused by the creation or absorption of single phonons, is calculated between scattering state eigenfunctions of the flat static surface. The eigenfunctions that are used in these calculations depend only trivially on all of the degrees of freedom except the motion normal to the surface. This golden rule approach can be used to include higher-order phonon processes but unless further approximations are made the resulting calculations are difficult to carry out.[16] As computing power has increased, distorted wave Born approximation calculations have been carried out using eigenfunctions in which several of the degrees of freedom are coupled, for instance, eigenfunctions of corrugated static surfaces[17] and surfaces with translational-rotational coupling.[1] The approach we are using in this paper is related to these extended distorted wave Born approximation calculations in that we treat the rotational diffraction on an equal footing with the elastic scattering.

The distorted wave Born approximation is less appropriate for calculating the elastic scattering probabilities when they are changed by the possibility of scattering inelastically. The simplest calculation of the elastic scattering probability under these conditions is to multiply the scattering probabilities by a Debye-Waller–like factor.[18] Another relatively simple calculation is to add a phenomenological local optical potential[19] to the rigid surface potential when doing a coupled channels calculation. The optical potential simulates the transfer of scattering probability from the elastic scattering to the inelastic scattering by absorbing intensity from the elastic scattering probability. This optical potential approach can be improved by solving for the nonlocal energy-dependent self-energy[20] that correctly describes the elastic scattering probability. A related approach is to include inelastic scattering in a scattering matrix calculation to study its effect on the elastic scattering line shapes.[21]

A unitary calculational scheme, in which all of the scattering intensity is accounted for and sums to unity, involves an extended coupled channels calculation,[22] extended in the sense that possible inelastic transitions are included in the coupled channels calculation. The calculation is done for several initial occupations of the lattice modes and then the scattering probabilities are thermally averaged with respect to these initial occupations to get scattering probabilities to compare with experiment. Since the phonon modes form continua and any number of phonons can be created or destroyed, it is necessary to truncate the set of inelastic processes that are allowed.

The present calculation is related to both the optical po-

tential approach and the extended coupled channels approach and forms a bridge between the two. It differs from the extended coupled channels approach in that the thermal averaging is done before the wave functions are calculated; it also differs in that the solutions are calculated iteratively instead of at one time. The final results of this calculation for the elastic scattering probability are identical to those of a self-energy calculation[20] mentioned above but are calculated using different intermediate quantities. In this calculation we chose to truncate the allowed phonon changes to include only one-phonon-change processes, but include all the phonon modes in the lattice. We also specify how to treat the situation in which particles can trap on the surface, a situation that can cause great difficulty if sufficient care is not taken.

We apply this method to HD scattering for two main reasons, the most important being that experiments have been performed on this system. The other reason is that with present computer power this method is most applicable to HD scattering. Significant savings in computation time result from being able to ignore the corrugation of the surface, as is discussed in Sec. V, and from treating broad as opposed to narrow selective adsorption resonances, because the iterative calculations converge faster. To study selective adsorption resonances and inelastic scattering simultaneously and to take advantage of the time savings mentioned above requires studying HD scattering.

This paper is organized as follows: Sec. II gives the general derivation of the thermal averaging, Sec. III contains a unitary one-phonon-change approximation using the results of the preceding section, Sec. IV discusses the use of stationary state scattering results to calculate the scattering probabilities, Sec. V gives the approximations that are made on the form of the gas-surface interaction potential, Sec. VI presents the result of some preliminary calculations using this method, and Sec. VII contains a summary of the main results of this paper.

II. THERMAL AVERAGING

In this section we show how thermally averaged scattering probabilities can be calculated in terms of amplitudes that are already thermally averaged. This procedure does not violate our concepts of statistical mechanics because the amplitudes for the particle are not thermally averaged with respect to the particle but with respect to the phonons from which the particle is scattering. We are averaging a reduced time evolution operator with respect to the phonon coordinates; the time evolution operator has been reduced by operating it on the initial state of the particle. We call this reduced time evolution operator an *amplitude-operator* throughout this text to remind the reader that it is both an operator on the phonon coordinates and an amplitude for the scattering particle. The thermally averaged amplitudes are the set of the thermal averages of products of this amplitude-operator with all possible combinations of phonon creation and destruction operators. This amplitude-operator can be used to calculate all the properties of the particle scattering from any surface so that all the thermally averaged properties can

be calculated from the thermally averaged amplitudes. These thermally averaged amplitudes obey a hierarchical set of equations of motion which can be solved and used to give the thermally averaged scattering without explicitly thermally averaging.

Our development of the amplitude-operator is based on studying the time evolution of the state of the system. We start at some initial time ($t = 0$) with the scattering particle in some initial state that is localized sufficiently far from the surface so that it is not interacting with it, then the state of the system is given by a product ket of that initial state, $|X(0)\rangle$, and the initial state of the phonons, $|\{n_i\}\rangle$, which is specified by the occupation of all the normal modes of the surface

$$|\Psi(0)\rangle = |X(0)\rangle \, |\{n_i\}\rangle \, . \tag{2.1}$$

The straightforward method of calculating the thermally averaged scattering probabilities is to calculate the scattering probabilities for the initial particle state scattering from each lattice state in an ensemble of surfaces and then averaging the scattering probabilities weighted by the thermal probability of each surface in the ensemble. Instead of this procedure, we show that we can calculate the thermally averaged scattering directly from thermally averaged amplitudes.

The time evolution of the state of the whole system, from which the scattering probabilities can be obtained, is given by operating on the state (2.1) with the exponential of the full Hamiltonian multiplied by the time

$$|\Psi(t)\rangle = e^{-iHt} |\Psi(0)\rangle \, . \tag{2.2}$$

Since the Hamiltonian couples the motion of the scattering particle with that of the phonons, the state is no longer a product state once the particle starts to interact with the surface but can be thought of as a sum of product states. Below we write this sum of states in terms of how the occupations of the phonon modes have changed.

A. Hamiltonian

The Hamiltonian is broken into three terms: the Hamiltonian, H_{lat}, of the lattice in the absence of the scattering particle, the Hamiltonian, H_{part}, of the particle in the absence of coupling to the phonons, and the potential, V_{int}, that couples the motion of the scattering particle with the motion of the phonon coordinates. The particle Hamiltonian includes both the kinetic energy of the particle and the potential that couples the particle with the lattice minus the interaction with the static lattice

$$H = H_{lat} + H_{part} + V_{int} \, . \tag{2.3}$$

The weak inelastic scattering and small changes in phonon occupations allows us to describe the lattice by a harmonic Hamiltonian because the subsequent anharmonic effects are even smaller in a real system. In

$$H_{lat} = \sum_\lambda \omega_\lambda a_\lambda^\dagger a_\lambda \, , \tag{2.4}$$

the phonon modes are labeled by a composite index λ which includes the momentum of the mode parallel to the surface, the polarization, and either the asymptotic

momentum normal to the surface far from the surface for bulk derived modes, or the decay length into the surface for modes that are localized to the surface.

In this section we make several approximations only to simplify the presentation. For example, we use a Hamiltonian for the scattering particle that just consists of the kinetic energy due to its center of mass motion and a potential energy due to the presence of the static lattice that depends on the position of the center of mass

$$H_{\text{part}} = \frac{p^2}{2m} + V(\mathbf{r}) \; . \tag{2.5}$$

The momentum of the center of mass is $\mathbf{p}$ and the position of the center of mass is $\mathbf{r}$. Throughout this paper lower case boldface letters refer to three-dimensional vectors (e.g., $\mathbf{r}$), boldface upper case letters refer to two-dimensional vectors that are perpendicular to the surface normal which we choose to be the z direction (e.g, $\mathbf{R}$), and italic versions of the boldface letters are the norm of the vector (e.g., p).

For simplicity we take only that term in the interaction, V_{int}, between the particle and the phonons that is linear in the phonon coordinates

$$V_{\text{int}} = \frac{1}{\sqrt{N}} \sum_{\lambda} [V_{\lambda}(\mathbf{r})a_{\lambda}^{\dagger} + \text{H.c.}] \; . \tag{2.6}$$

The factor of $N^{-1/2}$ associated with the sum over the modes of the lattice (N is the number of atoms in the surface) comes from writing the displacement of each lattice atom in terms of the normal coordinates of the lattice [see Sec. V, Eqs. (5.4)—(5.6)].

The procedure for thermal averaging that we present does not depend on either the neglect of the internal degrees of freedom of the scattering particle or the exclusion of more than the linear term in the interaction potential. We make these approximations to improve the clarity of the presentation. In particular, later we include the rotational degrees of freedom to study molecular hydrogen scattering.

B. Time evolution

Since we are not interested in the behavior of the lattice except to the extent that it affects the motion of the particle we define a quantity $\hat{\Psi}$ that we refer to as an amplitude-operator. It is an amplitude for the particle and an operator for the phonon coordinates with the time dependence of the lattice factored out

$$\hat{\Psi}(\mathbf{r},t) \equiv e^{iH_{\text{lat}}t} \langle \mathbf{r} \, | \, e^{-iHt} \, | \, \chi(0) \rangle \; . \tag{2.7}$$

In a related gas-surface scattering calculation Celli and Maradudin[20] use this amplitude-operator to calculate elastic scattering probabilities in the presence of inelastic scattering. The amplitude-operator and the time evolution operator of the uncoupled lattice give the time dependence of the molecule scattering from any initial set of phonon coordinates when they operate on that initial state. In particular, using Eqs. (2.1), (2.2), and (2.7), $\langle \mathbf{r} | \Psi(t) \rangle$ can be written as

$$\langle \mathbf{r} \, | \, \Psi(t) \rangle = e^{-iH_{\text{lat}}t} \hat{\Psi}(\mathbf{r},t) \, | \, \{n_i\} \rangle \; . \tag{2.8}$$

The utility of this amplitude-operator is that its time dependence is independent of the initial state of the lattice; this independence allows the calculation of the scattering from any particular surface in the ensemble using just this one operator. The equation of motion for $\hat{\Psi}$,

$$i\frac{\partial}{\partial t} \hat{\Psi}(\mathbf{r},t) = H_{\text{part}}(\mathbf{r})\hat{\Psi}(\mathbf{r},t) + \hat{V}_{\text{int}}(\mathbf{r},t)\hat{\Psi}(\mathbf{r},t) \tag{2.9}$$

is obtained by taking the partial derivative with respect to time of the defining equation (2.7). The two terms containing the lattice Hamiltonian cancel. The particle Hamiltonian commutes with the lattice Hamiltonian. The time dependence of the interaction potential is that due to the noninteracting lattice

$$\hat{V}_{\text{int}}(\mathbf{r},t) = e^{-iH_{\text{lat}}t} V_{\text{int}} e^{iH_{\text{lat}}t}$$

$$= \frac{1}{\sqrt{N}} \sum_{\lambda} [V_{\lambda}(\mathbf{r})e^{i\omega_{\lambda}t}a_{\lambda}^{\dagger} + \text{H.c.}] \; . \tag{2.10}$$

The time dependence of $\hat{V}_{\text{int}}$ is not that of any of the conventional approaches (Schrödinger, Heisenberg, or interaction picture) but is the interaction picture for the lattice, a picture in which operators have the time dependence of only part of zeroth-order Hamiltonian, i.e., that of the lattice Hamiltonian. We choose to treat the time dependence this way because we are only interested in the lattice time dependence as far as it affects the particle's motion. Since the time dependence is known exactly it can be removed from the calculation.

Since the lattice Hamiltonian commutes with any particle operator and does not change any particle state when operating on it, we can use the amplitude-operator to evaluate the expectation value of any particle operator. For example, consider

$$\langle \Psi(t) \, | \, O_{\text{part}} \, | \, \Psi(t) \rangle$$

$$= \int d^3r \int d^3r' \langle \{n_i\} \, | \, \hat{\Psi}^{\dagger}(\mathbf{r},t)$$

$$\times O_{\text{part}}(\mathbf{r},\mathbf{r}')\hat{\Psi}(\mathbf{r}',t) \, | \, \{n_i\} \rangle \; , \tag{2.11}$$

where we have inserted two complete sets of particle states (in the position representation) around the particle operator. Note that $O_{\text{part}}(\mathbf{r},\mathbf{r}')$ can be taken outside of the phonon matrix element. Since Eq. (2.11) is valid for any operator O_{part}, all the properties of the scattering particle are contained in the density matrix, which is $\hat{\Psi}$ times its Hermitian conjugate. Accordingly, thermally averaging the expectation of any particle operator just involves integrating over the thermally averaged density matrix

$$\langle \langle \Psi(t) \, | \, O_{\text{part}} \, | \, \Psi(t) \rangle \rangle_{\text{th}}$$

$$= \int d^3r \int d^3r' \, O_{\text{part}}(\mathbf{r},\mathbf{r}') \langle \hat{\Psi}^{\dagger}(\mathbf{r},t)\hat{\Psi}(\mathbf{r}',t) \rangle_{\text{th}} \; . \tag{2.12}$$

Calculating the thermally averaged density matrix from quantities that are independent of the initial state of the lattice is possible because the time evolution of the amplitude-operator is constructed to be independent of the initial state of the lattice.

C. Multiphonon expansion

To further simplify the calculation of the scattering probabilities we break up the amplitude-operator into amplitude-operators for each of which there is a specific change in the occupation of the lattice modes. In particular there is a term in which the occupation of each of the lattice modes has had no net change, a sum of terms in which exactly one mode has had a net increase or decrease of one phonon, and further terms for every possible net change. We write these terms by explicitly factoring out

all of the unpaired phonon operators from each term. Each phonon creation or destruction operator in the interaction potential which lead to these changes in phonon occupations, has associated with it both a sum over the modes of the lattice and a factor of $N^{-1/2}$, where N is the number of atoms in the lattice. We write this factor explicitly in front of the sum so that all of the newly defined amplitude-operators are not proportional to any power of the size of the system (see below). Thus, the decomposition of the amplitude-operator in terms of phonon-change amplitude-operators is given by

$$\hat{\Psi}(\mathbf{r},t) = \hat{\Psi}_{0ph}(\mathbf{r},t) + \frac{1}{\sqrt{N}} \sum_{\lambda} [a_{\lambda}^{\dagger}(t)\hat{\Psi}_{1ph}(\mathbf{r},t,\lambda,+) + a_{\lambda}(t)\hat{\Psi}_{1ph}(\mathbf{r},t,\lambda,-)] + \frac{1}{N}\sum_{\lambda,\lambda'} \cdots . \tag{2.13}$$

Each of these new phonon-change amplitude-operators can be written as a sum of terms that are amplitudes (i.e., they contain no phonon operators) times pairs of phonon operators such that the index of both the creation and the annihilation operator in each pair is the same. Associated with each pair of phonon operators there is a factor of N^{-1} and a sum over the lattice modes. There is only one sum with each pair of operators because we have taken only those terms in which the operators are paired; the rest of the terms from the same applications of the interaction potential are in higher-order phonon-change terms because they have more unpaired phonon operators. For example, the zero-phonon-change term can be written as

$$\hat{\Psi}_{0ph}(\mathbf{r},t) = \psi_{0ph}^{0}(\mathbf{r},t) + \frac{1}{N}\sum_{\lambda} \psi_{0ph}^{\lambda}(\mathbf{r},t)a_{\lambda}^{\dagger}a_{\lambda} + \frac{1}{N^2}\sum_{\lambda,\lambda'} \cdots . \tag{2.14}$$

All of the amplitudes and amplitude-operators discussed in this paper are independent of the size of the system in the limit that the size of the system becomes infinite because all sums of paired operators over $3N$ terms are canceled by a factor of N^{-1}. Some of the sums over lattice modes of unpaired operators should be restricted so as not to include the terms that are counted elsewhere because of pairing, but the corrections are not important or even relevant because all the restricted terms are negligible in the large N limit.

Since any expectation value over phonon states requires that all the phonon operators must be paired to give a nonzero result, the thermally averaged density matrix can be written as a sum of the thermal averages of the square of each phonon-change term

$$\langle \hat{\Psi}^{\dagger}(\mathbf{r},t)\hat{\Psi}(\mathbf{r}',t)\rangle_{th} = \langle \hat{\Psi}_{0ph}^{\dagger}(\mathbf{r},t)\hat{\Psi}_{0ph}(\mathbf{r}',t)\rangle_{th} + \frac{1}{N}\sum_{\lambda} [\langle \hat{\Psi}_{1ph}^{\dagger}(\mathbf{r},t,\lambda,+)a_{\lambda}a_{\lambda}^{\dagger}\hat{\Psi}_{1ph}(\mathbf{r}',t,\lambda,+)\rangle_{th}$$

$$+ \langle \hat{\Psi}_{1ph}^{\dagger}(\mathbf{r},t,\lambda,-)a_{\lambda}^{\dagger}a_{\lambda}\hat{\Psi}_{1ph}(\mathbf{r}',t,\lambda,-)\rangle_{th}] + \frac{1}{N^2}\sum_{\lambda,\lambda'} \cdots . \tag{2.15}$$

All of the creation and destruction operators on the right-hand side of this expression are explicitly paired, and all are summed over. In each of these expectation values there are many terms that contribute; contributing terms are called correlated if the index of one of the paired phonon operators is identical to that of another pair. In the large N limit all correlated terms have a factor of N^{-1} that is not associated with a sum and hence vanish as the number of lattice atoms becomes infinite (see Appendix A). This vanishing of correlated contributions allows each of these thermal expectation values of a product of operators to be written as a product of expectation values

$$\langle \hat{\Psi}^{\dagger}(\mathbf{r},t)\hat{\Psi}(\mathbf{r}',t)\rangle_{th} = \langle \hat{\Psi}_{0ph}^{\dagger}(\mathbf{r},t)\rangle_{th}\langle \hat{\Psi}_{0ph}(\mathbf{r}',t)\rangle_{th} + \frac{1}{N}\sum_{\lambda} [\langle \hat{\Psi}_{1ph}^{\dagger}(\mathbf{r},t,\lambda,+)\rangle_{th}(n_{\lambda}+1)\langle \hat{\Psi}_{1ph}(\mathbf{r}',t,\lambda,+)\rangle_{th}$$

$$+ \langle \hat{\Psi}_{1ph}^{\dagger}(\mathbf{r},t,\lambda,-)\rangle_{th}n_{\lambda}\langle \hat{\Psi}_{1ph}(\mathbf{r}',t,\lambda,-)\rangle_{th}] + \frac{1}{N^2}\sum_{\lambda,\lambda'} \cdots . \tag{2.16}$$

Although the left-hand side of Eq. (2.15) and the first term on the right-hand side of the same equation appear similar, the difference is that in the quantity on the right-hand side, all the phonon operators in each factor are ex-

plicitly paired; in the quantity on the left hand side, each factor contains unpaired operators that when paired with operators from the other factor give rise to the rest of the terms on the right-hand side of the equation.

D. Thermally averaged amplitudes

Thermally averaged n-phonon-change amplitudes can be defined by the thermal expectation value of the n-phonon-change amplitude-operators, in which we thermally average the paired phonon operators in the particle amplitude-operator. These thermally averaged amplitudes can be equivalently defined by taking the thermal expectation of the product of some phonon creation and destruction operators, which have the time dependence of the uncoupled lattice, with the amplitude-operator. This equivalence results from there being only one term in Eq. (2.13) that does not have any unpaired phonon operators when multiplied by the product of phonon operators. The zero-phonon-change amplitude

$$\psi_{0ph}(\mathbf{r},t) \equiv \langle \hat{\Psi}_{0ph}(\mathbf{r},t) \rangle_{th} = \langle \hat{\Psi}(\mathbf{r},t) \rangle_{th} \, , \qquad (2.17)$$

is the thermally averaged amplitude for the particle given that the lattice is in its initial state. We show that this amplitude describes the elastic scattering of the particle. There are two types of one-phonon-change amplitudes, those that are the thermally averaged amplitudes for the particle given that the occupation of exactly one-phonon mode has increased by one

$$\psi_{1ph}(\mathbf{r},t,\lambda,+) \equiv \langle \hat{\Psi}_{1ph}(\mathbf{r},t,\lambda,+) \rangle_{th}$$
$$= \frac{\sqrt{N}}{(n_{\lambda}+1)} \langle a_{\lambda}(t)\hat{\Psi}(\mathbf{r},t) \rangle_{th} \, , \qquad (2.18)$$

and those given that the occupation of exactly one mode has decreased by one

$$\psi_{1ph}(\mathbf{r},t,\lambda,-) \equiv \langle \hat{\Psi}_{1ph}(\mathbf{r},t,\lambda,-) \rangle_{th}$$
$$= \frac{\sqrt{N}}{n_{\lambda}} \langle a_{\lambda}^{\dagger}(t)\hat{\Psi}(\mathbf{r},t) \rangle_{th} \, . \qquad (2.19)$$

These amplitudes and the further n-phonon-change amplitudes describe the inelastic scattering of the particle. The density matrix can be written in terms of these thermally averaged amplitudes and the thermally averaged occupation numbers of the lattice modes as [see Eq. (2.16)]

$$\langle \hat{\Psi}^{\dagger}(\mathbf{r},t)\hat{\Psi}(\mathbf{r}',t) \rangle_{th} = \psi_{0ph}^{*}(\mathbf{r},t)\psi_{0ph}(\mathbf{r}',t) + \frac{1}{N}\sum_{\lambda}[\,\psi_{1ph}^{*}(\mathbf{r},t,\lambda,+)(n_{\lambda}+1)\psi_{1ph}(\mathbf{r}',t,\lambda,+)$$
$$+ \psi_{1ph}^{*}(\mathbf{r},t,\lambda,-)n_{\lambda}\psi_{1ph}(\mathbf{r}',t,\lambda,-)] + \frac{1}{N^{2}}\sum_{\lambda,\lambda'}\cdots \, . \qquad (2.20)$$

The advantage of writing the density matrix in terms of the thermally averaged amplitudes is that these amplitudes obey a hierarchical set of equations of motion and do not need to be explicitly thermally averaged.

The equation of motion for the zero-phonon-change amplitude, ψ_{0ph}, in which none of the lattice mode occupations have changed, is found by thermally averaging the equation of motion (2.9) for the amplitude-operator

$$i\frac{\partial}{\partial t}\psi_{0ph}(\mathbf{r},t) = H_{part}(\mathbf{r})\psi_{0ph}(\mathbf{r},t)$$
$$+ \frac{1}{N}\sum_{\lambda}[\,(n_{\lambda}+1)V_{\lambda}(\mathbf{r})\psi_{1ph}(\mathbf{r},t,\lambda,+)$$
$$+ n_{\lambda}V_{\lambda}^{*}(\mathbf{r})\psi_{1ph}(\mathbf{r},t,\lambda,-)] \, . \qquad (2.21)$$

The equations of motion for the one-phonon-change amplitudes, in which only one-phonon mode occupation has changed, are found by thermally averaging the same equation of motion after it has been multiplied by the appropriate creation or destruction operator and then scaling the resulting equation by the prefactor in Eqs. (2.18) and (2.19)

$$\left[i\frac{\partial}{\partial t} - \omega_{\lambda} \right]\psi_{1ph}(\mathbf{r},t,\lambda,+)$$
$$= H_{part}(\mathbf{r})\psi_{1ph}(\mathbf{r},t,\lambda,+) + V_{\lambda}^{*}(\mathbf{r})\psi_{0ph}(\mathbf{r},t)$$
$$+ \frac{1}{N}\sum_{\lambda'}[\,(n_{\lambda'}+1)V_{\lambda'}(\mathbf{r})\psi_{2ph}(\mathbf{r},t,\lambda,+,\lambda',+)$$
$$+ n_{\lambda'}V_{\lambda'}^{*}(\mathbf{r})\psi_{2ph}(\mathbf{r},t,\lambda,+,\lambda',-)] \, . \qquad (2.22)$$

The ω_{λ} term on the left-hand side of the equation comes from pulling the time-dependent creation operator through the time derivative. The zero-phonon-change term on the left-hand side becomes the term in the last sum when $\lambda = \lambda'$; for this term the two explicit operators (one from the premultiplication and the other from the potential) are paired together instead of with two unpaired operators in the amplitude-operator and the expectation becomes the occupation of that mode times the zero-phonon-change amplitude. The correlated contributions are again negligible because of unbalanced factors of N^{-1}.

The equations of motion for the two-phonon-change amplitudes can be defined in a manner similar to that for the one-phonon-change amplitudes, leading to a hierarchical set of equations of motion. This procedure for calculating thermally averaged properties is quite general for any system in which a few degrees of freedom are coupled to an infinite phonon system. The approximations we have made up to this point have been made just for the clarity of the presentation. For instance, the inclusion of anharmonic terms in the interaction potential just complicates the equations of motion for the thermally averaged amplitudes. In this case the n-phonon-change amplitudes would be coupled to more than just the $(n-1)$- and $(n+1)$-phonon-change amplitudes. Even though this approach is an exact solution to the scattering problem, a hierarchical set of equations of motion is useful only if the higher-order phonon-change terms are unimportant. For the contributions of the n-phonon-change terms to become unimportant in the limit that n goes to infinity, the coupling between the phonons and the scattering particle should be weak as is the case for thermal energy helium and molecular hydrogen scattering.

III. ONE-PHONON APPROXIMATION

For systems in which the inelastic scattering is weak, we truncate the set of thermally averaged amplitudes to include only zero- and one-phonon changes. The equations that describe this approximation come from those of the preceding section with the higher-order phonon-change amplitudes set to zero. The equation of motion for the zero-phonon-change amplitude is unchanged because the interaction potential we used included only the term linear in the phonon coordinates, i.e.,

$$\left[i\frac{\partial}{\partial t} - H_{part} \right] \psi_{0ph}(\mathbf{r},t) = \frac{1}{N} \sum_{\lambda,\sigma} n_{\lambda\sigma} V_{\lambda\sigma}(\mathbf{r}) \psi_{1ph}(\mathbf{r},t,\lambda,\sigma) \ . \tag{3.1}$$

We have made the one-phonon-increase and one-phonon-decrease amplitudes look similar by defining a notation; $\sigma = +$ or $-$, which refer to a net phonon increase or decrease, respectively, after the interaction, so that $n_{\lambda+} = n_\lambda + 1$, $n_{\lambda-} = n_\lambda$ and $V_{\lambda+} = V^*_{\lambda-} = V_\lambda$. In this notation the equations of motion for the one-phonon-change amplitudes are simple because they are only coupled to the zero-phonon-change amplitude

$$\left[i\frac{\partial}{\partial t} - \sigma\omega_\lambda - H_{part} \right] \psi_{1ph}(\mathbf{r},t,\lambda,\sigma) = V^*_{\lambda\sigma}(\mathbf{r}) \psi_{0ph}(\mathbf{r},t) \ . \tag{3.2}$$

In the approximation, the thermally averaged density matrix contains contributions from only the zero- and one-phonon-change amplitudes

$$P(\mathbf{r},\mathbf{r}',t) = \psi^*_{0ph}(\mathbf{r},t)\psi_{0ph}(\mathbf{r}',t)$$
$$+ \frac{1}{N} \sum_{\lambda,\sigma} \psi^*_{1ph}(\mathbf{r},t,\lambda,\sigma)\psi_{1ph}(\mathbf{r}',t,\lambda,\sigma) n_{\lambda\sigma} \ . \tag{3.3}$$

If the density matrix is evaluated at equal positions and integrated over all space it is constant in time

$$\frac{d}{dt} \int d^3r\, P(\mathbf{r},\mathbf{r},t) = 0 \ . \tag{3.4}$$

This can be seen by taking the time derivative inside the spatial integration and using the equations of motion to replace the time derivatives, then the Hermitian properties of the Hamiltonian can be used inside the integration to cancel all of the terms. The equal position density matrix is just the probability density for the scattering particle summed over all of the possible states of the lattice. That it is constant in time means that the one-phonon-change approximation is a unitary approximation. The same arguments apply to any finite phonon-change truncation of the set of amplitudes which will also be a unitary approximation.

IV. STATIONARY STATE SCATTERING

In this section we present the stationary state scattering results for the scattering probabilities, discuss the problems that arise in stationary state scattering theory when the zeroth-order Hamiltonian has bound states, and show

how the scattering probabilities can be calculated from the asymptotic forms of the scattering state wave functions. Central to the derivation of these results (see Appendix B) is a limiting process in which the initial momentum uncertainty of the wave packet goes to zero. Taking this limit allows the scattering to be calculated in terms of stationary state eigenfunctions of the Hamiltonian.

The scattering from the surface can be described in terms of the scattering state solutions of a Lippmann-Schwinger equation containing the static surface potential. The state $\chi^{(-)}$ is a scattering state with outgoing boundary conditions and is defined using a Lippmann-Schwinger equation with the advanced free-particle Green function G^a_0

$$\chi^{(-)}(\mathbf{r},\mathbf{k}) = e^{i\mathbf{k}\cdot\mathbf{r}} + \int d^3r'\, G^a_0(\mathbf{r},\mathbf{r}',E_\mathbf{k}) V(\mathbf{r}') \chi^{(-)}(\mathbf{r}',\mathbf{k}) \ . \tag{4.1}$$

Scattering states with incoming boundary conditions, $\chi^{(+)}$, can be defined in the same manner using the retarded Green function. The bound states of the static surface potential are defined by

$$(H_{part} - E_{n,\mathbf{K}})\chi(\mathbf{r},n,\mathbf{K}) = 0; \quad \int d^3r\, |\chi(\mathbf{r},n,\mathbf{K})|^2 = A \ , \tag{4.2}$$

where A is the area of the surface and n indexes the bound states at each value of $\mathbf{K}$. A complete set of states consists of both the bound states and either the incoming or the outgoing scattering states.

The propagation of a particle in the presence of the static surface is described by a retarded static surface Green function G^r_1 defined by

$$(E - H_{part} + i\eta)G^r_1(\mathbf{r},\mathbf{r}',E) = \delta^{(3)}(\mathbf{r}-\mathbf{r}') \ , \tag{4.3}$$

together with the boundary conditions that in the limit that as z goes to infinity, with z' finite, the Green function behaves like an outgoing plane wave. We use this Green function to write scattering states in the presence of inelastic scattering.

The scattering states in the presence of the coupling to the phonons are defined by a Lippmann-Schwinger equation similar to those with no coupling by using an outgoing static surface scattering state and the retarded static surface Green function. The Lippmann-Schwinger equation reduces to a set of equations coupling the different multiphonon amplitudes

$$\psi^{(+)}_{0ph}(\mathbf{r},\mathbf{k}) = \chi^{(+)}(\mathbf{r},\mathbf{k}) - \int d^3r'\, G^r_1(\mathbf{r},\mathbf{r}',E_\mathbf{k})$$
$$\times \frac{1}{N} \sum_{\lambda,\sigma} n_{\lambda\sigma} V_{\lambda\sigma}(\mathbf{r}') \psi^{(+)}_{1ph}(\mathbf{r}',\mathbf{k},\lambda,\sigma) \ , \tag{4.4}$$

$$\psi^{(+)}_{1ph}(\mathbf{r},\mathbf{k},\lambda,\sigma) = - \int d^3r'\, G^r_1(\mathbf{r},\mathbf{r}',E_\mathbf{k} - \sigma\omega_\lambda)$$
$$\times V^*_{\lambda\sigma}(\mathbf{r}') \psi^{(+)}_{0ph}(\mathbf{r}',\mathbf{k}) \ . \tag{4.5}$$

There is no boundary term on the right-hand side of this last equation because the boundary conditions are chosen so that the incident amplitude in the one-phonon-change states is zero.

A. Trapping

The bound states of the static surface potential appear as poles as a function of energy in the static surface Green function. Hence the one-phonon-change amplitudes diverge as a function of the phonon energy as the final-state energy $E_k - \sigma \omega_\lambda$ becomes equal to a bound-state energy with parallel wave vector equal to $\mathbf{K} - \sigma \mathbf{Q}_\lambda$. These divergences, which arise for finite temperature in any finite phonon-change truncation of the scattering states and for zero surface temperature in any approach, are due to trapping on the surface. If a stationary state is thought of as a constant incident flux of particles the continual increase of probability in the bound states leads to the paradox that the time-independent stationary state depends on time. This continual build up of particles means that there is no time-independent scattering state unless there is absorption of probability from the bound-state amplitudes; this absorption (and the resolution of this paradox) is provided by the imaginary part in the Green function. In the limit that the imaginary part of the Green function goes to zero all of the absorption, which is proportional to η, takes place from the bound-state amplitudes because they are diverging proportional to η^{-1}. The limit $\eta \to 0$ is well defined and produces a stable limiting value for the trapping probability (see Appendix B). Even though these scattering states involve a loss of probability due to trapping, the one-phonon approximation we are describing remains unitary.

The stationary state scattering wave functions also obey a coupled set of Schrödinger equations with the infinitesimal imaginary part included

$$(H_{\text{part}} - E_k - i\eta)\psi_{\text{0ph}}^{(+)}(\mathbf{r},\mathbf{k})$$
$$= -\frac{1}{N}\sum_{\lambda,\sigma} V_{\lambda\sigma}(\mathbf{r})n_{\lambda\sigma}\psi_{\text{1ph}}^{(+)}(\mathbf{r}',\mathbf{k},\lambda,\sigma) , \quad (4.6)$$

$$[H_{\text{part}} - (E_k - \sigma\omega_\lambda) - i\eta]\psi_{\text{1ph}}^{(+)}(\mathbf{r},\mathbf{k},\lambda,\sigma)$$
$$= -V_{\lambda\sigma}^*(\mathbf{r})\psi_{\text{0ph}}^{(+)}(\mathbf{r},\mathbf{k}) . \quad (4.7)$$

Solving these equations with a finite value of η remedies the divergence in the one-phonon-change amplitudes (see Appendix B). In practice it is simple to find a finite imaginary part that is small enough that the solutions of these equations for finite η give the same results as those in the limit that η goes to zero. In the numerical calculation that we describe in Sec. VI we choose to solve the Schrödinger equations instead of the Lippmann-Schwinger equations because using the latter would require either storing or recalculating the static surface Green function, G_1^r.

B. Scattering probabilities

To describe the scattering probabilities in the presence of the static surface potential, which cannot be treated as a perturbation, we have to calculate the matrix elements of the wave packet with the outgoing scattering states of the static surface potential. This approach is quite similar to that of the distorted wave Born approximation, and in fact it is a self-consistent improvement of that approximation. In particular, the probability to scatter into a state with a wave vector $\mathbf{k}_f$ is given by the square of the matrix element between the wave packet and the outgoing scattering state solution of the static surface

$$P(\mathbf{k}_f,t) = \langle\langle\Psi(t)|\chi^{(-)}(\mathbf{r},\mathbf{k}_f)\rangle\langle\chi^{(-)}(\mathbf{r},\mathbf{k}_f)|\Psi(t)\rangle\rangle_{\text{th}}$$

$$= \left|\int d^3r(\chi^{(-)})^*(\mathbf{r},\mathbf{k}_f)\psi_{\text{0ph}}^{(+)}(\mathbf{r},t)\right|^2 + \frac{1}{N}\sum_{\lambda,\sigma} n_{\lambda\sigma}\left|\int d^3r\chi^{(-)}(\mathbf{r},\mathbf{k}_f)^*\psi_{\text{1ph}}^{(+)}(\mathbf{r},t,\lambda,\sigma)\right|^2 . \quad (4.8)$$

In Appendix B we show that the first term gives the elastic scattering and the remaining terms give the inelastic scattering probabilities. The elastic and inelastic scattering in Eq. (4.8) can be written in terms of matrix elements of the interaction potential with respect to the zero-phonon-change scattering state amplitude and the outgoing static surface scattering states. In this form the inelastic amplitudes look like a typical golden rule rate in which the interaction potential causes a transition from the initial state to the final state. Note that this approach uses the incoming zero-phonon-change amplitude instead of the incoming static surface scattering state.

After a sufficiently long time such that all of the nontrapped particles have left the surface the probability to have scattered inelastically into a final state with wave vector $\mathbf{k}_f$ is given by [see the discussion following (B6)]

$$P_{\text{inel}}(\mathbf{k}_f) = \frac{m}{k_{zi}}\frac{1}{A}\frac{1}{N}\sum_{\lambda,\sigma} n_{\lambda\sigma}\left|\int d^3r\,[\chi^{(-)}(\mathbf{r},\mathbf{k}_f)]^*\right.$$
$$\left.\times V_{\lambda\sigma}^*(\mathbf{r})\psi_{\text{0ph}}^{(+)}(\mathbf{r},\mathbf{k}_i)\right|^2$$
$$\times (2\pi)\delta(E_{k_i} - \sigma\omega_\lambda - E_{k_f}) . \quad (4.9)$$

This result is identical to the distorted wave Born approximation result with the zero-phonon-change amplitude replacing the incident static surface potential scattering state, i.e., using the left-hand side of Eq. (4.4) to replace the first term on the right-hand side of Eq. (4.4) in Eq. (4.9). This expression illustrates why this approach is a

unitary extension of the distorted wave Born approximation because the elastic wave function from which the inelastic transitions are made is calculated self-consistently with the inelastic states to which the transitions are made. Furthermore, we see why the distorted wave Born approximation is not unitary and this approximation is; in the distorted wave Born approximation when a particle scatters inelastically the flux stays in the elastic channel

and continues to scatter leading to an overcounting of the inelastic scattering, whereas in this approach the flux is removed from the elastic channel leading to a flux conserving approximation. The trapping probabilities are the probabilities to be in one of the bound states of the static surface potential and are given by a similar expression with the outgoing scattering state replaced by a bound state

$$P_{\text{inel}}(n,\mathbf{K}_f)=\frac{m}{k_{zi}}\frac{1}{A}\frac{1}{N}\sum_{\lambda,\sigma}n_{\lambda\sigma}\left|\int d^3r\,[\chi^{(-)}(\mathbf{r},n,\mathbf{K}_f)]^*V_{\lambda\sigma}^*(\mathbf{r})\psi_{0\text{ph}}^{(+)}(\mathbf{r},\mathbf{k}_i)\right|^2(2\pi)\delta(E_{\mathbf{k}_i}-\sigma\omega_\lambda-E_{n,\mathbf{K}_f})\ . \tag{4.10}$$

The first term in Eq. (4.8) gives the elastic scattering probability which can be shown to be

$$P_{\text{el}}(\mathbf{k}_f)=\sum_{\mathbf{G}}\frac{m}{k_{zi}}(2\pi)\delta(E_{\mathbf{k}_i}-E_{\mathbf{k}_f})(2\pi)^2\delta^{(2)}(\mathbf{K}_i-\mathbf{K}_f-\mathbf{G})$$

$$\times\left|\frac{k_{zf}}{m}R(\mathbf{k}_f,\mathbf{k}_i)+\frac{1}{A}\int d^3r\int d^3r'\,[\chi^{(-)}(\mathbf{r},\mathbf{k}_f)]^*\Sigma(\mathbf{r},\mathbf{r}',E_{\mathbf{k}_i})\psi_{0\text{ph}}^{(+)}(\mathbf{r}',\mathbf{k}_i)\right|^2\ , \tag{4.11}$$

where $R(\mathbf{k}_f,\mathbf{k}_i)$ describes the amplitude to make a transition from the incident state $\mathbf{k}_i$ to the final state $\mathbf{k}_f$ by scattering from the static surface potential. It is proportional to the matrix element between the incoming scattering state and the outgoing scattering state. The sum over surface reciprocal-lattice vectors $\mathbf{G}$ makes explicit the possibility of elastic diffraction (or inelastic scattering due to internal excitations of the molecule as we discuss below) in the elastic scattering probability. The second term in the absolute value is the effect of the inelastic scattering on the elastic scattering; it is written in terms of the self-energy given by

$$\Sigma(\mathbf{r},\mathbf{r}',E_{\mathbf{k}})=\frac{1}{N}\sum_{\lambda,\sigma}n_{\lambda\sigma}V_{\lambda\sigma}(\mathbf{r})G_1^r(\mathbf{r},\mathbf{r}',E_{\mathbf{k}}-\sigma\omega_\lambda)V_{\lambda\sigma}^*(\mathbf{r}')\ . \tag{4.12}$$

This is the Born approximation to the self-energy of the full scattering system and can be understood in terms of its constituents: the potential $V_{\lambda\sigma}$ causes a transition to a one-phonon-change state, the molecule propagates with the energy $E_{\mathbf{k}}-\sigma\omega_\lambda$ until the potential $V_{\lambda\sigma}^*$ causes a transition back to the zero-phonon-change state. This process is summed over the possible phonons, weighted by the thermal occupation of each phonon mode.

The inelastic scattering probabilities can also be directly calculated from the asymptotic form of the one-phonon-change scattering states. The probability to scatter into a particular final state is given by the flux density in the one-phonon-change amplitude far from the surface divided by the incident flux and summed over all phonon modes that satisfy energy and momentum conservation

$$P_{\text{inel}}(\mathbf{k}_f)=\lim_{z\to\infty}\sum_{\mathbf{G}}\frac{k_{zf}}{k_{zi}}\frac{1}{N}\sum_{\lambda,\sigma}n_{\lambda\sigma}\,|\,\psi_{1\text{ph}}^{(+)}(\mathbf{r},\mathbf{k}_i,\lambda,\sigma)\,|^2\frac{k_{zf}}{m}(2\pi)\delta(E_{\mathbf{k}_i}-\sigma\omega_\lambda-E_{\mathbf{k}_f})(2\pi)^2\delta^{(2)}(\mathbf{K}_i-\sigma\mathbf{Q}_\lambda-\mathbf{G}-\mathbf{K}_f)\ .$$

$$\tag{4.13}$$

The trapping probability can be calculated from the behavior of the one-phonon-change amplitudes in the limit that the small imaginary part in the Green function (or Schrödinger equation) goes to zero. In the scattering state solutions calculated with a finite imaginary part there is a loss of probability from this system due to absorption from the bound-state amplitudes because particles would be trapping on the surface in a real scattering event. The trapping probability is then equal to the probability of absorption divided by the incident flux summed over all the phonon modes that satisfy parallel momentum conservation

$$P_{\text{inel}}(n,\mathbf{K}_f)=\lim_{\eta\to0}\sum_{\mathbf{G}}\frac{1}{N}\sum_{\lambda,\sigma}n_{\lambda\sigma}\eta^2\frac{1}{A}\int d^3r\,|\,\psi_{1\text{ph}}^{(+)}(\mathbf{r},\mathbf{k}_i,\lambda,\sigma)\,|^2$$

$$\times(2\pi)\delta(E_{\mathbf{k}_i}-\sigma\omega_\lambda-E_{n,\mathbf{K}_f})(2\pi)^2\delta^{(2)}(\mathbf{K}_i-\sigma\mathbf{Q}_\lambda-\mathbf{G}-\mathbf{K}_f)\ . \tag{4.14}$$

Similarly to the inelastic scattering probabilities, the elastic scattering probability (including diffractive and internal transitions) can be shown to be equal to the outgoing flux divided by the incident flux

$$P_{\text{el}}(\mathbf{k}_f)=\lim_{z\to\infty}\sum_{\mathbf{G}}\frac{k_{zf}}{k_{zi}}\,|\,\psi_{0\text{ph}}^{(+)}(\mathbf{r},\mathbf{k}_i)-\delta_{\mathbf{k}_f,\mathbf{k}_i}e^{i\mathbf{k}\cdot\mathbf{r}}\,|^2\frac{k_{zf}}{m}(2\pi)\delta(E_{\mathbf{k}_i}-E_{\mathbf{k}_f})(2\pi)^2\delta^{(2)}(\mathbf{K}_i-\mathbf{G}-\mathbf{K}_f)\ . \tag{4.15}$$

These last three expressions [(4.13)–(4.15)] are used to calculate the scattering probabilities once we have solved for the scattering states using Eqs. (4.6) and (4.7). When integrated over all momenta and summed over all bound states, these probabilities sum to one because this is a unitary approximation.

V. APPROXIMATIONS ON THE POTENTIAL

Although the equations presented in the preceding section could be solved for an arbitrary form of the potential, we show in this section, starting from a completely general form of the interaction potential, what assumptions lead to a Hamiltonian for which the scattering can be easily calculated and what form the equations of the last section take when applied to this form of the Hamiltonian. In particular, we choose a Hamiltonian for a flat surface so as to decouple the motion parallel to the surface from the motion perpendicular to it. This decoupling allows a much simpler numerical calculation of the wave functions.

The Hamiltonian consists of the kinetic energy of the scattering particle, the lattice Hamiltonian, and the potential that couples the scattering particle and the lattice. Later we regroup the terms in the pattern of Eq. (2.3), but here we keep all of the coupling terms together. The Hamiltonian for the general form is

$$H = T_{\text{part}} + H_{\text{lat}} + V . \tag{5.1}$$

The kinetic energy of the particle, T_{part}, here a molecule, consists of the translational kinetic energy of the particle plus its rotational kinetic energy. We neglect vibrational and electronic degrees of the molecule because the excitation energies are much higher than the other energies in the scattering problem. Accordingly

$$T_{\text{part}} = \frac{p^2}{2m} + \frac{L^2}{2I} , \tag{5.2}$$

where L is the angular momentum operator for the molecular rotations (a three-dimensional vector in spite of its being upper case) and I is the moment of inertia. The orientation of the molecule is specified by the angle of the molecular axis with respect to the surface normal θ and the angle of the orientation around the surface normal ϕ. The lattice Hamiltonian is the same as it was in the preceding section [Eq. (2.4)]

$$H_{\text{lat}} = \sum_\lambda \omega_\lambda a_\lambda^\dagger a_\lambda . \tag{5.3}$$

The displacements of the lattice atoms can be expanded in terms of the normal modes of the lattice[23]

$$\mathbf{u}_n = \frac{1}{\sqrt{N}} \sum_\lambda e^{i\mathbf{Q}_\lambda \cdot \mathbf{R}_n} \mathbf{e}(\lambda, z_n) \left[\frac{1}{2M\omega_\lambda} \right]^{1/2} (a_{\bar\lambda}^\dagger + a_\lambda) ,$$

$$\mathbf{Q}_{\bar\lambda} = -\mathbf{Q}_\lambda . \tag{5.4}$$

Here λ indexes the normal modes, $\mathbf{Q}_\lambda$ is the wave vector of the mode parallel to the surface, ω_λ is the frequency of the mode, and $\mathbf{e}(\lambda, z_n)$ is the polarization vector, which depends on the distance of the atom from the surface because there is no translational symmetry normal to the

surface. The polarization vectors obey the following orthonormality condition

$$\frac{1}{N} \sum_n \mathbf{e}^*(\lambda, z_n) \cdot \mathbf{e}(\lambda', z_n) e^{-i\mathbf{R}_n \cdot (\mathbf{Q}_\lambda - \mathbf{Q}_{\lambda'})} = \delta_{\lambda, \lambda'} . \tag{5.5}$$

Finally a_λ and $a_\lambda^\dagger$ are the creation and destruction operators for the phonon mode.

A. Interaction potential

In general, the interaction between the scattering particle and the lattice depends on the position of all the atoms in the lattice and all the molecular coordinates. Since the mean-square displacements of the lattice atoms are small compared to the characteristic lengths of the potential a Taylor series expansion of the potential in terms of the displacements of the lattice atoms should converge rapidly

$$V(\mathbf{r}, \theta, \phi, \{\mathbf{u}_j\}) = V_0(\mathbf{r}, \theta, \phi) + \sum_{n,\alpha} \frac{\partial V}{\partial u_{n,\alpha}} \Bigg|_{\{\mathbf{u}_j\}=0} u_{n,\alpha}$$

$$+ \frac{1}{2} \sum_{n,\alpha} \sum_{m,\beta} \frac{\partial^2 V}{\partial u_{n,\alpha} \partial u_{m,\beta}} \Bigg|_{\{\mathbf{u}_j\}=0} u_{n,\alpha} u_{m,\beta} . \tag{5.6}$$

We truncate this expansion at the term linear in the phonon coordinates, consistent with the one-phonon-change approximation we have made previously.

Now we regroup the terms in the Hamiltonian so that all the terms that are independent of the phonon coordinates are grouped together.[24] In addition, we make part of the flat surface approximation, we ignore any dependence on the position of the particle parallel to the surface in the first term in the potential,

$$H_{\text{part}} = T_{\text{part}} + V_0(z, \theta) . \tag{5.7}$$

The rest of the flat surface approximation is made in Eq. (5.10).

The linear term in the coupling between the phonons and the scattering particle can be written in a manner that makes it easy to see all of the approximations that we make

$$V_{\text{int}} = \sum_{\mathbf{G}} \sum_{\alpha, z_n} \frac{1}{\sqrt{N}} \sum_\lambda e^{i(\mathbf{Q}_\lambda + \mathbf{G}) \cdot \mathbf{R}} V_{1\alpha}$$

$$\times (\mathbf{G}, \mathbf{Q}_\lambda, z, z_n, \theta, \phi) e_\alpha(\lambda, z_n)$$

$$\times \left[\frac{1}{2M\omega_\lambda} \right]^{1/2} (a_{\bar\lambda}^\dagger + a_\lambda) . \tag{5.8}$$

We have expanded the coordinates of the lattice atoms in terms of the normal modes of the lattice Eq. (5.4), and expressed the dependence of the potential on the position of the particle in the plane of the surface by Fourier transforming the potential with respect to the sum of the parallel wave vector of the phonon mode and a reciprocal-lattice vector. The dependence of the potential on the phonon wave vector and the reciprocal-lattice vector is given by an integral over the surface Wigner-Sietz

cell (SWSC) of the potential summed over the lattice sites in the surface

$$V_{1\alpha}(\mathbf{G},\mathbf{Q}_\lambda,z,z_n,\theta,\phi)$$

$$= \frac{1}{a}\int_{\text{SWSC}} d^2R \sum_{\mathbf{R}_n} e^{-i(\mathbf{Q}_\lambda+\mathbf{G})\cdot(\mathbf{R}-\mathbf{R}_n)} \frac{\partial V}{\partial u_{n,\alpha}}\bigg|_{\{u_j\}=0} .$$

(5.9)

This is still a completely general form for the linear coupling term in the potential.

The approximation that we make for the coupling potential is given by restricting the form that $V_{1\alpha}$ takes to

$$V_{1\alpha}(\mathbf{G},\mathbf{Q}_\lambda,z,z_n,\theta,\phi)$$

$$= -\delta_{\alpha,z}\delta_{\mathbf{G},0}\delta_{z_n,0}H(\mathbf{Q}_\lambda)\left[\frac{\partial V_0(z,\theta)}{\partial z}\right] . \quad (5.10)$$

This expression includes the rest of the flat surface approximation; we keep only coupling to the phonon motion normal to the surface $\delta_{\alpha,z}$, do not allow umklapp processes (i.e., $\mathbf{G}=0$), and do not allow coupling of any other component of the motion with rotation of the molecule around the surface normal. For simplicity we also assume that the scattering particle only couples to the phonons through the projection on the top surface layer $\delta_{z_n,0}$. Finally we assume that the dependence of the potential on the parallel wave vector of the phonon that is being coupled to and the dependence on the height of the particle above the surface and its orientation are separable. The dependence on the parallel wave vector is assumed to be Gaussian[25]

$$H(\mathbf{Q}_\lambda)=e^{-(Q_\lambda^2/2Q_c^2)} . \quad (5.11)$$

This last assumption greatly simplifies numerical calculations because the only dependence of the phonon amplitude on the wave vector of the phonon comes in through the net energy transfer to the motion normal to the surface and an overall scale factor. This simplification is discussed further below.

This separability assumption can also be thought of as a local height approximation, i.e., that the effect of the phonons is to locally shift the origin of the potential without changing its shape in the z direction. If this potential is then expanded in terms of the phonon coordinates the coefficient of the linear term is proportional to the partial derivative of the uncoupled term with respect to the height above the surface. Then the Fourier transform of $H(\mathbf{Q})$ gives the effect of a lattice vibration at one surface point on the local height of the surface at another surface point as a function of the distance between the two points. The local height approximation should be a good approximation close to the surface where the effective height is dominated by the closest atoms; further from the surface where the potential is determined by more and more atoms the approximation should break down. Fortunately the inelastic scattering is dominated by the region of the potential close to the turning point so that the breakdown of this approximation should not be important. Within this approximation the neglect of the layers below the top

is equivalent to assuming that only the top layer affects the local height in the potential. Again, this neglect should be a good approximation close to the surface.

The interaction potential can now be written in a form similar to Eq. (2.6)

$$V_{\text{int}}=-\frac{\partial V_0(z,\theta)}{\partial z}\frac{1}{\sqrt{N}}\sum_\lambda (M_\lambda e^{-i\mathbf{Q}_\lambda\cdot\mathbf{R}}a_\lambda^\dagger+\text{H.c.}) .$$

(5.12)

The dependence on the height above the surface and on the orientation with respect to the surface is independent of the phonon to which the scattering particle is coupled. The dependence on the position parallel to the surface comes in through a factor that conserves the total wave vector of the system parallel to the surface. The factor M_λ contains all the information about the strength of the coupling to each phonon mode

$$M_\lambda=\left[\frac{1}{2M\omega_\lambda}\right]^{1/2} e_z(\lambda,0)H(\mathbf{Q}_\lambda) . \quad (5.13)$$

Below we see that M_λ is related to a weighted phonon density of states.

B. Scattering states

Because of the form of the potential we have assumed the parallel wave vector and the azimuthal quantum number are conserved and hence the form of the static surface scattering states simplifies

$$\chi^{(-)}(\mathbf{r},\theta,\phi,\mathbf{k}_f,l_f,m)=e^{i\mathbf{K}_f\cdot\mathbf{R}}e^{im\phi}\chi^{(-)}(z,\theta,k_{zf},l_f,m) .$$

(5.14)

The remaining part of the wave function is independent of the incident parallel wave vector. The zero-phonon-change amplitude, on the other hand, still depends on the full incident wave vector because the coupling to the phonons depends on the parallel wave vector

$$\psi_{0\text{ph}}^{(+)}(\mathbf{r},\theta,\phi,\mathbf{k}_i,l_i,m)=e^{i\mathbf{K}_i\cdot\mathbf{R}}e^{im\phi}\psi_{0\text{ph}}^{(+)}(z,\theta,\mathbf{k}_i,l_i,m) .$$

(5.15)

The scattering probabilities depend on the matrix element of the derivative of the static surface potential between these two scattering states.

The details of the phonons come into the scattering probabilities through a weighted projected density of states

$$C(\mathbf{Q},\omega)=\frac{1}{N}\sum_{\lambda,\sigma} n_{\lambda\sigma} |M_\lambda|^2(2\pi)\delta(\omega-\sigma\omega_\lambda)$$

$$\times(2\pi)^2\delta^{(2)}(\mathbf{Q}-\sigma\mathbf{Q}_\lambda) . \quad (5.16)$$

This density of states is projected onto the surface layer by the $e_\alpha(\lambda,0)$ factor in the definition of M_λ, and weighted by the thermal occupation of the modes, by the amplitude of the mode, and by the (local-height) phonon-cutoff function $H(\mathbf{Q})$. The weighted phonon density of states indicates how likely the particle is to interact with a phonon at a particular frequency and parallel wave vector. It

is also worth a reminder at this point that $C(\mathbf{Q},\omega)$ includes both phonon creation and annihilation events through σ. The inelastic scattering probability is given by the product of three factors: the inverse of the incident velocity, the squared matrix element of the derivative of the static surface potential between the incoming zero-phonon-change state and the outgoing static surface state, and the weighted phonon density of states

$$P_{\text{inel}}(\mathbf{k}_f, l_f) = \frac{m}{k_{zi}} \left| \left\langle \chi^{(-)}(z, \theta, k_{zf}, l_f, m) \right| \right.$$

$$\left. \times \frac{\partial V_0(z,\theta)}{\partial z} \left| \psi_{0\text{ph}}^{(+)}(z, \theta, \mathbf{k}_i, l_i, m) \right\rangle \right|^2$$

$$\times C(\mathbf{K}_i - \mathbf{K}_f, E_i - E_f) . \tag{5.17}$$

This equation is Eq. (4.9) rewritten in the form appropriate for the flat surface approximation. One nice feature of this approximation is that, given the matrix element for one final z component of the wave vector, the scattering probability for any wave vector with that z component can be calculated without recalculating the scattering state wave functions. Since these wave functions are calculated by numerically solving a Schrödinger equation, the savings in computer time can be considerable.

To rewrite Eqs. (4.6) and (4.7) in the form appropriate for the flat surface approximation it is useful to define some energies and wave vectors. The *incident* energy due to both the energy in center of mass motion normal to the surface and the rotational energy is given by

$$E_{zi} = \frac{k_{zi}^2}{2m} + \frac{l_i(l_i+1)}{2I} . \tag{5.18}$$

The change in energy in motion normal to the surface and the rotational energy due to exciting a phonon of wave vector $\mathbf{Q}$ and frequency ω is given by

$$\Delta E_z = E_{zi} - E_{zf} = \omega + \frac{(\mathbf{K}_i - \mathbf{Q})^2}{2m} - \frac{K_i^2}{2m} . \tag{5.19}$$

We are going to expand the motion of the molecule in terms of spherical harmonics with respect to its rotation so it is useful to define the kinetic energy the incident molecule would have in each rotational state far from the surface

$$\frac{k_{zl}^2}{2m} = E_{zi} - \frac{l(l+1)}{2I} . \tag{5.20}$$

It is also useful to define the same quantities for the molecules that have scattered inelastically

$$\frac{k_{zl}^2(\Delta E_z)}{2m} = \frac{k_{zl}^2}{2m} - \Delta E_z . \tag{5.21}$$

These wave vectors are used in the Schrödinger equations that the scattering states obey.

We can take advantage of the fact that the one-phonon-change amplitudes only depend on the energy in the motion normal to the surface and on the rotational motion up to a scale factor and calculate many of the amplitudes at the same time by scaling the one-phonon-change amplitudes by M_λ and defining an amplitude that only depends on the change in that energy

$$\psi_{1\text{ph}}^{(+)}(\mathbf{r}, \theta, \phi, \mathbf{k}_i, l_i, m, \lambda, \sigma)$$

$$= M_\lambda e^{i(\mathbf{K}_i - \sigma\mathbf{Q}_\lambda)\cdot\mathbf{R}} e^{im\phi} \psi_{1\text{ph}}^{(+)}(z, \theta, \Delta E_z) \big|_{\mathbf{Q}=\sigma\mathbf{Q}_\lambda; \omega=\sigma\omega_\lambda} .$$

$$\tag{5.22}$$

Here ΔE_z is evaluated at $\omega = \sigma\omega_\lambda$ and $\mathbf{Q} = \sigma\mathbf{Q}_\lambda$. If Eq. (4.13) for the inelastic scattering probability is written using the wave function defined above, there is a factor $|M_\lambda|^2$ associated with the sum over phonon modes. If we integrate the inelastic scattering probability over possible parallel wave vectors we can define a new phonon density of states that is a measure of how strongly phonons lead to a particular change in the energy

$$C(\Delta E_z) = \int \frac{d\omega}{(2\pi)} \int \frac{d^2Q}{(2\pi)^2} C(\mathbf{Q},\omega)(2\pi)\delta\left[\omega - \left(\Delta E_z - \frac{(\mathbf{K}_i - \mathbf{Q})^2}{2m} + \frac{K_i^2}{2m}\right)\right]$$

$$= \frac{1}{N} \sum_{\lambda,\sigma} n_{\lambda\sigma} |M_\lambda|^2 (2\pi)\delta\left[\sigma\omega_\lambda - \left(\Delta E_z - \frac{(\mathbf{K}_i - \sigma\mathbf{Q}_\lambda)^2}{2m} + \frac{K_i^2}{2m}\right)\right] . \tag{5.23}$$

We use Eq. (4.13) rewritten using this phonon density of states to calculate the inelastic scattering probabilities.

C. Coupled channels

For molecular hydrogen scattering the potential only depends weakly on the orientation of the molecule and the rotational energy splittings are comparable to the scale of the incident energies so that is is useful to formulate the scattering problem in a coupled-channels approach by ex-

panding the potential in Legendre polynomials and the wave functions in spherical harmonics. These expansions can be truncated after a few terms. The expansion of the potential and its derivative are given by

$$V_0(z,\theta) = \sum_l V_l(z) P_l(\cos\theta) , \tag{5.24}$$

$$\frac{\partial V_0(z,\theta)}{\partial z} = \sum_l V_l'(z) P_l(\cos\theta) . \tag{5.25}$$

Since the wave functions are expanded in spherical harmonics, we need the spherical harmonic matrix elements of the potential

$$V_{ll'}(z) = \sum_{l''} V_{l''}(z) \int d\Omega \, Y_{lm}^*(\theta,\phi) P_{l''}(\cos\theta) Y_{l'm}(\theta,\phi) \ . \tag{5.26}$$

These matrix elements still depend on the azimuthal quantum number m, but that quantity is constant during the scattering process so we suppress this dependence. To simplify the wave functions we suppress all of the initial conditions in writing down the wave functions. To suppress the azimuthal dependence of the wave function we define a spherical harmonic with the azimuthal dependence removed

$$Y_{lm}(\theta) = e^{-im\phi} Y_{lm}(\theta,\phi) \ . \tag{5.27}$$

Using this function we can write the expansions of the wave functions as

$$\psi_{0\text{ph}}^{(+)}(z,\theta) = \sum_l \psi_{0\text{ph}}^{(+)}(z,l) Y_{lm}(\theta) \ , \tag{5.28}$$

$$\psi_{1\text{ph}}^{(+)}(z,\theta,\Delta E_z) = \sum_l \psi_{1\text{ph}}^{(+)}(z,l,\Delta E_z) Y_{lm}(\theta) \ . \tag{5.29}$$

We solve for these wave functions numerically and use the solutions to calculate the thermally averaged scattering probabilities.

The wave functions we have defined above obey a coupled set of differential equations that are the formulations of Eqs. (4.5)—(4.7) in the approximations that we have made for the potential

$$-\left[\frac{1}{2m}\frac{d^2}{dz^2} + \frac{k_{zl}^2}{2m} + i\eta \right] \psi_{0\text{ph}}^{(+)}(z,l) + \sum_{l'} V_{ll'}(z)\psi_{0\text{ph}}^{(+)}(z,l') = \int \frac{d\Delta E_z}{(2\pi)} C(\Delta E_z) \sum_{l'} V_{ll'}(z)\psi_{1\text{ph}}^{(+)}(z,l',\Delta E_z) \ , \tag{5.30}$$

$$-\left[\frac{1}{2m}\frac{d^2}{dz^2} + \frac{k_{zl}^2(\Delta E_z)}{2m} + i\eta \right] \psi_{1\text{ph}}^{(+)}(z,l,\Delta E_z) + \sum_{l'} V_{ll'}(z)\psi_{1\text{ph}}^{(+)}(z,l',\Delta E_z) = \sum_{i'} V_{ll'}'(z)\psi_{0\text{ph}}^{(+)}(z,l') \ . \tag{5.31}$$

The first term on the left-hand side of both equations contains the kinetic-energy operator minus the kinetic energy in each channel of the molecule far from the surface, the second term contains the static surface potential that reflects the molecule away from the surface and that couples different rotational channels within the same phonon-change amplitude. The right-hand side of the first equation is the coupling of the zero-phonon-change amplitude to all of the one-phonon-change amplitudes, and the right-hand side of the second equation is the coupling of each one-phonon-change amplitude to the zero-phonon-change amplitude. These terms are asymmetric because of the way in which the one-phonon-change amplitudes were scaled. We solve these equations with a finite imaginary part that is small enough that the results do not change if it is made smaller, typically it must be much smaller than all of the widths of the resonances in the problem.

By discretizing the energy mesh for the one-phonon-change amplitudes these equations could be solved by a large coupled channels calculation, but in situations in which the sum of the results of a distorted wave Born approximation are not much greater than one it can be faster to solve these equations iteratively. For the first iteration we set the one-phonon-change amplitudes to zero and solve for the zero-phonon-change amplitude; this gives the scattering from the static surface. Then we use this result for the zero-phonon-change amplitude to calculate the one-phonon-change amplitudes; this gives the distorted wave Born approximation results for the inelastic scattering probabilities. Then these amplitudes are used to calculate the zero-phonon-change amplitude and the calculation proceeds iteratively.

D. Scattering probabilities

The boundary conditions that the amplitudes must satisfy are that the amplitudes decay to zero into the surface

$$\lim_{z \to -\infty} \psi_{0\text{ph}}^{(+)}(z,l), \psi_{1\text{ph}}^{(+)}(z,l,\Delta E_z) = 0 \ . \tag{5.32}$$

The zero-phonon-change amplitude far from the surface consists of a unit amplitude incoming plane wave in the incident channel and outgoing plane waves in all the rotational channels that have positive kinetic energy far from the surface

$$\lim_{z \to \infty} \psi_{0\text{ph}}^{(+)}(z,l) = e^{-ik_{zi}z}\delta_{l,l_i} + R_l e^{ik_{lz}z}; \quad k_{zl}^2 > 0 \ . \tag{5.33}$$

Those rotational channels that do not have sufficient energy must also decay away from the surface. The allowed channels for the one-phonon-change amplitudes are all outgoing plane waves

$$\lim_{z \to \infty} \psi_{1\text{ph}}^{(+)}(z,l,\Delta E_z) = R_l(\Delta E_z) e^{ik_{lz}(\Delta E_z)z}; \quad k_{zl}^2(\Delta E_z) > 0 \ . \tag{5.34}$$

The forbidden channels must also decay to zero away from the surface. Solving the coupled Schrödinger equations, Eqs. (5.30) and (5.31), for these boundary conditions gives the scattering probabilities.

The elastic and rotationally inelastic scattering probabilities are given by the outgoing flux in each channel divided by the incident flux [see Eq. (4.15)]

$$P_l = \frac{k_{zl}}{k_{zi}} R_l^2 \ . \tag{5.35}$$

The inelastic scattering probabilities are given by the ratio of fluxes times the phonon density of the states due to the scaling of the amplitudes [see Eqs. (4.13) and (5.22)]

$$P_l(\Delta E_z) = \frac{k_{zl}(\Delta E_z)}{k_{zi}} C(\Delta E_z) \, | \, R_l(\Delta E_z) \, |^2 \; . \qquad (5.36)$$

The trapping probabilities are due to the absorption caused by the infinitesimal imaginary part in the Schrödinger equation, and are given by the probability density in the bound states times the absorption rate [see Eq. (4.14)]

$$P_n = \frac{2m}{k_{zi}} \sum_l \int dz \, | \, \psi^{(+)}_{1ph}(z, l, E_{zi} - E_n) \, |^2 \eta^2 C(E_{zi} - E_n) \; .$$

$$(5.37)$$

Since this is a unitary approximation these probabilities all sum to one

$$\sum_l P_l + \sum_l \int \frac{d\Delta E_z}{(2\pi)} P_l(\Delta E_z) + \sum_n P_n = 1 \; . \qquad (5.38)$$

In Sec. VI we calculate these probabilities for the case of HD scattering from copper.

These probabilities have been integrated over all possible parallel momenta that lead to the same change in the energy in the motion of the molecule normal to the surface. To recover the full distribution over all of the individual final states it is just necessary to multiply the probability that has been calculated for the change in normal energy appropriate to that final state by the integrand of Eq. (5.23). This integrand is the product of the phonon density of states and the δ function that determines the final normal component of the energy from the properties of the phonons.

The flat surface approximation discussed in this section is useful because it greatly reduces the number of final states that have to be integrated over. This reduction arises from the decoupling of the motion normal to the surface from that in the plane of the surface. It is a useful approximation for studying rotationally inelastic scattering from uncorrugated surfaces because of this simplification. It is not a useful approximation for quantitatively calculating scattering probabilities for corrugated surfaces, but by calculating the interaction of inelastic scattering with rotational transitions it should be possible to qualitatively discuss scattering from a corrugated surface.

VI. RESULTS

To demonstrate the method presented in this paper we use it to calculate scattering probabilities for HD scattering from copper and compare the results with the results of the same calculation using a distorted wave Born approximation. The main purposes of this section are to demonstrate that it is possible to carry out the calculations that we have outlined in this paper and to show how selective adsorption resonances and inelastic scattering can affect each other. More extensive calculations are presented in a subsequent paper along with the details of the potential, the phonon spectrum, and the numerical

techniques that we use.

The differences between the distorted wave Born approximation and this self-consistent one-phonon approximation are most obvious at a selective adsorption resonance. At the energies near the resonance we have chosen to study, the HD molecule can scatter from the uncorrugated static copper surface into either an $l = 0$ or an $l = 1$ rotational state. Above the resonance but near it most molecules leave the surface rotationally excited, in an $l = 1$ state. The $l = 2$ rotational state plays a significant role in the rigid surface scattering when at this selective adsorption resonance the molecule can make a virtual transition into the $l = 2$ rotational state and the second lowest bound state of the potential. When the molecule can make this transition it tends to spend a long time near the surface in this rotationally excited state. The scattering probabilities are greatly affected by this resonance with the elastic, $l = 0$, scattering probability increasing to one near the center of the resonance. These scattering probabilities can be seen in the top panel of Fig. 1, the solid curve is the elastic, $l = 0$, scattering probability from a static surface, and the dashed curve is the rotationally inelastic, $l = 1$, scattering.

The shape of the elastic scattering probability as a function of incident energy is characteristic of a Fano resonance. This is not surprising because selective adsorption resonances, Fano resonances, and Feshbach resonances all
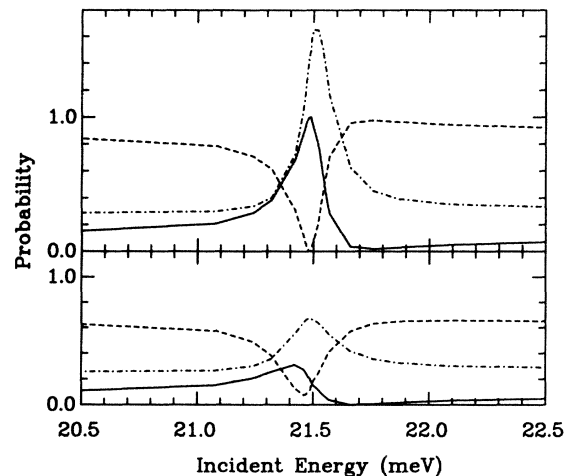

FIG. 1. Comparison of two methods for calculating scattering probabilities. The system is HD scattering at normal incidence from a zero-temperature copper surface. The top panel shows as a function of incident energy a static surface calculation of the elastic (solid curve, $l = 0$), rotationally inelastic (dashed curve, $l = 1$), and a distorted wave Born approximation calculation of the total phonon inelastic scattering probability (dashed-dotted curve). The bottom panel shows the same probabilities calculated using the self-consistent one-phonon approximation outlined in this paper. The structure in these curves is due to a selective adsorption resonance in which the HD molecule makes a virtual rotational transition to an $l = 2$ state in the second bound state of the static surface potential. The three probabilities in the top panel sum to a total probability greater than one, especially at the resonance, while the three probabilities in the bottom panel sum to one at all values of the incident energy.

result from the coupling of a bound state into a continuum of states, and all have similar lineshapes.

The elastic and rotationally inelastic probabilities sum to one for all incident energies in the static surface calculation; the distorted wave Born approximation for the inelastic scattering probabilities does not alter the static surface scattering probabilities. For the distorted wave Born approximation to be valid the inelastic scattering probability should be small compared to one. Far from the resonances the inelastic scattering probability, seen in the dotted curve in the top panel of Fig. 1, calculated using the distorted wave Born approximation is about as large as it can be for this approximation to remain valid. At the resonance this condition is clearly not satisfied as the inelastic scattering probability exceeds unity. The total probabilities calculated using these methods range from about 1.3 to 2.1. The width of the Lorentzian that can be fit to the enhancement of the inelastic scattering peak is the same as the width of the Fano resonance that can be fit to the static surface scattering probabilities.

The bottom panel of Fig. 1, for comparison, shows the results of the same calculation done using the method developed in this paper. Since this approximation is unitary the scattering probability is one for all incident energies; numerically unitarity is satisfied to the same accuracy as it is for the static surface calculation of the elastic and rotationally inelastic scattering probabilities. In this approximation the elastic and rotationally inelastic scattering probabilities are affected by the inelastic scattering probabilities. The peak in the elastic scattering probability is strongly reduced, much more strongly than the dip in the rotationally inelastic scattering probability. This suggests that dips due to selective adsorption resonances should be easier to observe experimentally than peaks. The width of the enhancement peak in the inelastic scattering has increased due to the interaction between the selective adsorption resonance and the inelastic scattering; the increase is roughly a factor of 2. This increase in the resonance width indicates that the inelastic lifetime of the resonance is comparable to the inherent rotational width.

VII. SUMMARY

The central features discussed in this paper are: (1) when the scattering is weak we justify expanding the scattering wave functions in terms of n-phonon-change operator-amplitudes, (2) these n-phonon-change amplitude operators are thermally averaged to describe the averaged scattering in terms of thermally averaged amplitudes, (3) the scattering probabilities are calculated using stationary scattering states when the interaction time is long compared to the characteristic times in the substrate, (4) the calculation can be simplified for some specific assumptions about the interaction potential, and (5) the inelastic scattering and selective adsorption resonances affect each other. The first three points reflect what we feel is the correct way to treat thermal energy helium and molecular hydrogen scattering from surfaces on which they physisorb. The fourth point details the simplification of the scattering calculation for a specific system in

which the corrugation of the surface does not play an important role and the fifth point is a result of applying these approximations to molecular hydrogen scattering. These points are detailed as follows.

(1) When the inelastic scattering is sufficiently weak that in a typical scattering event only a few phonons are created or destroyed, the scattering process can be reasonably described in terms of how the occupation of the lattice has changed. Helium and molecular hydrogen scattering at thermal energies from surfaces on which they physisorb satisfy the weak inelastic scattering criterion due to their low mass and their weak interaction with the surface. Since the elastic scattering is a quantum-mechanical process and is both observable and distinguishable from the inelastic scattering, it is necessary to treat the elastic scattering quantum mechanically and separately from the inelastic scattering. It is also important to treat the inelastic scattering in terms of the changes in the phonon modes because the inelastic scattering probabilities reflect the discrete nature of the phonon excitations of each mode. Doing the calculation self-consistently allows the range of validity of the calculation to be extended to resonant elastic scattering situations in which a perturbative approach would break down.

(2) In calculating scattering probabilities it is useful to be able to thermally average the results without having to do an explicit ensemble average of calculated scattering probabilities. In this paper we have presented a method of doing the thermal averaging by calculating the scattering in terms of thermally averaged n-phonon-change amplitudes. This part of the calculation is exact and is useful in any situation in which the expansion in terms of phonon exchanges, discussed in the preceding section, is applicable.

(3) The scattering probabilities for these systems can be calculated using stationary state scattering wave functions because the resolution with which the energy of the incident particle is defined is much smaller than typical phonon frequencies in the lattice. Stationary state calculations are useful both for their simplicity and because they emphasize the quantum-mechanical nature of the scattering process that is of interest in the scattering experiments. Since scattering experiments are performed for a better understanding of the gas-surface interaction potential and quantum-mechanical scattering, due its discrete nature, is usually more sensitive to the details of the potential, stationary state calculations are better suited to discriminate between possible potentials.

(4) The flat surface approximation is used because it speeds up the calculation while still including some of the important aspects of the potential and allowing the possibility of studying resonance phenomena. It is an approximation in which we neglect the corrugation of the surface while still treating the motion of the particle parallel to the surface. The simplification comes from the separability of the motion parallel and perpendicular to the surface. This approximation also allows separate calculation of the importance of the details of the potential and of the importance of the details of the phonon spectrum on the scattering probabilities.

(5) Our preliminary calculations show that selective ad-

sorption resonances increase the inelastic scattering at resonance conditions and that inelastic scattering broadens selective adsorption resonances. This last result will not emerge from a low-order perturbative approach. Future work will be directed toward studying in more detail how inelastic scattering and selective adsorption resonances affect each other as well as how finite substrate temperature affects the scattering process.

ACKNOWLEDGMENTS

APPENDIX A: THERMAL AVERAGING

In this appendix we discuss the thermal averaging procedure that we use in Sec. II of this paper.[26] We show that in the limit that the number of modes in the substrate goes to infinity, the contribution of correlated terms to the density matrix goes to zero. When the correlated contributions are unimportant, the thermal averages of products of operators can be written as products of thermal averages of the operators. In particular, we are interested in the thermal averages of the amplitude-operators that describe the time evolution of the amplitude of the scattering particle; these are the thermally averaged n-phonon-change amplitudes we use to calculate the scattering probabilities.

In all of the terms that contribute to a thermal expectation value each phonon creation operator must be paired with an annihilation operator; correlated terms are those in which two pairs of operators are paired together. The correlated terms do not contribute to the expectation value because they are inversely proportional to the size of the lattice (N^{-1}) due to the removal of a sum over a number of terms proportional to the size of the system by the requirement that the mode indices of two pairs of operators be equal. For the uncorrelated terms the factor of N^{-1} is cancelled by the sum over $3N$ terms that is missing in the correlated terms. These factors and sums in the amplitude operators come from the form of the interaction potential, Eq. (2.12), which has both a sum over the modes of the lattice and a factor of $N^{-1/2}$ associated with each phonon creation and annihilation operator.

By suppressing the spatially dependent functions associated with each phonon operator, all of the terms in the left-hand side of Eq. (2.15) for the density matrix can be written in the form

$$\frac{1}{\sqrt{N}}\sum_{\lambda_1}\frac{1}{\sqrt{N}}\sum_{\lambda_2}\cdots\frac{1}{\sqrt{N}}\sum_{\lambda_n}\langle a_{\lambda_1}a_{\lambda_2}^\dagger\cdots a_{\lambda_n}\rangle_{\text{th}},$$

(A1)

with arbitrary numbers of creation and destruction operators. The only terms in this expression that are nonzero are the terms which have no unpaired phonon operators. When all the operators are paired there are the same number of sums over the phonon modes, as there are factors of N^{-1}, each sum having $3N$ terms. The contributing terms can be written in the form

$$\frac{1}{N}\sum_{\lambda_1}\frac{1}{N}\sum_{\lambda_2}\cdots\frac{1}{N}\sum_{\lambda_n}\langle a_{\lambda_1}^\dagger a_{\lambda_1}a_{\lambda_2}^\dagger a_{\lambda_2}\cdots a_{\lambda_n}^\dagger a_{\lambda_n}\rangle_{\text{th}}.$$

(A2)

Here all of the phonon operators are paired in the same way that they are on the right-hand side of Eq. (2.15), which has been written in terms of operators and amplitude-operators that have the pairing already explicit. The uncorrelated terms in Eq. (A2) are those in which we replace the average of the product of paired operators by the product of the averages of the paired operators

$$\frac{1}{N}\sum_{\lambda_1}\langle a_{\lambda_1}^\dagger a_{\lambda_1}\rangle_{\text{th}}\frac{1}{N}\sum_{\lambda_2}\langle a_{\lambda_2}^\dagger a_{\lambda_2}\rangle_{\text{th}}\cdots\frac{1}{N}\sum_{\lambda_n}\langle a_{\lambda_n}^\dagger a_{\lambda_n}\rangle_{\text{th}}.$$

(A3)

In this expression all factors of N^{-1} are balanced by sums over the lattice modes. On the other hand, correlated terms have at least two of the paired operators paired with each other and are of the form

$$\frac{1}{N}\frac{1}{N}\sum_{\lambda_1}\langle a_{\lambda_1}^\dagger a_{\lambda_1}a_{\lambda_1}^\dagger a_{\lambda_1}\rangle_{\text{th}}$$

$$\times\frac{1}{N}\sum_{\lambda_2}\langle a_{\lambda_2}^\dagger a_{\lambda_2}\rangle_{\text{th}}\cdots\frac{1}{N}\sum_{\lambda_n}\langle a_{\lambda_n}^\dagger a_{\lambda_n}\rangle_{\text{th}}.$$

(A4)

Since each of the correlated terms has at least one factor of N^{-1} associated with it that is not balanced by a sum over the phonon modes these terms do not contribute in the limit that the number of lattice atoms goes to infinity. The vanishing of the correlated terms allows us to rewrite the density matrix in Eq. (2.15) in the form of Eq. (2.16), i.e., to write the average of products of operators as the product of operator averages. Then we can define the n-phonon-change amplitudes that we use to calculate the thermally averaged scattering.

As an example of how terms from the right-hand side of Eq. (2.15) contribute to the right-hand side of Eq. (2.16) let us consider one of the terms from the square of the zero-phonon-change amplitude-operator [see Eq. (2.14) for the definition of these operators]

$$\frac{1}{N}\sum_{\lambda_1}\frac{1}{N}\sum_{\lambda_2}\langle(\hat{\Psi}_{0\text{ph}}^{\lambda_1})^\dagger\hat{\Psi}_{0\text{ph}}^{\lambda_2}\rangle_{\text{th}}=\frac{1}{N}\sum_{\lambda_1}\frac{1}{N}\sum_{\lambda_2}\sum_{\{n_i\}}\frac{\exp\left[-\beta\sum_i\omega_i n_i\right]}{\left[\sum_{\{n_i\}}\exp\left[-\beta\sum_i\omega_i n_i\right]\right]}(\psi_{0\text{ph}}^{\lambda_1})^*\psi_{0\text{ph}}^{\lambda_2}\langle\{n_i\}|a_{\lambda_1}^\dagger a_{\lambda_1}a_{\lambda_2}^\dagger a_{\lambda_2}|\{n_i\}\rangle.$$

(A5)

First consider the uncorrelated contributions, those in which $\lambda_1 \neq \lambda_2$, rewriting the exponential of a sum as a product of exponentials

$$\frac{1}{N}\sum_{\lambda_1}\frac{1}{N}\sum_{\lambda_2}\langle(\hat{\Psi}_{0\mathrm{ph}}^{\lambda_1})^\dagger\hat{\Psi}_{0\mathrm{ph}}^{\lambda_2}\rangle_{\mathrm{th}}=\frac{1}{N}\sum_{\lambda_1}\frac{1}{N}\sum_{\lambda_2\neq\lambda_1}\frac{\sum\limits_{\{n_i\}}\prod\limits_{i}e^{-\beta\omega_i n_i}}{\left[\sum\limits_{\{n_i\}}\prod\limits_{i}e^{-\beta\omega_i n_i}\right]}(\psi_{0\mathrm{ph}}^{\lambda_1})^*\psi_{0\mathrm{ph}}^{\lambda_2}{n_i=\lambda_1}{n_i=\lambda_2}\,. \tag{A6}$$

Now write the sum over all sets of occupation numbers of the products over all modes as the product over all modes of the sums of the occupations for each mode

$$\sum_{\{n_i\}}\prod_{i}=\prod_{i}\sum_{n_i=0}^{\infty}\,. \tag{A7}$$

All the factors in the numerator other than those containing λ_1 and λ_2 cancel similar factors in the partition function leaving

$$\frac{1}{N}\sum_{\lambda_1}\frac{1}{N}\sum_{\lambda_2}\langle(\hat{\Psi}_{0\mathrm{ph}}^{\lambda_1})^\dagger\hat{\Psi}_{0\mathrm{ph}}^{\lambda_2}\rangle_{\mathrm{th}}$$

$$=\frac{1}{N}\sum_{\lambda_1}\frac{1}{N}\sum_{\lambda_2(\neq\lambda_1)}(\psi_{0\mathrm{ph}}^{\lambda_1})^*\psi_{0\mathrm{ph}}^{\lambda_2}$$

$$\times\frac{\sum\limits_{n=0}^{\infty}ne^{-\beta\omega_{\lambda_1}n}\sum\limits_{n=0}^{\infty}ne^{-\beta\omega_{\lambda_2}n}}{\sum\limits_{n=0}^{\infty}e^{-\beta\omega_{\lambda_1}n}\sum\limits_{n=0}^{\infty}e^{-\beta\omega_{\lambda_2}n}}\,. \tag{A8}$$

These two ratios just give the thermal expectation of the occupation of each of the modes

$$\frac{1}{N}\sum_{\lambda_1}\frac{1}{N}\sum_{\lambda_2}\langle(\hat{\Psi}_{0\mathrm{ph}}^{\lambda_1})^\dagger\hat{\Psi}_{0\mathrm{ph}}^{\lambda_2}\rangle_{\mathrm{th}}$$

$$=\frac{1}{N}\sum_{\lambda_1}\frac{1}{N}\sum_{\lambda_2(\neq\lambda_1)}(\psi_{0\mathrm{ph}}^{\lambda_1})^*\psi_{0\mathrm{ph}}^{\lambda_2}n_{\lambda_1}n_{\lambda_2}$$

$$=\frac{1}{N}\sum_{\lambda_1}\frac{1}{N}\sum_{\lambda_2(\neq\lambda_1)}\langle\hat{\Psi}_{0\mathrm{ph}}^{\lambda_1}\rangle_{\mathrm{th}}^*\langle\hat{\Psi}_{0\mathrm{ph}}^{\lambda_2}\rangle_{\mathrm{th}}\,. \tag{A9}$$

These and all the other uncorrelated terms are the contributions to the right-hand side of Eq. (2.16). Now consider the correlated terms; the calculation for these terms remains the same until

$$\frac{1}{N^2}\sum_{\lambda_1}(\psi_{0\mathrm{ph}}^{\lambda_1})^*\psi_{0\mathrm{ph}}^{\lambda_1}\frac{\sum\limits_{n=0}^{\infty}n^2e^{-\beta\omega_{\lambda_1}n}}{\sum\limits_{n=0}^{\infty}e^{-\beta\omega_{\lambda_1}n}}$$

$$=\frac{1}{N^2}\sum_{\lambda_1}(\psi_{0\mathrm{ph}}^{\lambda_1})^*\psi_{0\mathrm{ph}}^{\lambda_1}(2n_{\lambda_1}^2+n_{\lambda_1})$$

$$\neq\frac{1}{N^2}\sum_{\lambda_1}\langle\hat{\Psi}_{0\mathrm{ph}}^{\lambda_1}\rangle_{\mathrm{th}}^*\langle\hat{\Psi}_{0\mathrm{ph}}^{\lambda_1}\rangle_{\mathrm{th}}\,. \tag{A10}$$

Although this result is of a different form from the terms

in Eq. (A8), there is an additional N^{-1} factor associated with losing a sum over the phonon modes so that the difference in form is unimportant. This factor causes the contributions of the correlated terms to go to zero in the limit that the number of lattice atoms goes to infinity. The restricted sum in Eq. (A9) can be made unrestricted in the same limit because the error is also proportional to N^{-1}.

APPENDIX B: STATIONARY STATE SCATTERING

In this appendix we outline the derivation of the results in Sec. IV of this paper. First we show how to calculate the scattering probabilities in terms of matrix elements of the zero-phonon-change scattering state by taking the limit that the initial momentum uncertainty of the wave packet goes to zero. Then we show that the same scattering probabilities can be calculated from the asymptotic form of the zero- and one-phonon-change scattering states.

The derivation of the results in this Appendix requires four limits to be taken in this order: the imaginary part η that determines the boundary conditions goes to zero, the wave packet start far enough from the surface that it is not interacting with it, the initial momentum uncertainty of the wave packet goes to zero, and the final time minus the initial time (t_f-t_i) goes to infinity. The first two and the last limits are properties of description of the calculation; the imaginary part has to be small enough that the normalization of the incident plane wave is not affected by it, we choose to have the particle start in a state that is independent of the surface, and want to measure the state of the particle after it has ceased interacting with the surface.

The third limit is a property of the scattering system and may not always be valid. To take this limit (the initial momentum uncertainty going to zero) the interaction time of the scattering process should be longer than the characteristic time scales of the phonons. The interaction time is set by the time difference from the time when the wave packet first interacts with the phonons to the time when all of the incident wave packet has entered the interaction region. A lower bound on the interaction time, set by the energy-time uncertainty principle, is Planck's constant divided by the energy resolution of the incident wave packet. A lower bound on this lower bound is set by the energy resolution of the scattering experiment. Since the times scales of the phonons are their oscillation periods and the phonon frequencies go continuously to zero, there are always phonons in the surface with time scales longer than the interaction time. For this reason stationary state scattering is unable to describe all of the

scattering processes, but if the interaction time is longer than most relevant time scales and if the low-frequency phonons do not dominate the scattering process it should be able to describe the scattering within the resolution of the experiment. In particular, if low-energy modes are not important in the stationary state scattering calculation they are not important in a wavepacket scattering situation because wave packets will not strongly excite modes for which the oscillation period is longer than the interaction time.

To derive the matrix elements for the scattering probabilities we expand the initial wave packet in terms of the scattering state solutions in the one-phonon-change approximation. Then we use the spectral representation of the Green function to convert the time dependent exponentials into energy-conserving δ functions in the limit that the time difference goes to infinity. Finally the amplitude factors that describe the initial wave packet become a δ function.

The initial wave packet can be expanded in incoming plane waves

$$\phi(\mathbf{r},t)=\int \frac{d^3k}{(2\pi)^3}a(\mathbf{k})e^{-i\mathbf{k}\cdot\mathbf{r}}e^{-iE_k(t-t_i)}, \tag{B1}$$

where the time dependence gives the free motion of the particle. The expansion coefficient, $a(\mathbf{k})$, is sharply peaked around the incident wave vector $\mathbf{k}_i$. The boundary conditions that the Lippmann-Schwinger equations for the zero- and one-phonon-change amplitudes obey allow us to expand the initial wave packet in terms of these scattering states with the same coefficients as the expansion in plane waves

$$\psi_{0ph}(\mathbf{r},t)=\int \frac{d^3k}{(2\pi)^3}a(\mathbf{k})\psi_{0ph}^{(+)}(\mathbf{r},\mathbf{k})e^{-iE_k(t-t_i)}, \tag{B2}$$

$$\psi_{1ph}(\mathbf{r},t,\lambda,\sigma)=\int \frac{d^3k}{(2\pi)^3}a(\mathbf{k})\psi_{1ph}^{(+)}(\mathbf{r},\mathbf{k},\lambda,\sigma)e^{-iE_k(t-t_i)}. \tag{B3}$$

This time dependence gives the full time dependence of the scattering particle in the one-phonon-change approximation. Inserting the equation for the one-phonon-change amplitude into Eq. (4.7), gives the expansion of the state of the scattering particle at any time in terms of outgoing scattering states of the static surface. To write the scattering probability in the form of Eq. (4.9) the one-phonon-change amplitudes are written in terms of the zero-phonon-amplitude using the Lippmann-Schwinger Eq. (4.5), and the static surface Green function is written in terms of its spectral representation

$$G_1^r(\mathbf{r},\mathbf{r}',E)=\int \frac{d^3k}{(2\pi)^3}\frac{\chi^{(-)}(\mathbf{r},\mathbf{k})[\chi^{(-)}(\mathbf{r}',\mathbf{k})]^*}{E-E_k+i\eta}$$
$$+\int \frac{d^2K}{(2\pi)^2}\sum_n \frac{\chi(\mathbf{r},n,\mathbf{K})[\chi(\mathbf{r}',\mathbf{K},n)]^*}{E-E_{n,\mathbf{K}}+i\eta}. \tag{B4}$$

The sum over n in the second sum in the spectral representation is restricted to run only over the bound states for a particular value of $\mathbf{K}$; since all of the $E_{n,\mathbf{K}}$ must be less than zero, some values of $\mathbf{K}$ have no bound states for sufficiently large energy in the motion parallel to the surface. The normalization of the scattering states allows one three-dimensional spatial and one three-dimensional k-space integral to be done trivially, leaving

$$P(\mathbf{k}_f,t_f)=\frac{1}{N}\sum_{\lambda,\sigma}n_{\lambda\sigma}\left|\int \frac{d^3k}{(2\pi)^3}a(\mathbf{k})\frac{e^{-iE_k(t_f-t_i)}}{E_k-\sigma\omega_\lambda-E_{k_f}+i\eta}\int d^3r(\chi^{(-)})^*(\mathbf{r},\mathbf{k}_f)[V_{\lambda\sigma}(\mathbf{r})]^*\psi_{0ph}^{(+)}(\mathbf{r},\mathbf{k})\right|^2. \tag{B5}$$

This expression is valid for any time, in particular the limit that $t_f-t_i\to\infty$ in which we calculate the scattering probabilities.

Expanding the square of the absolute value as a product of complex conjugates gives

$$P(\mathbf{k}_f,t_f)=\frac{1}{N}\sum_{\lambda,\sigma}n_{\lambda\sigma}\int \frac{d^3k}{(2\pi)^3}\int \frac{d^3k'}{(2\pi)^3}[a(\mathbf{k})]^*a(\mathbf{k}')\frac{e^{-i(E_k-\sigma\omega_\lambda-E_{k_f}+i\eta)(t_f-t_i)}}{E_k-\sigma\omega_\lambda-E_{k_f}+i\eta}\frac{e^{i(E_{k'}-\sigma\omega_\lambda-E_{k_f}-i\eta)(t_f-t_i)}}{E_{k'}-\sigma\omega_\lambda-E_{k_f}-i\eta}$$

$$\times \left[\int d^3r(\chi^{(-)})^*(\mathbf{r},\mathbf{k}_f)[V_{\lambda\sigma}(\mathbf{r})]^*\psi_{0ph}^{(+)}(\mathbf{r},\mathbf{k})\right]^*$$

$$\times \left[\int d^3r(\chi^{(-)})^*(\mathbf{r},\mathbf{k}_f)[V_{\lambda\sigma}(\mathbf{r})]^*\psi_{0ph}^{(+)}(\mathbf{r},\mathbf{k}')\right]. \tag{B6}$$

Each of the factors with time exponentials become energy δ functions in the limit that the time difference goes to infinity and the imaginary part goes to zero, as can be seen by converting each expression into a time integral. Because the interaction potential conserves parallel momentum, we can factor from each of the matrix elements a parallel momentum conserving δ function

$$\frac{1}{A}(2\pi)^2\delta^{(2)}(\mathbf{K}_f+\sigma\mathbf{Q}_\lambda+\mathbf{G}-\mathbf{K}), \tag{B7}$$

which gives unity when integrated over. The expansion coefficients have chosen so that the overlap integral over $\mathbf{k}$ is zero if one of the arguments is displaced by a surface reciprocal-lattice vector

$$\int \frac{d^3k}{(2\pi)^3} a(\mathbf{k}) a(\mathbf{k}+\mathbf{G}) = 0 , \tag{B8}$$

and their modulus squared becomes a δ function as the initial momentum uncertainty goes to zero. Integrating over the δ functions gives the inelastic scattering probability result, Eq. (4.8). Replacing the outgoing static surface scattering state by a bound state and performing the same manipulations gives Eq. (4.9) for the trapping probability.

The derivation of the elastic scattering probability proceeds in the same manner, complicated by the presence of outgoing states scattered from the static surface. The elastic scattering from the static surface is described by a reflection coefficient, $R(\mathbf{k}_f,\mathbf{k}_i)$ that includes the possibility of diffraction

$$\int d^3r (\chi^{(-)})^*(\mathbf{r},\mathbf{k}_f) \chi^{(+)}(\mathbf{r},\mathbf{k}_i)$$

$$= \sum_{\mathbf{G}} R(\mathbf{k}_f,\mathbf{k}_i)(2\pi)^3 \delta^{(2)}(\mathbf{K}_i - \mathbf{K}_f - \mathbf{G}) \frac{k_{zf}}{m} \delta(E_i - E_f) . \tag{B9}$$

Inserting Eq. (4.5) into Eq. (4.4) gives an equation for the zero-phonon-change scattering state in terms of itself and the self-energy, Eq. (4.11). The elastic scattering probability is given by inserting the resulting expression into the first term on the right-hand side of Eq. (4.7). After factoring out δ functions from all of the terms using the same tricks that we have used for the inelastic scattering probabilities for the terms in which the self-energy ap-

pears, the derivation of Eq. (4.10) proceeds in much the same manner as the derivation of Eq. (4.8). The second term, containing the self-energy, in Eq. (4.10) cancels the part of the elastic scattering intensity that has been lost to inelastic scattering. The energy conserving δ function restricts possible outgoing states to those that have the same energy as the incident particle, i.e., elastic scattering.

Rotational degrees of freedom only complicate these derivations by adding a rotational state subscript to almost all of the factors. The rotational transitions can be treated in the same way that diffraction was treated in the elastic scattering probability.

The rest of this Appendix is concerned with the calculation of these scattering probabilities from the asymptotic forms of the scattering states. For the inelastic scattering probabilities we need the asymptotic form of the static surface Green function in the limit that the z component of the first argument goes to infinity

$$\lim_{z \to \infty, z > z', E_\mathbf{k} > 0} G_1^r(\mathbf{r},\mathbf{r}',E)$$

$$= \int \frac{d^2K'}{(2\pi)^2} \frac{-im}{k_z'} e^{i\mathbf{K}' \cdot \mathbf{R}} e^{ik_z' z} [\chi^{(-)}(\mathbf{r}',\mathbf{k}')]^* , \tag{B10}$$

$$(k_z')^2 = 2mE - (K')^2 ,$$

where the $\mathbf{K}'$ integration is restricted to those values for which $(k_z')^2 > 0$. Using this form and Eq. (4.5), the asymptotic form of the wave function is

$$\lim_{z \to \infty, E_\mathbf{k} > 0} \psi_{1ph}^{(+)}(\mathbf{r},\mathbf{k},\lambda,\sigma) = -\frac{-im}{k_z'} e^{i\mathbf{K}' \cdot \mathbf{R}} e^{ik_z' z} \left[\int d^3r' [\chi^{(-)}(\mathbf{r}',\mathbf{k}')]^* V_{\lambda\sigma}(\mathbf{r}')^* \psi_{0ph}^{(+)}(\mathbf{r}',\mathbf{k}) \right] ,$$

$$\mathbf{K}' = \mathbf{K} - \sigma \mathbf{Q}_\lambda, \quad (k_z')^2 = 2m(E_\mathbf{k} - \sigma\omega_\lambda) - (K')^2 . \tag{B11}$$

The flux density in this state for large distances (squaring it and multiplying by the outgoing velocity) divided by the incident velocity gives the contribution from each mode to the inelastic scattering probability. Summing this result over all of the phonon modes weighted by the thermal occupation of each mode and multiplying by energy and parallel momentum conserving δ functions gives the result for the inelastic scattering distribution Eq. (4.12). A similar treatment of the elastic scattering probability yields Eq. (4.10). These results show that the scattering probabilities can be given by the flux in each outgoing channel of the zero- and one-phonon-change amplitudes divided by the incident flux.

The expression for the trapping probability, Eq. (4.9) can be calculated from the behavior of the static surface Green function in the limit that the infinitesimal imaginary part goes to zero

$$\lim_{\eta \to 0, E \to E_{n,\mathbf{K}}} G_1^r(\mathbf{r},\mathbf{r}',E) = \int \frac{d^2K'}{(2\pi)^2} \frac{\chi(\mathbf{r},n,\mathbf{K}')\chi(\mathbf{r}',n,\mathbf{K}')^*}{E - E_{n,\mathbf{K}'} + i\eta} . \tag{B12}$$

Using this expression the one-phonon-change amplitude at the bound-state energy becomes

$$\lim_{\eta \to 0,} \psi_{1ph}[(\mathbf{r},\mathbf{k},\lambda,\sigma)] = \frac{1}{i\eta} \int \frac{d^2K'}{(2\pi)^2} \chi(\mathbf{r},n,\mathbf{K}') \left[\int d^3r' \chi(\mathbf{r}',n,\mathbf{K}')^* V_{\lambda\sigma}(\mathbf{r}')^* \psi_{0ph}^{(+)}(\mathbf{r}',\mathbf{k}) \right] ,$$

$$\mathbf{K}' = \mathbf{K} - \sigma \mathbf{Q}_\lambda, \quad E_{n,\mathbf{K}} = m(E_\mathbf{k} - \sigma\omega_\lambda) . \tag{B13}$$

Since the bound-state wave functions are normalized to the area of the surface, Eq. (4.2), squaring the amplitude, integrating the result over all space, dividing by the area of the surface, and multiplying by the imaginary part squared gives the contribution to the trapping for each phonon mode. Summing over all the phonon modes

weighted by the thermal occupation and multiplying by energy and parallel momentum conserving δ functions gives the result for the trapping probability Eq. (4.13). This result can also be derived from the absorption of probability from the system due to the small imaginary part and trapping. In this case we have to evaluate Eq.

(B13) for energies near the bound state, square the amplitudes, multiply by the absorption rate, η, and integrate over both all space and the energies near the bound states. For small enough η all the matrix elements are constant so the energy integral is just the integral of a Lorentzian, which gives the additional factor of η that appears in Eq. (B13).

The only difficulty that arises in using these results for the flat surface approximation is that the spectral representation of the Green function no longer has the same form as it does in Eq. (B4) because the motions parallel

and perpendicular to the surface decouple. In particular, in the bound-state terms there are the same number of bound states for every parallel momentum, some of which have a positive total energy. In a real system the slightest coupling of the two motions would couple these positive energy states to the continuum and they are no longer bound states. This defect of the flat surface approximation is not important for one-phonon-change scattering at normal incidence but would complicate the interpretation of the results for off-normal scattering conditions when the final parallel momentum can be high.

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