OFFICE OF NAVAL RESEARCH

Contract N00014-89-J-1530

Task No. NR372-160

TECHNICAL REPORT NO. 32

EXACT THEORY OF ONE-PHONON AMPLITUDES IN DIFFRACTIVE ATOM-SURFACE SCATTERING

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Prepared for publication

in

The Structure of Surfaces III

Proceedings of the Third International

Conference on the Structure of Surfaces,

eds. M. A. Van-Hove et al., Springer Verlag (New York (1991))

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November 1990

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER TECHNICAL REPORT NO. 32	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER N00014-01
4. TITLE (and Subtitle) EXACT THEORY OF ONE-PHONON AMPLITUDES IN DIFFRACTIVE ATOM-SURFACE SCATTERING		5. TYPE OF REPORT & PERIOD COVERED TECHNICAL REPORT 1/01/90-12/31/90 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) M. FLATTE		8. CONTRACT OR GRANT NUMBER(s) N00014-89-J-1530
9. PERFORMING ORGANIZATION NAME AND ADDRESS UNIVERSITY OF CALIFORNIA PHYSICS DEPARTMENT, SANTA BARBARA, CA 93106 CONTRACTS & GRANTS, CHEADLE HALL, ROOM 3227		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS TASK NO. 372-160
11. CONTROLLING OFFICE NAME AND ADDRESS OFFICE OF NAVAL RESEARCH ELECTRONICS & SOLID STATE PHYSICS PROGRAM 800 N. QUINCY, ARLINGTON, VA 22217		12. REPORT DATE November 14, 1990 13. NUMBER OF PAGES - 2 -
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) OFFICE OF NAVAL RESEARCH DETACHMENT 1030 EAST GREEN STREET PASADENA, CA 91106		15. SECURITY CLASS. (of this report) UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

"APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED"

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

REPORTS DISTRIBUTION LIST FOR ONR PHYSICS DIVISION OFFICE

18. SUPPLEMENTARY NOTES

The Structure of Surfaces III, Proceedings of the Third International Conference on the Structure of Surfaces, eds. M. A. Van-Hove et al., Springer Verlag (New York: (1991))

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Atom-Surface Scattering, Atom-Surface Potential, Long-Wavelength-Phonon Amplitudes, Reprints (THD) ← is derived

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

We derive an expression for the probability of creating or annihilating one long-wavelength surface or bulk phonon during a scattering event, which depends on the bulk elastic constants but is independent of the details of the atom-target potential and of force constant changes near the surface. This expression is exact if the inelastic scattering is "weak" (the meaning of which is explained in the text). This theory should be experimentally verifiable, e.g. for 20 meV He atoms scattered from a W-surface. Key words 5

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Exact Theory of One-Phonon Amplitudes in Diffractive Atom-Surface Scattering

Michael E. Flatté

This paper is an extension of a previous paper, **Exact Theory of One-Phonon Amplitudes in Atom-Surface Scattering**, by Michael E. Flatté and Walter Kohn. That paper derives an expression for the probability of creating or annihilating one long-wavelength phonon in an atom-surface scattering event for a system with negligible diffraction. The expression is independent of the atom-surface potential and of force constant changes near the surface. It is exact if the inelastic scattering is weak. This paper derives a result with the same qualitative features for systems with arbitrary diffraction.

Determining the atom-surface potential is a complicated problem which is very important for such fields as corrosion, catalysis and surface diffusion. Atom-surface scattering experiments are good probes of this potential. It is useful for an experimenter to know that some phonons will be ineffective in probing this potential. Our paper proves that this category includes all long-wavelength phonons when the total inelastic scattering is weak.

Furthermore, an exact expression for the scattering probability which is independent of the atom-surface potential may be useful for calibrating other experiments.

Exact Theory of One-Phonon Amplitudes in Diffractive Atom-Surface Scattering

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(To be published in the proceedings of the Third International Conference on the Structure of Surfaces (ICSOS-3))

Abstract I derive an expression for the probability of creating or annihilating one long-wavelength surface or bulk phonon during a scattering event in a system with diffraction scattering. This expression depends on the *bulk* elastic constants but is independent of force constant changes near the surface and of the details of the atom-target potential. If the inelastic scattering is weak (as defined in the text), the expression is exact.

In a system where the only elastic scattering is specular, the bulk elastic constants of the target and the quantum numbers of the decoupled atom-target system entirely determine the probability for the weak inelastic creation (or annihilation) of a long-wavelength phonon [1]. A heuristic explanation follows of why an expression with similar qualities should also exist for systems with non-specular elastic scattering. In particular, the expression is independent of (1) deviations of force constants from bulk values near the surface of a target uncoupled to atoms and (2) the functional form of the atom-target interaction potential $V(\vec{r};\{\vec{u}_i\})$. where $\vec{r}$ is the position of the colliding atom and $\vec{u}_i$ the displacement of the i'th target atom.

Displacements in the surface region associated with a phonon of small wave-vector $\vec{q}$ are quasi-rigid for $(qa)^{-1}$ layers perpendicular to the surface, where a is the lattice constant. If $qa \ll 1$, force constant changes in a few layers near the surface are irrelevant to the displacements associated with this phonon.

The functional form of V is irrelevant because to lowest order in qa, the first-order expression for the probability is proportional to

$$\left[\int_{\mathbf{V}} \langle \Psi_o^{(1)}|\vec{r}\rangle \frac{\partial V(\vec{r})}{\partial z} \langle \vec{r}|\Psi_o^{(2)}\rangle d\vec{r}\right]^2 . \qquad (1)$$

Here $V(\vec{r}) = V(\vec{r};\{\vec{0}\})$ and the $|\Psi_o\rangle$'s are wave functions of the atom-rigid target system with the same crystal momentum parallel to the surface

($\vec{K}$) and energy (E). When there is only elastic scattering, the case with a rigid target, for a given $\vec{K}$ and E there is a discrete set of asymptotic perpendicular momenta $k_{\vec{G}}$ the atom may have. These channels, incoming if $k_{\vec{G}} < 0$, outgoing if $k_{\vec{G}} > 0$, are labelled by surface reciprocal lattice vectors $\vec{G}$. The atom involved in an inelastic scattering process where $qa \ll 1$ will emerge near one of these channels. The probability that the atom emerges near channel $\vec{G}_o$ is calculated by choosing the amplitude of all incoming channels except $\vec{0}$ to be 0 for $|\Psi_o^{(1)}\rangle$, and the amplitude of all outgoing channels except $\vec{G}_o$ to be 0 for $|\Psi_o^{(2)}\rangle$. When both wave functions are normalized to unit incoming flux in channel $\vec{0}$, the integral represents the total force applied in transferring the atom from incoming channel $\vec{0}$ to outgoing channel $\vec{G}_o$. This is rigorously given by the change in perpendicular momentum per unit time and area, *i.e.*, $-\hbar(k_{\vec{0}} + k_{\vec{G}})$.

The results are exact in the limit where the following conditions are satisfied:

$$\frac{\hbar}{Mcb} \ll 1 \qquad (2a) \qquad \frac{m}{M}\left(\frac{V_o}{\hbar\omega_D}\right)^2 \ll 1 \qquad (2b) \qquad E_a \lesssim \hbar\omega_D \qquad (2c)$$

$$k_B T \lesssim \hbar\omega_D \qquad (2d) \qquad qa \ll 1 \qquad (2e),$$

where c is a characteristic velocity of a phonon in the target, b is the range of the atom-target potential and V_o is its depth. m is the mass of the colliding atom and E_a is its incident energy. M is the mass of a target atom, ω_D is the Debye frequency, and T is the temperature of the target.

The condition (2a) allows one to stop the expansion of V after the first order term

$$V(\vec{r};\{\vec{u}_i\}) = V(\vec{r}) + \vec{u}_i \cdot \nabla_{\vec{u}_i} V(\vec{r};\{\vec{0}\}) \qquad (3)$$

Condition (2b) ensures that in calculating the inelastic scattering, the last term in (3) can be treated to lowest order.

Derivation of the Probability for Production of Long-Wavelength Phonons

This derivation requires the use of a variational principle developed for multichannel scattering in nuclear collisions [2]. The following assumptions simplify this presentation: (1) the atom only interacts with the uppermost layer of target atoms and (2) the units are chosen so that the

target's volume and the area of its interacting surface are 1. The results remain unchanged if these assumptions are dropped.

To first order in $\{u_i\}$, the Hamiltonian consists of an unperturbed Hamiltonian H_o, which ignores phonon coupling to the colliding atom, and H_1, which couples the atom linearly to the phonons.

$$H = H_{particle} + H_{target} + V(\vec{r}, \{\vec{u}_i\}) = H_o + H_1 + \mathcal{O}(u^2) \qquad (4)$$

where

$$H_o = \frac{p^2}{2m} + \sum_{\vec{q},\nu} \hbar\omega_{\vec{q},\nu} n_{\vec{q},\nu} + V(\vec{r}) \quad (5a) \qquad H_1 = \sum_{i,\alpha} \frac{\partial V}{\partial u_{i,\alpha}}(\vec{r}) u_{i,\alpha}. \quad (5b)$$

Here α denotes a cartesian coordinate and $n_{\vec{q},\nu} = a^{\dagger}_{\vec{q},\nu} a_{\vec{q},\nu}$ is the occupation of phonon mode $\vec{q},\nu$, where ν is the phonon's branch.

Let $|\Psi^{(1)}\rangle$ and $|\Psi^{(2)}\rangle$ be two wave functions for the combined target-atom system with the same E and $\vec{K}$. Their asymptotic form is

$$\langle \vec{r}|\Psi^{(\mu)}\rangle = \sum_{\{n\},\vec{G}} |\{n\}\rangle e^{\imath(\vec{K}_{\{n\}}+\vec{G})\cdot\vec{R}} \left[A^{(\mu)}_{\vec{G},\{n\}} e^{-\imath k_{\vec{G},\{n\}} z} + B^{(\mu)}_{\vec{G},\{n\}} e^{\imath k_{\vec{G},\{n\}} z} \right] \quad (6)$$

where the sum is carried out over all surface reciprocal lattice vectors $\vec{G}$ and phonon occupations $\{n\}$, $\vec{R}$ is the atom's displacement parallel to the surface, and

$$\vec{K}_{\{n\}} = \vec{K} - \sum_{\vec{q},\nu} n_{\vec{q},\nu}\vec{q}, \quad k^2_{\vec{G},\{n\}} + (\vec{K}_{\{n\}} + \vec{G})^2 = \frac{2m}{\hbar^2}(E - \sum_{\vec{q},\nu} \hbar\omega_{\vec{q},\nu} n_{\vec{q},\nu}). \qquad (7)$$

Choose two trial functions $|\Psi^{(1)}_t\rangle$ and $|\Psi^{(2)}_t\rangle$, such that $A^{(2)}_{\vec{G},\{n\},t} = A^{(2)}_{\vec{G},\{n\}}$ and $B^{(1)}_{\vec{G},\{n\},t} = B^{(1)}_{\vec{G},\{n\}}$. Then the equation

$$\int_{\mathbf{V}} \langle \Psi^{(1)}_t|\vec{r}\rangle (H - E) \langle \vec{r}|\Psi^{(2)}_t\rangle d\vec{r} = \frac{-\imath\hbar^2}{m} \sum_{\vec{G},\{n\}} k_{\vec{G},\{n\}} B^{(1)*}_{\vec{G},\{n\}} \delta B^{(2)}_{\vec{G},\{n\}}, \quad (8)$$

where $\delta B^{(2)}_{\vec{G},\{n\}} = B^{(2)}_{\vec{G},\{n\},t} - B^{(2)}_{\vec{G},\{n\}}$, is correct to first order in the errors of the wave functions.

This variational principle is of value because the integral can be evaluated analytically to lowest order in qa for trial functions which are eigenfunctions of H_o. These wavefunctions have the form [3]

$$\langle\vec{r}|\Psi_{\vec{K},E,\{n\}}\rangle = |\{n\}\rangle \sum_{\vec{G}} e^{\imath(\vec{K}_{\{n\}}+\vec{G})\cdot\vec{r}}\phi_{\vec{G},\vec{K},E,\{n\}}(z) \tag{9}$$

The set of all $\phi_{\vec{G}}(z)$ for a given $\vec{K}$, E and $\{n\}$ satisfy the following coupled equations, where $E_a = E - \sum_{\vec{q},\nu}\hbar\omega_{\vec{q},\nu}n_{\vec{q},\nu}$ and $\sum_{\vec{H}} e^{\imath\vec{H}\cdot\vec{r}}V_{\vec{H}}(z) = V(\vec{r})$:

$$\left[-\frac{\hbar^2\partial_z^2}{2m} - (E_a - \frac{\hbar^2(\vec{K}_{\{n\}}+\vec{G})^2}{2m})\right]\phi_{\vec{G}}(z) = -\sum_{\vec{G}'} V_{\vec{G}-\vec{G}'}(z)\phi_{\vec{G}'}(z). \tag{10}$$

Let $|\Psi^{(2)}_{\{n_2\},o}\rangle$ be an eigenfunction of H_o with energy E, crystal momentum $\vec{K}$ and $|\{n_2\}\rangle = |\ldots n_{\vec{q},\nu}\ldots\rangle$ for which $A_{\vec{0}} = (m/\hbar k_{\vec{0}})^{1/2}$ and all other A's are 0. Let $|\Psi^{(1)}_{\{n_1\},o}\rangle$ be an eigenfunction of H_o with eigenvalues E, $\vec{K}$ and $|\{n_1\}\rangle = |\ldots n_{\vec{q},\nu}+1\ldots\rangle$ for which $A_{\vec{0}} = (m/\hbar k_{\vec{0}})^{1/2}$ and $B_{\vec{G}_o}$ is the only nonzero B.

For these trial functions, the integral is $\int_{\mathbf{V}}\langle\Psi^{(1)}_{\{n_1\},o}|\vec{r}\rangle H_1\langle\vec{r}|\Psi^{(2)}_{\{n_2\},o}\rangle d\vec{r}$. Expanding the $\vec{u}_i$ in normal modes and rewriting yields

$$H_1 = \sum_{\vec{q},\nu,\alpha} e^{-\imath\vec{q}\cdot\vec{R}}u_{\vec{q},\nu,\alpha}\sum_i \frac{\partial V}{\partial u_{i,\alpha}}(\vec{r})e^{-\imath\vec{q}\cdot(\vec{R}_i-\vec{R})} + \text{c.c.} \tag{11}$$

The second exponential can be ignored if the wavelength of the phonon is much larger than the range of the coupling potential, similar to a and b, since unless $q(R_i - R) \ll 1$ $(\partial V/\partial u_i)$ will vanish. Furthermore, $\sum_i \partial V/\partial u_{i,\alpha}(\vec{r}) = -\partial V(\vec{r})/\partial r_\alpha$ since $V(\vec{r};\{u_i\})$ depends only on $\vec{r} - \vec{u}_i$. Finally, defining $\vec{u}_{\vec{q},\nu} = \vec{U}_{\vec{q},\nu}(a^\dagger_{\vec{q},\nu} + a_{-\vec{q},\nu})$ yields

$$H_1 = -\sum_{\vec{q},\nu,\alpha} e^{-\imath\vec{q}\cdot\vec{R}}\frac{\partial V}{\partial r_\alpha}(\vec{r})U_{\vec{q},\nu,\alpha}(a^\dagger_{\vec{q},\nu} + a_{-\vec{q},\nu}) + \text{c.c.} \tag{12}$$

Transforming the resulting integral with (5a) and Green's Theorem yields

$$(n_{\vec{q},\nu}+1)^{1/2}U_{\vec{q},\nu,\alpha}\sum_{\vec{G},\vec{G}',\alpha}\int_{\mathbf{S}} dS\Big[e^{-\imath\vec{G}\cdot\vec{R}}\phi^{(1)*}_{\vec{G},\{n_1\}}(z)\frac{\partial}{\partial r_\alpha}\hat{n}\cdot\nabla\phi^{(2)}_{\vec{G}',\{n_2\}}(z)$$
$$-\hat{n}\cdot\nabla\left(e^{-\imath\vec{G}\cdot\vec{R}}\phi^{(1)*}_{\vec{G},\{n_1\}}(z)\right)\frac{\partial}{\partial r_\alpha}\phi^{(2)}_{\vec{G}',\{n_2\}}(z)\Big] \tag{13}$$

where $\hat{n}$ is the unit normal to the surface S which bounds V. Because of the small difference in atomic energy and parallel crystal momentum between $|\Psi^{(1)}_{\{n_1\},o}\rangle$ and $|\Psi^{(1)}_{\{n_2\},o}\rangle$, $\phi^{(1)*}_{\vec{G},\{n_1\}}$ may be replaced by $\phi^{(1)*}_{\vec{G},\{n_2\}}$. The vanishing of the resulting integrals for $n_x(\partial/\partial x)$ and $n_y(\partial/\partial y)$ and evaluation of the remainder yields

$$\frac{\hbar^2 U_{\vec{q},\nu,\alpha}(n_{\vec{q},\nu}+1)^{1/2}}{2m}\sum_{\vec{G}}\left[\phi^{(1)*}_{\vec{G}}\frac{\partial^2\phi^{(2)}_{\vec{G}}}{\partial r_\alpha \partial z}-\frac{\partial\phi^{(1)*}_{\vec{G}}}{\partial z}\frac{\partial\phi^{(2)}_{\vec{G}}}{\partial r_\alpha}\right]_{z=\infty} \tag{14}$$

Since $k_{\vec{G}_o}B^{(1)*}_{\vec{G}_o,\{n_2\},o}B^{(2)}_{\vec{G}_o,\{n_2\},o} = k_{\vec{0}}A^{(1)*}_{\vec{0},\{n_2\},o}A^{(2)}_{\vec{0},\{n_2\},o}$, expression (14) is zero if α denotes x or y, and when α denotes z it is $-(n_{\vec{q},\nu}+1)^{1/2}U_{\vec{q},\nu,z}\hbar(k_{\vec{0}}+k_{\vec{G}_o})$.

The differential probability of scattering an atom into final angle Ω with energy E_a, per unit incident perpendicular flux is

$$\frac{d^2P}{d\Omega dE_a} = (2\pi\hbar^2 k_{\vec{0}}/m)|\delta B^{(2)}_{\vec{G}_o,\{n_1\}}/A^{(2)}_{\vec{0},\{n_2\}}|^2\rho(E_a)g(\hbar\omega_{\vec{q},\nu},\vec{Q}) \tag{15}$$
$$= (k_{\vec{0}}k/4\pi^2)(k_{\vec{0}}+k_{\vec{G}})^2U^2_{\vec{q},\nu,z}(n_{\vec{q},\nu}+1)|B^{(2)}_{\vec{G}_o,\{n_2\},o}/A^{(2)}_{\vec{0},\{n_2\}}|^2 g(\hbar\omega_{\vec{q},\nu};\vec{Q})$$

where k is the atom's final momentum, $\rho(E_a)$ is the density per unit energy of atomic states with momentum in final angle Ω, and $g(\hbar\omega_{\vec{q},\nu};\vec{Q})$ is the density per unit energy of phonons with frequency $\omega = \omega_{\vec{q},\nu}$ and surface wavevector $\vec{Q}$.

For a target which is isotropic in the long wavelength limit, $U_{\vec{q},\nu,z}$ and $g(\hbar\omega_{\vec{q},\nu};\vec{Q})$ are well known, depend only on bulk elastic constants, density, ω and Q, and are given in simple form in Ref. 1. For non-isotropic targets, $U_{\vec{q},\nu,z}$ and $g(\hbar\omega_{\vec{q},\nu};\vec{Q})$ depend in a more complicated way on the bulk elastic constants, density, Miller indices of the surface, ω and $\vec{Q}$.

Acknowledgments

This work is supported by the National Science Foundation through a graduate fellowship and Grant No. DMR87-03434 and by the U.S. Office of Naval Research through Grant No. N00014-89-J-1530.

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