# Large-angle inelastic electron scattering from adsorbate vibrations: Basic theory

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This paper formulates the theory of large-angle inelastic electron scattering from vibrational motions of the crystal surface. We focus attention on the scattering from an ordered overlayer of adsorbed molecules, but the formulation developed here is applicable to a variety of other situations, so long as the surface structure is periodic. The emphasis is on incorporation of multiple scattering of the electron from the adsorbate-substrate combination as it either approaches or exits from a site where vibrational excitation occurs. The method here makes explicit contact with earlier theories of low-energy electron diffraction from surfaces, and theories of angle-resolved photoemission. By synthesizing elements of these theories with a model of the electron-phonon coupling, we obtain general expressions for the energy variation of the inelastic cross section and its angular variation. A separate paper reports a series of numerical calculations based on the present formalism for a  $c(2 \times 2)$  overlayer of CO on the Ni(100) surface.

### I. INTRODUCTION

The purpose of the present paper is to provide a theoretical description of large-angle inelastic electron scattering from the vibrational motions of an ordered monolayer of adsorbed molecules on a semi-infinite crystalline substrate. We wish to present the analysis in a form that relates the required ingredients to earlier analyses of the lowenergy electron diffraction (LEED) by crystals and angle-resolved photoemission. We also set down a structure of sufficient generality that it may readily be adapted to other problems in this general area. A separate paper describes application of the formalism presented here to a description of large-angle scattering from vibrations of a  $c(2 \times 2)$  layer of CO molecules on a Ni(100) surface. Before we turn to the details of the presentation, perhaps some introductory remarks will clarify our motivation for pursuing these questions.

For many years, there has been considerable interest in understanding the nature of the bonding between adsorbed molécules and surfaces. Before this can be done, it is clearly essential to obtain information about the details of the bonding-site geometry. Also, the normal vibrational modes of the adsorbate-substrate combination have been the focus of numerous studies, because a great deal may be inferred about site geometry from them, and because it is clear that thermal vibrations in the surface crucially influence a variety of phenomena there.

From the experimental point of view, it is difficult to probe atomic vibrations of surface atoms, and of molecules adsorbed on the surface. Infrared-absorption studies have been carried out for a number of adsorbates,<sup>1</sup> but the experiments are difficult because the number of surface molecules exposed to the incident radiation is not large, unless powdered samples with large surface-tovolume ratios are employed. Then one does not have the simplicity of probing molecules on one particular well-characterized face of a single crystal. During the past year or two, the observation of "giant" Raman signals from adsorbates has generated great excitement.<sup>2</sup> We have here a powerful form of optical surface spectroscopy if the phenomenon emerges as reasonably general, and not confined to the limited number of (poorly characterized) adsorbate-substrate systems explored so far.<sup>3</sup>

While optical spectroscopy may provide information about vibrational frequencies of adsorbates, and limited information about site symmetry can follow in principle from selection rules (the Raman-scattering technique has considerable potential here), the amount of structural information that may be extracted from optical probes of infrared or visible frequency is severely limited by the very long wavelength of the probing light, when compared to crystal lattice constants and molecular bond lengths. A short-wavelength probe has the potential of providing information not only on site symmetry, but also on bond lengths and other fine details of the local environment of an adsorbate.

The last remark suggests that the study of the inelastic scattering of low-energy electrons from vibrations of the surface is an experimental method of substantial power. Here we have a shortwavelength probe that penetrates only a small number of atomic layers into the substrate. Energy

resolution sufficient to resolve vibrational modes of light adsorbates on tungsten was first achieved by Propst and Piper,<sup>4</sup> and shortly afterwards a pioneering set of experiments by Ibach and collaborators<sup>5-7</sup> explored phonons on clean semiconductor surfaces, and adsorbates on both semiconductors and metals. Now, inelastic electron scattering is an active topic of experimental study in numerous laboratories. The spectrometer developed by Ibach achieved an energy resolution of 5 meV  $(40 \text{ cm}^{-1})$  which, so far as we know, remains the highest-resolution electron spectrometer developed to date. This resolution is sufficient to study highfrequency vibration modes of adsorbates on a variety of surfaces, and phonons on clean semiconductor surfaces, and studies of substrate phonons on stepped and adsorbate-covered surfaces have been reported recently.<sup>8</sup>

With the exception of recent experiments discussed below, all studies of electron-energy loss by phonons (EELS) examine inelastics that emerge very close to the specular direction. These electrons suffer very-small-angle deflections in the inelastic event; the angular distribution consists of an intense, narrow lobe that emerges near the specular (and also Bragg) direction, and a broad but considerably weaker background which forms the thermal diffuse background in LEED experiments. The intense lobe of inelastics that emerges near the specular has its origin in the long-range electrostatic potential set up in the vacuum above the crystal by surface vibrations. A vibrating atom in a crystal surface, or adsorbate on the surface, possesses a time-dependent electric dipole moment, from symmetry considerations alone. The long-range dipole fields produced by the oscillating dipoles lead to intense, small-angle inelastic scattering; the dipole-scattering mechanism operates even on the surface of a nominally nonpolar semiconductor such as silicon.<sup>5-9</sup> The width in angle of the near-specular dipolar lobe9 is  $\Delta \theta \approx \hbar \omega_0 / 2E_0$ , where  $\omega_0$  is the frequency of the phonon excited in the scattering event, and  $E_0$  is the incident electron energy.

A selection rule very similar to that invoked in infrared spectroscopy has been introduced also into electron-energy-loss spectroscopy,<sup>9</sup> in the small-angle dipole-dominated regime. This is that strong scattering is produced only by vibrational modes that involve motions normal to the surface. For an adsorbate on a metal, on a site of high symmetry where the normal modes can be decomposed into those with motion normal to the surface and those with motion parallel to the surface, to first approximation the transverse modes do not scatter at all.

Thus, small-angle EELS spectroscopy provides

access only to a limited number of vibrational modes of an adsorbate. These are the same as those studied by infrared spectroscopy. In fact, for scattering from the CO stretch vibration on Ni, the values of the dynamic effective charge extracted from EELS data using the theory of Evans and Mills compare well with those extracted from infrared studies.<sup>10,11</sup>

Outside of the "dipole lobe," most particularly where the wave-vector change  $\Delta \vec{k}$  becomes on the order of  $a_0^{-1}$ , where  $a_0$  is a typical bond length of the surface structure of interest, the electron suffers upon inelastic scattering, and it is clear that the selection rule for small-angle scattering breaks down. Here there are large phase differences between scattered waves which originate from different portions of the structure, and the electron no longer sees simply the potential from a point dipole and its image. Thus, at large scattering angles, with no selection rule operative, one has access to all the vibrational modes of the adsorbate, and not only those which involve motion normal to the surface.

One sees this very clearly in the data of Ho. Wallis, and Plummer,<sup>12</sup> who report the first EELS data which scan not only the near-specular scattering but large-angle scattering as well. These authors study H adsorbed on W(100), and identify three energy-loss features (80, 130, and 160 MeV) as the three vibrational modes of H on a bridge site between two tungsten atoms. Far from the specular, all modes scatter with comparable intensity, but very close to the specular, the intensity of the 130-meV peak is larger than the remaining two by roughly a factor of 100. The 130-meV peak is thus the vibration normal to the surface, with dipole scattering responsible for the nearspecular enhancement of the scattering intensity. The large-angle spectra provide all the normal modes, while the near-specular data allow one to select the mode polarized normal to the surface.

As remarked earlier, our aim here is to put forth a theoretical description of EELS valid for large scattering angles where a full microscopic description of the scattering potentials of the adsorbate-substrate system is required. We conclude this section with a description of the relationship between the formulation developed here and other work.

Roundy and Mills<sup>13</sup> presented the first discussion of large-angle EELS, with analysis of the information on surface vibrations of the clean substrate one may extract from such data. The calculations presented there illustrate the sensitivity of qualitative features in the loss spectra to the force constants which enter the lattice dynamical description of the surface region. While their dis-

cussion is framed within a rather general description of the scattering process, resort was made to a simple description of the electron-phonon coupling in the end. The scheme set forth there does not lend itself to practical exploitation at a deeper level.

More recently, Davenport, Ho, and Schrieffer<sup>14</sup> presented analysis of the inelastic scattering of electrons from vibrations of a CO molecule presumed adsorbed on the substrate. The focus of their treatment is on the coupling of the electron to the particular molecule whose vibrational motion is excited in the scattering process. In fact, they presume the surface has no effect in the problem whatsoever, save to orient the axis of the CO molecule in space. Thus the calculation they carry out is inelastic scattering from a CO molecule isolated and in free space, but with its symmetry axis pinned in direction.

We believe that an essential feature of the problem is diffraction and subsequent backscattering of the electrons from other molecules in the near vicinity of the one where phonon excitation occurs, and from the substrate as well. Only a fraction of the incident electron wave is directly backscattered in a direction that avoids subsequent contact with other adsorbed molecules or the substrate. A large portion of the incident wave is either forward scattered or side scattered, and experiences subsequent interactions before emerging from the system. Also, the incident wave does not only reach the excitation site directly, but may do so after scattering off the substrate or other adsorbates. Thus we view the fundamental theoretical problem as one which requires utilization of the multiple scattering techniques developed in recent years in LEED theory, and the theory of angleresolved photoemission. In fact, we phrase our discussion in language that makes explicit contact with both bodies of theory.

In our view, there is more involved than simply a proper and complete calculation of the scattering intensities. The Bragg diffraction of the incident wave before phonon excitation, and subsequent diffraction of the scattered wave afterward, provide interference effects and structure in the energy (and angular) dependence of the cross section, sensitive to the details of the adsorbate-site symmetry and the arrangement of nearby molecules. Thus, in addition to providing vibrational frequencies, the complete study of large-angle EELS allows one to obtain structural information very similar to that obtained with LEED studies and angular-resolved photoemission. We show here that the EELS spectrum is potentially very rich; the scattering intensity from each of the normal modes contains, in principle, its own characteristic

structural data. Unfortunately, the large-angle EELS experiments reported to date present data on only a limited range of impact angles.<sup>12</sup>

One aim of the present investigation, and the numerical calculations reported in a separate paper, is to outline the theoretical expectations within the framework of calculations comparable to the current state of the art in LEED theory and angleresolved photoemission. It is necessary to make approximations at certain points. We shall try to point out where these occur, and their consequences.

### II. DERIVATIVE FORM OF THE ELECTRON-ENERGY-LOSS SCATTERING AMPLITUDE

We consider in this section the inelastic scattering of electrons by phonons from a semi-infinite substrate upon which an ordered layer of adsorbed molecules has been arranged. As remarked in Sec. I, our interest here is in large-angle scattering, where explicit resort to multiple scattering methods is required for the description of the interaction of the electron with the adsorbate-substrate system. We concentrate here on one-phonon processes, though the method outlined can, in principle, be extended to higher-order scatterings. This is our first examination of the theory of large-angle scattering, and at various points we do introduce simplifying approximations. We shall point these out where they occur, and subsequent work will explore a number of these points.

The geometry we explore is illustrated in Fig. 1. We place a master origin in one particular unit cell, and  $\vec{S}_{\nu}$  is a translation vector between the master origin, and an equivalent origin in unit cell  $\nu$ . The unit cell is semi-infinite in extent and consists of an adsorbed molecule and a semi-infinite array of substrate atoms. Thus  $\vec{S}_{\nu}$  lies parallel to



FIG. 1. Schematic illustration of the geometry that is employed in the present analysis. We show an ordered layer of adsorbed diatomic molecules on a substrate with two substrate atoms in each layer of the semi-infinite unit cell.

the surface.

For the case where an ordered layer of adsorbate molecules is present, each phonon mode of the adsorbate-substrate system is characterized by a wave vector  $\vec{Q}_{\parallel}$  parallel to the surface. This wave vector lies within the two-dimensional Brillouin zone appropriate to the structure. For each value of  $\vec{Q}_{\mu}$ , we have a denumerably infinite set of normal modes of the system. Suppose the substrate, rather than taken to be semi-infinite, is presumed to consist of N equivalent layers parallel to the surface, with m substrate atoms from each layer in the basic unit cell. Then with a single adsorbed diatomic molecule associated with each unit cell, as presumed in Fig. 1, we have 3(2 + mN) phonon modes associated with each value of  $\vec{Q}_{\parallel}$ . We index each mode by a quantum number  $\alpha$ , so the pair  $(\overline{Q}_{\mu}\alpha)$  labels the vibrational modes of the system. The vibrational wave function may then be specified by stating the set of occupation numbers  $\{n_{O_{\mu}\alpha}\}$  of the array of normal modes. We denote the vibrational wave function by the symbol  $|\{n_{\bar{Q}_{||}\alpha}\}\rangle$ ; this wave function depends on the instantaneous positions  $\{\vec{R}\} = (\vec{R}_1, \dots, \vec{R}_M)$  of all the nuclei in the system.

We consider the interaction of an electron with the system, where far from the substrate the incoming portion of the electron wave function is a plane wave of wave vector  $\vec{k}^{(I)}$ . From the point of view of this electron, the solid is an array of potentials arranged in the spirit of the muffin-tin approximation, each displaced from the equilibrium site (and possibly distorted in form) by the vibrational motion of the nuclei. In the adiabatic approximation, the wave function of the initial state of the system assumes the product form, with  $\vec{r}$ the position of the electron:

$$|\psi_{I}(\vec{r},\{\vec{R}\})\rangle = |\psi_{e}(\vec{r},\{\vec{R}\})\rangle |\{n_{\vec{O},\alpha}\}_{I}\rangle, \qquad (2.1)$$

where  $|\{n_{\bar{Q}_{\parallel}\alpha}\}_{I}\rangle$  is the initial vibrational state, and  $|\varphi_{e}(\bar{r}, \{\bar{R}\})\rangle$  the wave function of the electron, which is dependent on the instantaneous positions of the array of nuclei.

In the final state, the phonon occupation numbers  $\{n_{\vec{Q}_{\parallel}}\alpha\}_F$  may differ from those in the initial state, and the electron is an outgoing wave of wave vector  $\vec{k}^{(F)}$ , which will not be in the Bragg direction if  $\vec{Q}_{\parallel} \neq 0$  phonons are created or destroyed in the scattering process. If phonons of wave vector  $\vec{Q}_{\parallel}^{(1)}, \vec{Q}_{\parallel}^{(2)}, \ldots$  are created or destroyed, then the direction and magnitude of  $\vec{k}^{(F)}$  is determined uniquely by the consideration of energy conservation and wave-vector conservation that applies to wave-vector components parallel to the surface. We have  $\vec{k}_{\parallel}^{(F)} = \vec{k}_{\parallel}^{(f)} + \vec{G}_{\parallel} - \sum_i \sigma_i \vec{Q}_i^{(i)}$ , where  $\vec{G}_{\parallel}$  is a reciprocal-lattice vector of the two-dimensional array of unit cells, and if a phonon of wave vector  $\vec{Q}_{\parallel}^{(i)}$  is created,  $\sigma_i = +1$ , while  $\sigma_i = -1$  if the phonon is destroyed.

We may describe the scattering process through use of the *T* matrix of the adsorbate-substrate pair combined with the one-electron Green's function  $G(\vec{r}, \vec{r}')$ . The derivation, in its initial stages, parallels the description of elastic scattering of electrons from the substrate<sup>15</sup> [low-energy electron diffraction (LEED)]. Let us denote the matrix element for scattering the electron from  $\vec{k}^{(I)}$  to  $\vec{k}^{(F)}$ with creation or absorption of an array of phonons by  $M(\vec{k}^{(I)}, \vec{k}^{(F)}; \{\sigma_i \vec{Q}_{\parallel}^{(i)}; \alpha_i\})$ . Then we have

$$M(\vec{\mathbf{k}}^{(I)}, \vec{\mathbf{k}}^{(F)}; \{\sigma_{i}\vec{\mathbf{Q}}_{\parallel}^{(i)}; \alpha_{i}\}) = \langle \{n_{\vec{\mathbf{Q}}_{\parallel}\,\alpha}\}_{F} |\langle \vec{\mathbf{k}}^{(F)}| GT | \vec{\mathbf{k}}^{(I)} \rangle \times |\{n_{\vec{\mathbf{Q}},\alpha}\}_{I} \rangle.$$
(2.2)

In Eq. (2.2),  $|\vec{k}^{(I)}\rangle$  and  $|\vec{k}^{(F)}\rangle$  are plane waves that describe the incoming and outgoing electron, G is a free-electron Green's function corrected for inner-potential shifts and inelastic damping as in LEED calculations, while T is the T matrix that describes the multiple scattering of electrons off the solid. The T matrix depends parametrically on the instantaneous positions of the ion cores in the adiabatic approximation. Thus Eq. (2.2) provides the following prescription. We consider the scattering of the electron from an array of potentials with the *i*th potential displaced slightly from the equilibrium position to  $\vec{R}_i \neq \vec{R}_i^{(0)}$ . Given the resulting T matrix, which directs the electron away from the Bragg directions by virtue of the disorder associated with the ion displacements, we then compute a transition-matrix element that depends on the ionic coordinates after integrating out the electron coordinate. Finally, one takes the matrix element of the resulting object between the initial and final vibrational states over nuclear displacement amplitudes.

This prescription is nontrivial to carry through in complete generality, and it is necessary to introduce a sequence of approximations to render the analysis tractable. Here, we concentrate on onephonon processes, as remarked earlier. Upon assuming the amplitude of the vibrational motion is small, we may express the one-phonon cross section in terms of a derivative of the T matrix with respect to the nuclear displacements. We find, in the end, an approximate expression for the onephonon cross section sufficiently simple that explicit numerical calculations (nontrivial in nature) may be carried through.

Our principle task is to analyze the structure of the *T* matrix, since once this is determined the relevant integrations in Eq. (2.2) may be evaluated in a straightforward manner. If  $V(\vec{r}, \{\vec{R}\})$  is the crystal potential seen by the incoming electron with nuclei displaced from their lattice sites, then as in LEED theory,<sup>15</sup> we may write

$$T(\vec{\mathbf{r}}, \vec{\mathbf{r}}'; \{\vec{\mathbf{R}}\}) = \delta(\vec{\mathbf{r}} - \vec{\mathbf{r}}')V(\vec{\mathbf{r}}, \{\vec{\mathbf{R}}\})$$
$$+ \int d^3 r'' V(\vec{\mathbf{r}}, \{\vec{\mathbf{R}}\})G(\vec{\mathbf{r}} - \vec{\mathbf{r}}'')$$
$$\times T(\vec{\mathbf{r}}'' \vec{\mathbf{r}}'; \{\vec{\mathbf{R}}\}). \qquad (2.3)$$

For a particular, specified set of nuclear coordinates  $\{\vec{R}\}$ , we define an electron scattering amplitude  $f(\vec{k}^{(F)}, \vec{k}^{(I)}; \{\vec{R}\})$  through the relation

$$f(\mathbf{k}^{(\mathbf{F})}, \mathbf{k}^{(I)}; \{\mathbf{R}\}) = \langle \mathbf{\bar{k}}^{(F)} | GT | \mathbf{\bar{k}}^{(I)} \rangle$$

$$\equiv \frac{1}{V} \int d^{3}r' d^{3}r'' d^{3}r''' \exp(-i\mathbf{\bar{k}}^{(F)} \cdot \mathbf{\bar{r}}') \times G(\mathbf{\bar{r}}' - \mathbf{\bar{r}}'')T(\mathbf{\bar{r}}'', \mathbf{\bar{r}}'''; \{\mathbf{\bar{R}}\}) \exp(+i\mathbf{\bar{k}}^{(I)} \cdot \mathbf{\bar{r}}'''),$$
(2.4)

where V is the basic quantization volume. Then

$$M(\vec{k}^{(I)}, \vec{k}^{(F)}; \{\sigma_i \vec{Q}^{(i)}_{\parallel}; \alpha_i\}) = \langle \{n_{\vec{Q}_{\parallel}\alpha}\}_F | f(\vec{k}^{(F)}, \vec{k}^{(I)}; \{\vec{R}\}) | \{n_{\vec{Q}_{\parallel}\alpha}\}_I \rangle.$$
(2.5)

Our basic procedure will be to expand the T matrix in powers of the displacement  $\vec{u}_j = \vec{R}_j - \vec{R}_j^{(0)}$  of the *j*th nucleus from its equilibrium positions. The one-phonon cross section is then formed by taking the matrix element of the leading term between initial and final vibrational wave functions, where the final phonon configuration differs from the initial one by a single quantum of one normal mode.

By expanding the T matrix in the fashion just outlined, our ability to explore one issue becomes limited. This is the question of how the Debye-Waller factor, or perhaps a more general analog, is to enter the one-phonon cross section. While we may introduce Debye-Waller factors into our final expressions through use of single-site t matrices corrected for vibrational motion, as in LEED theory, the validity of such a scheme should be studied with care. For the LEED problem, Laramore and Duke<sup>16</sup> have examined this issue and concluded that correction of the single-site tmatrices in this fashion leads to cross sections accurate to some 20%. We believe the question should be reexamined, most particularly to explore the dependence of the corrections on surface geometry (the position of the adsorbed layer relative to the substrate, for example). We hope to turn to this issue in future work; a model of the lattice dynamics of the adsorbate-substrate system more sophisticated than that used here must also be developed to do this.

To discuss the explicit form of the expansion of the scattering amplitude  $f(\vec{k}^{(F)}, \vec{k}^{(X)}; \{\vec{R}\})$  in powers of the nuclear displacements  $\vec{u}_j$ , it is convenient to turn to an explicit model of the adsorbate-substrate system, and to a simple picture of the lattice dynamics of the surface region. We consider an ordered monolayer of diatomic molecules ABarranged on a substrate in a  $c(2\times 2)$  structure. This structure is realized for CO on the (100) surface of Ni at half coverage, and we have carried out explicit calculations of large-angle vibrationalloss cross sections for this particular structure. While the formal development below refers to it explicitly, the reader will recognize that the extension to more general geometries is straightforward.

We also simplify the description of the surfacelattice dynamics by presuming the masses of the two constituents of the adsorbed molecule are small compared to those of the substrate atoms. Then the vibrational frequencies of the adsorbed species are large compared to the substrate phonon frequencies, and the motion of the substrate atoms may be ignored. In most electron-energy-loss studies of vibrational spectra of adsorbates on metals to data, this assumption is well satisfied. Finally, we ignore interactions between adsorbate molecules, and treat each as an independent entity with six normal modes. For an adsorption site of high symmetry, the normal modes may decomposed into motion perpendicular to the surface and motion parallel to it. Then for motion normal to the surface, we have the stretch mode, present in the gas phase and modified by bonding of the molecule to the substrate and a second mode which involves motion of the center of mass of the molecule against the substrate. Also, we have the "wagging modes" that involve transverse motions. In phonon language, this last assumption amounts to presuming the adsorbed overlayer leads to six new surface phonon branches, each of which is dispersionless. In the recent literature,<sup>17</sup> we find discussions of interactions between adsorbates at high coverage and the resulting dispersion in the surface phonon spectra. While we ignore the effect of dispersion at the moment, we plan to include it in later studies, since large-angle electron-energyloss spectroscopy offers a unique experimental probe of it, if the dispersion is sufficiently large to be resolved experimentally.

Then if  $u_A^{(i)}(\nu)$  and  $u_B^{(i)}(\nu)$  are the *i*th Cartesian coordinates of the displacement of nuclei A and B for the molecule in unit cell  $\nu$ , we have, with  $\{\vec{\mathbf{R}}^{(0)}\}$ , the collection of equilibrium positions of the nuclei

$$f(\vec{\mathbf{k}}^{(F)}, \vec{\mathbf{k}}^{(I)}; \{\vec{\mathbf{R}}\}) = f(\vec{\mathbf{k}}^{(F)}, \vec{\mathbf{k}}^{(I)}; \{\vec{\mathbf{R}}^{(0)}\}) + \sum_{\nu} \sum_{i} \left(\frac{\partial f}{\partial R_{A}^{(i)}(\nu)}\right)_{0} u_{A}^{(i)}(\nu) + \sum_{\nu} \sum_{i} \left(\frac{\partial f}{\partial R_{B}^{(i)}(\nu)}\right)_{0} u_{B}^{(i)}(\nu) + \cdots$$

$$(2.6)$$

The derivatives in Eq. (2.6) are evaluated at the equilibrium positions of the nuclei. The term  $f(\vec{k}^{(F)}, \vec{k}^{(I)}; \{\vec{R}^{(0)}\})$  describes elastic scattering of electrons from the rigid lattice (the LEED process), while the second terms lead to the one-phonon loss processes, calculated as described above. In what follows, we retain only the one-phonon term, since the first has vanishing matrix elements between initial and final phonon states where the array of vibrational occupation numbers  $\{n_{\vec{Q}_{\parallel}\alpha}\}$  differ.

Now from Eq. (2.4), it follows that

$$\begin{pmatrix} \frac{\partial f}{\partial R_{A}^{(i)}(\nu)} \\ = \frac{1}{V} \int d^{3}r' d^{3}r''' \exp(-i\vec{k}^{(F)} \cdot \vec{r}') G(\vec{r}' - \vec{r}'') \\ \times \left( \frac{\partial T(\vec{r}'', \vec{r}'''; \{\vec{R}\})}{\partial R_{A}^{(i)}(\nu)} \right)_{0} \exp(+i\vec{k}^{(I)} \cdot \vec{r}''') . \quad (2.7)$$

The integrations in Eq. (2.7) are to be carried through by placing the master origin in unit cell 0, as illustrated in Fig. 1. Now shift the origin to unit cell  $\nu$  by writing  $\vec{r}' = \vec{\rho}' + \vec{S}_{\nu}$ , and similarly for  $\vec{r}''$  and  $\vec{r}'''$ . Then we have

$$\left(\frac{\partial f}{\partial R_{A}^{(i)}(\nu)}\right)_{0} = \exp\left[i\,\vec{S}_{\nu}\cdot(\vec{k}^{(I)}-\vec{k}^{(F)})\right] \int \frac{d^{3}\rho'}{V} d^{3}\rho'' d^{3}\rho''' \\
\times \exp\left(-ik^{(F)}\cdot\vec{\rho}'\right)G(\vec{\rho}'-\vec{\rho}'')\exp\left(i\vec{k}^{(I)}\cdot\vec{\rho}'''\right)\left(\frac{\partial T(\vec{\rho}''+\vec{S}_{\nu},\vec{\rho}'''+\vec{S}_{\nu};\{\vec{R}\})}{\partial R_{A}^{(i)}(\nu)}\right)_{0}.$$
(2.8)

Simple consideration of invariance of the *T*-matrix derivative under a translation of *all* vectors in its argument (including the nuclear positions) under the same translation  $\tilde{S}_{\nu}$  shows that

$$\frac{\left(\frac{\partial T(\vec{\rho}'' + \vec{S}_{\nu}, \vec{\rho}''' + \vec{S}_{\nu}; \{\vec{R}\})}{\partial R_{A}^{(i)}(\nu)}\right)_{0} \equiv \left(\frac{\partial T(\vec{\rho}'', \vec{\rho}'''; \{\vec{R}\})}{\partial R_{A}^{(i)}(0)}\right)_{0}, \qquad (2.9)$$

so we have the identity

$$\left(\frac{\partial f}{\partial R_{A}^{(i)}(\nu)}\right)_{0} = \exp[i\vec{S}_{\nu}\cdot(\vec{k}^{(I)}-\vec{k}^{(F)})]\left(\frac{\partial f}{\partial R_{A}^{(i)}(0)}\right)_{0}, \qquad (2.10)$$

with an identical relation for  $[\partial f/\partial R_B^{(i)}(\nu)]_0$ . Then with  $\Delta \vec{k} = \vec{k}^{(I)} - \vec{k}^{(F)}$ , we have for the matrix element  $\mathcal{M}(\vec{k}^{(I)}, \vec{k}^{(F)}; \{\sigma_i \vec{Q}_{\parallel c}^{(i)}; \alpha_i\})$  the form

$$M(k^{(I)}, k^{(F)}; \{\sigma_{i} Q_{\parallel}^{(i)}; \alpha_{i}\}) = \sum_{i} \left[ \left( \frac{\partial f}{\partial R_{A}^{(i)}(0)} \right)_{0} \sum_{\nu} \exp(i \Delta \vec{k} \cdot \vec{S}_{\nu}) \langle \{n_{\vec{Q}_{\parallel}\alpha}\}_{F} | u_{A}^{(i)}(\nu) | \{n_{\vec{Q}_{\parallel}\alpha}\}_{I} \rangle + \left( \frac{\partial f}{\partial R_{B}^{(i)}(0)} \right)_{0} \sum_{\nu} \exp(i \Delta \vec{k} \cdot \vec{S}_{\nu}) \langle \{n_{\vec{Q}_{\parallel}\alpha}\}_{F} | u_{B}^{(i)}(\nu) | \{n_{\vec{Q}_{\parallel}\alpha}\}_{I} \rangle \right].$$

$$(2.11)$$

Now, for our diatomic molecule, upon assuming the adsorption site has symmetry sufficiently high that the normal modes can be decomposed into motions normal or parallel to the surface, we can write the nuclear displacements in terms of phonon annihilation and creation operators  $a_{Q_{\parallel}}^{\star}$ . We have

$$u_{\mathbf{A}}^{(i)}(\nu) = \left(\frac{\hbar}{2M_{\mathbf{A}}N_{\mathbf{S}}}\right)^{1/2} \sum_{\mathbf{\tilde{Q}}_{\parallel}^{j}} \frac{\sin\theta_{j}^{(i)}}{(\omega_{j})^{1/2}} \left(a_{\mathbf{\tilde{Q}}_{\parallel}^{j}} + a_{\mathbf{\tilde{Q}}_{\parallel}^{j}}^{\dagger}\right) \exp(i\mathbf{\tilde{Q}}_{\parallel} \cdot \mathbf{\tilde{S}}_{\nu})$$
(2.12a)

and also

$$u_{B}^{(i)}(\nu) = \left(\frac{\hbar}{2M_{B}N_{S}}\right)^{1/2} \sum_{\bar{\mathbb{Q}}_{\parallel}^{j}} \frac{\cos\theta_{j}^{(i)}}{(\omega_{j})^{1/2}} \left(a_{\bar{\mathbb{Q}}_{\parallel}^{j}} + a_{-\bar{\mathbb{Q}}_{\parallel}^{j}}^{\dagger}\right) \exp(i\vec{\mathbb{Q}}_{\parallel} \cdot \vec{S}_{\nu}).$$
(2.12b)

In Eqs. (2.12),  $M_A$  and  $M_B$  are the masses of the two nuclei,  $N_S$  is the number of unit cells parallel to the surface, and  $\omega_j$  the frequency of normal mode j. Finally, the sum on  $\overline{Q}_{\parallel}$  is confined to the two-dimensional Brillouin zone of the structure. For a diatomic molecule which vibrates against a rigid substrate, the explicit form of the coefficients  $\cos\theta_j^{(i)}$  and  $\sin\theta_j^{(i)}$  are given in Appendix A.

Now suppose our electron is scattered from the initial state  $\mathbf{\hat{k}}^{(I)}$  to the final state  $\mathbf{\hat{k}}^{(F)}$ , with creation of a phonon  $(\mathbf{\hat{Q}}_{\parallel i})$ . Then if  $\mathbf{\hat{G}}_{\parallel}$  is a reciprocal-lattice vector associated with the two-dimensional array of unit cells, we have

$$M(\vec{k}^{(I)}, \vec{k}^{(F)}; +\vec{Q}_{\parallel}j) = \left(\frac{\hbar N_{a}}{2\omega_{j}}\right)^{1/2} (1 + \bar{n}_{j})^{1/2} \sum_{\vec{G}_{\parallel}} \delta_{\vec{k}_{\parallel}}^{(F)}; \vec{k}_{\parallel}^{(I)} - \vec{Q}_{\parallel} + \vec{G}_{\parallel} \left[\sum_{i} \frac{\sin \theta_{i}^{(i)}}{(M_{A})^{1/2}} \left(\frac{\partial f}{\partial R_{A}^{(i)}}\right)_{0} + \sum_{i} \frac{\cos \theta_{i}^{(i)}}{(M_{B})^{1/2}} \left(\frac{\partial f}{\partial R_{B}^{(i)}}\right)_{0}\right].$$
(2.13)

In Eq. (2.13),  $\bar{n}_j = [\exp(\bar{n} \omega_j/k_B T) - 1]^{-1}$  is the Bose-Einstein factor associated with the normal mode of frequency  $\omega_j$ ,  $\bar{k}_{\parallel}^{(F)}$  and  $\bar{k}_{\parallel}^{(I)}$  are the projections of the wave vectors  $\bar{k}^{(F)}$  and  $\bar{k}^{(I)}$  onto the plane parallel to the surface, and  $\delta_{\bar{k}_{\parallel},\bar{k}_{\parallel}^{(I)}}$  is unity when  $\bar{k}_{\parallel} = \bar{k}_{\parallel}^{(I)}$  and is zero otherwise. Also,  $R_A^{(i)}$  and  $R_B^{(i)}$  are nuclear displacements in the unit cell where the master origin is placed.

We see in Eq. (2.13) a number of important features in the structure of the scattering amplitude. For example, for each normal mode of the molecule, the matrix element is a coherent superposition of an amplitude for scattering from nucleus A, and an amplitude for scattering from nucleus B. In the cross section, which is proportional to  $|M(\vec{k}^{(I)}, \vec{k}^{(F)}; \vec{q}_{\parallel}j)|^2$ , there is thus an interference term in addition to the sum of the square of the amplitude for scattering from site A and scattering from site B. We can see that in general, for fixed incident and scattered electron directions, we expect a distinctly different energy dependence of the loss cross section for scattering from each normal mode of the adsorbed molecule, since the magnitude of each contribution to the cross section, and most particularly the sign of the interference term, will differ for each mode.

Consider, for example, scattering from the modes that involve motions normal to the surface. The high-frequency mode, with frequency  $\omega_{\perp}^{(\perp)}$ , is the "A-B stretch" mode in the gas phase. In the gas phase, the masses oscillate nearly 180° out of phase; when the molecule is chemisorbed, presumably the relative motions are still roughly opposed, so  $\sin \theta_j^{(\perp)}$  and  $\cos \theta_j^{(\perp)}$  will differ in sign. On the other hand, the low-frequency mode  $\omega^{(1)}$ involves primarily a motion of the center of mass against the substrate, so here  $\sin\theta_i^{(1)}$  and  $\cos\theta_i^{(1)}$ will have the same sign. Thus, a comparison of the energy variation of the cross section for these two modes, with scattering angles fixed, will provide direct information about interference effects; for our simple model, as one sees from Appendix A, both  $\sin\theta_i^{(\perp)}$  and  $\cos\theta_i^{(\perp)}$  may be calculated once the two vibrational frequencies are known.

From the remarks above, it is clear that the energy and angle variation of the energy-loss cross sections associated with the array of vibrational modes of the adsorbed layer contains a rich store of information about the molecular motion, and the local environment in its near vicinity. We next turn to an analysis of the derivatives  $(\partial f/\partial R_A^{(i)})_0$ , which are the fundamental quantities that enter the theory. Before we do this, however, we pause to state the relation between the matrix element  $M(\bar{k}^{(I)}, \bar{k}^{(F)}; \bar{\mathbf{Q}}_{\parallel}j)$  and the integrated intensity of the electrons scattered by the mode of polarization j.

Note that for a given value of  $\vec{k}^{(F)}$  and  $\vec{k}^{(I)}$ , there

will be a single, unique value of  $\vec{Q}_{\parallel}$  that renders the sum of  $\vec{G}_{\parallel}$  nonzero in Eq. (2.13). This is found by forming the difference  $\vec{R}_{\parallel}^{(F)} - \vec{k}_{\parallel}^{(I)}$ , which in general lies outside the two-dimensional Brillouin zone formed from our array of unit cells. One finds the (unique) reciprocal lattice vector that translates  $\vec{k}_{\parallel}^{(F)} - \vec{k}_{\parallel}^{(I)}$  back into the first zone, and chooses  $\vec{Q}_{\parallel}$  equal to the resulting wave vector.

Now we form the following quantities. Suppose the incoming electron beam makes the angle  $\theta_0$ with the normal to the surface, and suppose we examine scattered electrons that emerge with angle  $\theta_s$  relative to the normal. Let  $[dP(\vec{k}_I, \vec{k}_F)/d\Omega] d\Omega$  be the *fraction* of the incoming electrons which emerge onto the solid angle  $d\Omega$ , after scattering inelastically off the vibrational mode of polarization j. Then if  $E_I$  is the energy of the electrons in the vacuum and S is the surface area of the sample, one may show that

$$\frac{dP(\vec{\mathbf{k}}_{I},\vec{\mathbf{k}}_{F})}{d\Omega} = \frac{mE_{I}\cos^{2}\theta_{s}}{2\pi^{2}\hbar^{2}\cos\theta_{0}}S|M(\vec{\mathbf{k}}^{(I)},\vec{\mathbf{k}}^{(F)};\vec{\mathbf{Q}}_{\parallel}j)|^{2}.$$
(2.14)

We have ignored the difference in energy between the incident and scattered electron to derive this formula.

Examining the prefactors which enter Eq. (2.14), one sees the cross section is explicity proportional to the number of molecules per unit area  $n_* = N_*/S_*$ . This is because a factor  $N_s^{1/2}$  appears in Eq. (2.13) and a factor 1/S appears in Eq. (3.18). These are to be squared when substituted in Eq. (2.14). From the explicit factor of  $n_s$  that appears in Eq. (2.14), one cannot conclude that in our theory the cross section scales directly as the number of molecules per unit area. Even though we ignore the coverage dependence of the vibrational frequencies at the present level of development, the matrix element  $M(\dots)$  is to be calculated by summing the full multiple-scattering series, including scatterings from other molecules within the adsorbed layer. Thus, an implicit dependence on coverage for a structure of given symmetry is contained in  $|M(\vec{k}^{(I)}, \vec{k}^{(F)}; \vec{Q}_{\parallel}j)|^2$ .

# III. ANALYSIS OF THE ELECTRON-PHONON COUPLING AMPLITUDES

In this section, we analyze the derivatives  $[\partial f/\partial R_A^i]_0$  of unit cell 0 that enter the theory of electron energy-loss spectroscopy (EELS) in the previous subsection. For the moment, we use notation more general than that which applies to the simple lattice-dynamical model employed in Sec. II.

We have, to repeat the definition for completeness at unit cell 0,

$$\begin{pmatrix} \frac{\partial f}{\partial R^{\alpha}_{A}} \end{pmatrix}_{0} = \frac{1}{V} \int \int \int d^{3}r' d^{3}r'' d^{3}r''' \exp(-i\vec{k}^{(F)} \cdot \vec{r}') \\ \times G(\vec{r}' - \vec{r}'') \left( \frac{\partial T(\vec{r}'', \vec{r}'''; \{\vec{R}\})}{\partial R^{\alpha}_{A}} \right)_{0} \\ \times \exp(i\vec{k}^{(I)} \cdot \vec{r}'''), \qquad (3.1)$$

where  $\alpha$  instead of *i* is chosen as the Cartesian coordinate. In the discussion of the previous section, atom A was a nucleus in the adsorbed diatomic molecule, but in more general discussions we shall wish to consider scattering produced by motion of the substrate nuclei, as well as the nuclei in the adsorbed molecule. We may write Eq. (3.1) in the more schematic form

$$\left(\frac{\partial f}{\partial R_{A}^{\alpha}}\right)_{0} = \langle \vec{k}^{(F)} | G\left(\frac{\partial T\left(\{\vec{R}\}\right)}{\partial R_{A}^{\alpha}}\right)_{0} | \vec{k}^{(I)} \rangle.$$
(3.2)

Noting the Kronecker delta in Eq. (2.13), we define

$$\left(\frac{\partial f(\mathbf{G}_{\mathbf{I}})}{\partial R_{\mathbf{A}}^{\alpha}}\right)_{0} = \left(\frac{\partial f}{\partial R_{\mathbf{A}}^{\alpha}}\right)_{0} \delta_{\mathbf{k}_{\mathbf{I}};\mathbf{k}_{\mathbf{I}}|\mathbf{I}} - \check{\mathbf{G}}_{\mathbf{I}} + \check{\mathbf{G}}_{\mathbf{I}} \right).$$
(3.3)

A similar definition is used for the B atom.

Now the integral equation satisfied by the T matrix may be written in the schematic form

$$T(\{\vec{R}\}) = V(\{\vec{R}\}) + V(\{\vec{R}\}) GV(\{\vec{R}\}) + V(\{\vec{R}\}) GV(\{\vec{R}\}) GV(\{\vec{R}\}) + \cdots,$$
(3.4)

where G is independent of the atomic positions. Then differentiation with respect to  $R_A^{(\alpha)}$  gives

$$\frac{\partial T(\{\vec{R}\})}{\partial R^{\alpha}_{A}} = \frac{\partial V(\{\vec{R}\})}{\partial R^{\alpha}_{A}} + \frac{\partial V(\{\vec{R}\})}{\partial R^{\alpha}_{A}} G[V(\{\vec{R}\}) + V(\{\vec{R}\}) GV(\{\vec{R}\}) + \cdots] + [V(\{\vec{R}\})G + V(\{\vec{R}\})GV(\{\vec{R}\})G + \cdots] \frac{\partial V(\{\vec{R}\})}{\partial R^{\alpha}_{A}} + [V(\{\vec{R}\})G + V(\{\vec{R}\})GV(\{\vec{R}\})G + \cdots] \frac{\partial V(\{\vec{R}\})}{\partial R^{\alpha}_{A}} [GV(\{\vec{R}\}) + GV(\{\vec{R}\})GV(\{\vec{R}\}) + \cdots] = \frac{\partial V(\{\vec{R}\})}{\partial R^{\alpha}_{A}} + \frac{\partial V(\{\vec{R}\})}{\partial R^{\alpha}_{A}} GT(\{\vec{R}\}) + T(\{\vec{R}\})G \frac{\partial V(\{\vec{R}\})}{\partial R^{\alpha}_{A}} + T(\{\vec{R}\})G \frac{\partial V(\{\vec{R}\})}{\partial R^{\alpha}_{A}} GT(\{\vec{R}\}) .$$
(3.5)

Now Eq. (3.5) is quite general; we evaluate both sides by taking the limit  $\{\vec{R}\} \rightarrow \{\vec{R}^{(0)}\}$ . When this is done, and the result inserted into Eq. (3.2), we have

$$\left(\frac{\partial f(\mathbf{G}_{\parallel})}{\partial R_{\mathbf{A}}^{\alpha}}\right)_{0} = \langle \vec{\mathbf{k}}^{(F)} | (G + GT_{0}G) [\partial V(\{\vec{\mathbf{R}}\}) / \partial R_{\mathbf{A}}^{\alpha}]_{0} (1 + GT_{0}) | \vec{\mathbf{k}}^{(I)} \rangle \delta_{\vec{\mathbf{k}}}^{\alpha} \mathcal{O}_{\parallel} \hat{\mathbf{k}}_{\parallel}^{(I)} - \tilde{\mathbf{Q}}_{\parallel} + \tilde{\mathbf{G}}_{\parallel}, \qquad (3.6)$$

where  $T_0$  is the T matrix, evaluated with all nuclei fixed at the equilibrium sites. If we write out the right-hand side of Eq. (3.6) in explicit form

$$\left(\frac{\partial f(\mathbf{G}_{\parallel})}{\partial R_{A}^{\alpha}}\right)_{0} = \frac{1}{V} \int \int \int d^{3}r \, d^{3}r' \, d^{3}r'' \exp(-i\,\vec{\mathbf{k}}^{(F)}\cdot\vec{\mathbf{r}}) \left(G(\vec{\mathbf{r}}-\vec{\mathbf{r}}')+\int \int d^{3}r_{1}d^{3}r_{2}G(\vec{\mathbf{r}}-\vec{\mathbf{r}}_{1})T_{0}(\vec{\mathbf{r}}_{1}\vec{\mathbf{r}}_{2})G(\vec{\mathbf{r}}_{2}-\vec{\mathbf{r}}')\right) \\
\times \left(\frac{\partial V(\vec{\mathbf{r}}',\{\vec{\mathbf{R}}\})}{\partial R_{A}^{\alpha}}\right)_{0} \left(\delta(\vec{\mathbf{r}}'-\vec{\mathbf{r}}'')+\int \int G(\vec{\mathbf{r}}'-\vec{\mathbf{r}}_{3})T_{0}(\vec{\mathbf{r}}_{3},\vec{\mathbf{r}}'')d^{3}r_{3}\right) \exp(i\,\vec{\mathbf{k}}^{(I)}\cdot\vec{\mathbf{r}}'')\,\delta_{\vec{\mathbf{k}}}^{+}|_{\parallel}^{F})\cdot\vec{\mathbf{q}}_{\parallel} +\vec{\mathbf{q}}_{\parallel} +\vec{\mathbf{q}}_{\parallel} .$$
(3.7)

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While the expressions in Eqs. (3.6) and (3.7) have a cumbersome appearance, they can be arranged in a form that makes their physical content quite clear. This can be seen by noting that the combination  $(G + GT_0G)$  is precisely the propagator  $g_{PE}$  that enters the theory of angle-resolved photoemission.<sup>18</sup> If an electron is emitted from a point in the lattice, then the combination  $\langle \vec{k}^{(F)} | (G + GT_0G) \rangle$ describes the propagation of the electron from the point of emission to the detector, which is oriented to accept electrons with wave vector  $\vec{k}^{(F)}$ . As the electron propagates to the detector, it may do so directly  $\langle \langle \vec{k}^{(F)} | G \rangle$  or may arrive at the detector after multiple scattering off the lattice  $\langle\langle \mathbf{\tilde{k}}^{(F)} | GT_0 G \rangle$ . The combination  $(1 + GT_0) | \mathbf{\tilde{k}}^{(I)} \rangle$  is precisely the wave function that enters LEED theory. It describes the incoming electron, which propagates to the point in the lattice (engaging in multiple scattering along the way) where it interacts with a displaced atom through the term  $[\partial V(\{\mathbf{\tilde{R}}\})/\partial R_A^{\alpha}]_0$ . Thus Eq. (3.6) may be rewritten to read

$$\left(\frac{\partial f(\{\vec{\mathbf{R}}\},\vec{\mathbf{G}}_{\parallel})}{\partial R_{A}^{\alpha}}\right)_{0} = \langle \vec{\mathbf{k}}^{(P)} | g_{PE} \left[ \partial V(\{\vec{\mathbf{R}}\}) / \partial R_{A}^{\alpha} \right]_{0} | \psi_{LEED}^{(I)} \rangle .$$
(3.8)

$$|\psi_{\text{EELS}}\rangle = g_{\text{PE}}\left(\frac{\partial V(\{\vec{R}\})}{\partial R_{A}^{\alpha}}\right)_{0}|\psi_{\text{LEED}}^{(I)}\rangle , \qquad (3.9)$$

then

$$\left(\frac{\partial f(\{\vec{\mathbf{R}}\},\vec{\mathbf{G}}_{\parallel})}{\partial R_{A}^{\alpha}}\right)_{0} = \langle \vec{\mathbf{k}}^{(F)} | \psi_{\text{EELS}} \rangle . \qquad (3.10)$$

Thus from Eq. (3.8) we see that once we are able to develop a method for calculating the potential derivative  $(\partial V/\partial R_A^{\alpha})_0$ , the computational technology developed in LEED theory, and in the theory of angle-resolved photoemission may be brought to bear on the calculation of the EELS intensity. We next turn to an analysis of each of these three factors and the method of synthesizing them. First, we direct our attention to the calculation of  $(\partial V(\{\bar{\mathbf{R}}\})/\partial R_A^{\alpha})_0$ , which is a new piece of required information.

First consider the behavior of the derivative of the crystal potential with atomic displacement. We arrange spherically symmetric potentials about a series of lattice sites, in the spirit of the muffintin approximation:

$$V(\vec{\mathbf{r}}, \{\vec{\mathbf{R}}\}) = \sum_{i} v_{i}(|\vec{\mathbf{r}} - \vec{\mathbf{R}}_{i}|). \qquad (3.11)$$

In Eq. (3.11),  $\vec{R}_i$  is the instantaneous position of the center of the potential associated with unit cell *i*. Then we have, invoking the muffin-tin approximation in the calculation of the potential derivative,

$$\left(\frac{\partial V(\{\vec{\mathbf{R}}\})}{\partial R^{\alpha}_{A}}\right)_{0} = \left(\frac{\partial v_{A}(|\vec{\mathbf{r}} - \vec{\mathbf{R}}_{A}|)}{\partial R^{\alpha}_{A}}\right)_{0}.$$
 (3.12)

If  $\rho_A = |\vec{\mathbf{r}} - \vec{\mathbf{R}}_A|$ , then we may rewrite Eq. (3.12) to read

$$\left(\frac{\partial V(\{\vec{\mathbf{R}}\})}{\partial R_{A}^{\alpha}}\right)_{0} = \left(\frac{\partial v_{A}}{\partial \rho_{A}}\right)_{0} \left(\frac{\partial \rho_{A}}{\partial u_{A}^{\alpha}}\right)_{u_{A}^{\alpha}=0}, \qquad (3.13)$$

where  $\vec{R}_A = \vec{R}^{(0)} + \vec{u}_A$ . If  $\hat{x}_{\alpha}$  is a unit vector in the direction of Cartesian axis  $\alpha$ , then the derivative  $(\partial \rho_A / \partial u_A^{\alpha})_0$  is readily calculated to yield

$$\left(\frac{\partial V(\{\vec{\mathbf{R}}\})}{\partial R_{A}^{\alpha}}\right)_{0} = -\left(\frac{dv_{A}(\rho_{A})}{d\rho_{A}}\right)(\hat{x}_{\alpha}\cdot\hat{\rho}_{A}).$$
(3.14)

Note that  $(dv_A/d\rho_A)$  is nonzero only within the muffin-tin sphere, and this depends on only the magnitude and not the direction of  $\vec{\rho}_A$ . While the use of the muffin-tin procedure seems reasonable for large scattering angles and large momentum transfers, its use prohibits us from making explicit contact with the earlier theories of small-angle scattering by the dipolar mechanism. We return to this point in the concluding remarks of Sec. IV.

The expression in Eq. (3.14) must now be incorporated into the calculation of  $|\psi_{\rm ELLS}\rangle$ , the wave function which traces the entire trajectory of the electron including the multiple-scattering events before and after the electron emits the vibrational quantum which deflects it from one of the Bragg directions. We next turn to an analysis of  $|\psi_{\rm EELS}\rangle$ , through use of the layer by layer method that has formed the basis of a number of LEED and angleresolved photoemission calculations. If Eq. (3.9) is written out explicitly, we have

$$|\psi_{\text{EELS}}\rangle = G(1+T_0G) \left(\frac{\partial V(\{\vec{R}\})}{\partial R_A^{\alpha}}\right)_0 (1+GT_0) |\vec{k}^{(I)}\rangle \\ \times \delta_{\vec{k}} (\vec{P}, \vec{k}_{\parallel}^{(I)}, -\tilde{c}_{\parallel} + \tilde{c}_{\parallel}) .$$
(3.15)

As we trace through the sequence of multiple scatterings, we divide them into those that occur within a given layer and those that transfer the electron from one layer to another. Suppose first we concentrate on all possible scatterings that occur within the same layer, layer A, which contains the nucleus at which the inelastic-scattering event occurs. Let  $t_{\bar{R}_A}$  denote the single-site t matrix that sums multiple scatterings off the particular atom where the inelastic event occurs. This operator obeys the integral equation (here, and in what follows, we use  $\bar{R}_A$  to denote the equilibrium site position vector)

$$t_{\vec{\mathbf{r}}_{A}}(\vec{\mathbf{r}},\vec{\mathbf{r}}') = v_{A}(\vec{\mathbf{r}})\delta(\vec{\mathbf{r}}-\vec{\mathbf{r}}') + \int d^{3}r''v_{A}(\vec{\mathbf{r}})G(\vec{\mathbf{r}},\vec{\mathbf{r}}'')t_{\vec{\mathbf{r}}_{A}}(\vec{\mathbf{r}}'',\vec{\mathbf{r}}').$$
(3.16)

Here  $v_A(\vec{\mathbf{r}})$  is the spherically symmetric muffin-tin potential associated with this nucleus. We begin by isolating in Eq. (3.15) all those scatterings which involve the particular site  $\vec{\mathbf{R}}_A$  (recall that for the moment, we confine our attention to only those scattering events that take place within the layer where the inelastic event occurs). We have

$$|\psi_{\text{EELS}}\rangle = G \left( 1 + \sum_{\vec{R} \neq \vec{R}_{A}} t_{\vec{R}} G + \sum_{\vec{R} \neq \vec{R}'} \sum_{\vec{R}' \neq \vec{R}_{A}} t_{\vec{R}} G t_{\vec{R}'} G + \cdots \right) (1 + t_{\vec{R}_{A}} G) \left( \frac{\partial V(\{\vec{R}\})}{\partial R_{A}^{\alpha}} \right)_{0} (1 + G t_{\vec{R}_{A}})$$

$$\times \left( 1 + \sum_{\vec{R} \neq \vec{R}_{A}} G t_{\vec{R}} + \sum_{\vec{R}' \neq \vec{R}} \sum_{\vec{R} \neq \vec{R}_{A}} G t_{\vec{R}} G t_{\vec{R}'} + \cdots \right) |\vec{k}^{(I)}\rangle \, \delta_{\vec{k}} |_{||}^{(F)}; \, \vec{k}_{||}^{(I)} - \vec{\delta}_{||} + \vec{G}_{||} \, .$$

$$(3.17)$$

We note that in Eq. (3.17), in the multiple sums over  $\vec{\mathbf{R}}$ , successive scatterings from the same site are to be avoided, since these are included fully when scattering from a single site is described by the full t matrix rather than the potential  $v_A$ . By expressing  $t_{\vec{\mathbf{R}}}(\vec{\mathbf{r}},\vec{\mathbf{r}}')$  and  $G(\vec{\mathbf{r}},\vec{\mathbf{r}}')$  in partial-wave expansions, we may then introduce a layer scattering matrix, as in LEED theory, which formally carries through the summation of the multiple-scattering sequence that appears in Eq. (3.17). To do

this, one must consider excitation of a phonon mode of a particular wave vector  $\vec{Q}_{\parallel}$  (even though the mode is excited through interaction with a single site), since  $\vec{Q}_{\parallel}$  controls the kinematics, i.e., the direction of the outgoing electron once the incident electron direction is specified.

For the sequence of multiple scatterings within the layer A, the amplitude of the outgoing wave is controlled by the matrix

$$Q_{\vec{G}_{\parallel}\vec{G}_{\parallel}}^{(A_{\alpha})^{\pm\pm}} = \frac{16\pi^{2}im}{S\hbar^{2}} \sum_{L_{1}L_{2}} \sum_{L_{3}L_{4}} \frac{Y_{L_{1}}[\vec{k}_{\pm}^{(F)}(\vec{G}_{\parallel})]}{k_{\pm}^{(F)}(\vec{G}_{\parallel})} (\underline{1} - \underline{t}_{\vec{R}_{A}} \underline{G}_{\vec{k}}^{(A_{A})})_{L_{1}L_{2}}^{-1} \times (F_{A}^{\alpha})_{L_{2}L_{3}} (\underline{1} - \underline{G}_{\vec{k}}^{(A_{A})})_{L_{3}L_{4}}^{-1} Y_{L_{4}}^{*} (\vec{k}_{\pm}^{(I)}(\vec{G}_{\parallel})) .$$

$$(3.18)$$

The form of this matrix, and its explicit relation to  $|\psi_{\text{EELS}}\rangle$  is discussed in Appendix B.

In Eq. (3.18), if  $\vec{k}_{\parallel}^{(I)}$  is the projection of the wave vector of the incoming electron on the plane parallel to the surface, then the wave vector  $\vec{k}^{(F)}$  is determined by considerations of energy conservation and by the kinematical relation (for phonon emission)

$$\vec{k}_{\parallel}^{(F)} = \vec{k}_{\parallel}^{(I)} - \vec{Q}_{\parallel} + \vec{G}_{\parallel}.$$
(3.19)

The wave vectors  $\vec{k}_{1}^{(F)}(\vec{G}_{\parallel})$  and  $\vec{k}_{1}^{(I)}(G_{\parallel})$  are calculated by the following prescription. An electron with wave vector  $\vec{k}$ , after suffering a two-dimensional Bragg scattering, has projection  $\vec{k}_{\parallel} + \vec{G}_{\parallel}$  onto the plane of the surface, where  $\overline{G}_{\scriptscriptstyle \parallel}$  is the reciprocal-lattice vector through which it has been deflected. Its component normal to the surface is complex in general, by virtue of the inelastic scattering present in the medium. The prescription for calculating the complex wave vector is stated below. By  $\vec{k}_{\downarrow}^{(F)}(\vec{G}_{\parallel})$ , we describe a wave which reaches the plane with nucleus A from above and by  $\vec{k}^{(F)}(\vec{G}_{\mu})$  we describe a wave which reaches the plane from below. Thus  $\vec{k}_{+}^{(F)}(\vec{G}_{\parallel})$  has negative imaginary part while  $\vec{k}^{(F)}(\vec{G}_{\parallel})$  has positive imaginary part. In summing the multiple-scattering series where the electron reaches a given plane by all possible paths, all combinations of the indices + and - will be encountered.

As in earlier work, the symbol L stands for the pair (lm) of integers required to label the spherical harmonic  $Y_L(\hat{k})$ , and we have

$$\frac{(\underline{G}_{\vec{k}}^{AA})_{LL}}{(\underline{F}_{\vec{k}})_{LL}} = + \frac{8\pi mk_0}{i\hbar^2} \sum_{L_1} \sum_{\vec{p} \neq 0} i^{l_1} a(LL'L_1) h_{l_1}^{(1)}(k_0 |\vec{p}|) \times Y_{L_1}(\vec{p}) \exp(-i\vec{k}\cdot\vec{p}),$$
(3.20)

which is identical to the planar structure factor

used in LEED theory.<sup>15</sup> The sum on  $\vec{p}$  is a sum over lattice sites in layer A, and  $a(LL'L_1)$  is in essence a Clebsch-Gordan coefficient, with definition given in Eq. (32) of Ref. 15. While  $G_k^{A}$  is the same planar structure factor as that encountered in LEED theory, note that in contrast to the LEED (or photoemission) problem, we have to sum over multiple-scattering events that the electron experiences before, as well as after, phonon emission.

To continue with a description of the factors in Eq. (3.18), the factor  $(F_A^{\alpha})_{LL}$ , is obtained from the spherical wave expansion of the combination

 $(1+t_{\overline{R}_A}G)[\partial V(\{\overline{R}\})/\partial R^{\alpha}_A]_0(1+Gt_{\overline{R}_A}),$ 

which is the electron-phonon matrix element formed from rigid displacement of the bare potential combined with multiple scatterings of the electron off the site as it enters and as it leaves. One can write this factor in the form, upon using Eq. (3.14),

$$(F_{A}^{\alpha})_{LL}, = (i)^{l'-l} \exp[i(\delta_{l}^{A} + \delta_{l}^{A})]$$

$$\times \int d^{3}\rho_{A} R_{l}^{(F)}(\rho_{A}) Y_{L}^{*}(\hat{\rho}_{A}) (\hat{\chi}_{\alpha} \cdot \hat{\rho}_{A})$$

$$\times \frac{dv_{A}(\rho_{A})}{d\rho_{A}} R_{l}^{(I)}(\rho_{A}) Y_{L}, (\hat{\rho}_{A}). \qquad (3.21)$$

Here  $\delta_i^A$  and  $\delta_i^A$ , are the phase shifts for scattering off the potential at  $\vec{R}_A$ , while  $R_i^{(F)}$  and  $R_i^{(f)}$  are the radial solutions to the Schrödinger equation within the muffin-tin sphere. All quantities indexed l' are to be computed at the incident electron energy and all those indexed l are to be computed at the outgoing energy, though the energy change of the electron is so small these differences can be ignored to excellent approximation. The integral on angle may be separated out explicitly in Eq. (3.21), to leave

$$(F_{A}^{\alpha})_{LL}, = (i)^{I'-I} \exp[i(\delta_{I}^{A} + \delta_{I'}^{A})]I(L, \alpha, L')$$

$$\times \int_{0}^{R_{A}} d\rho_{A} \rho_{A}^{2} R_{I}^{(F)}(\rho_{A}) \frac{dv_{A}(\rho_{A})}{d\rho_{A}} R_{I'}^{(I)}(\rho_{A}),$$
(3.22)

with  $R_A$  the muffin-tin radius and

$$I(L, \alpha, L') = \int d\Omega(\hat{\rho}_{A}) Y_{L}^{*}(\dot{\rho}_{A}) (\hat{x}_{\alpha} \cdot \hat{\rho}_{A}) Y_{L} \cdot (\dot{\rho}_{A}).$$
(3.23)

The use of the full solution to the Schrödinger equation in the radial integral in Eq. (3.22) rather than the spherical Bessel function  $j_I(\rho_A)$  means the expression fully includes multiple scatterings described by the factors  $1 + t_{\tilde{R}_A}^{\alpha} G$  appended to the right and left of  $[\partial V(\{\bar{R}\})/\partial R_A^{\alpha}]_0$  in the definition of  $F_A^{\alpha}$ .

We also need the partial-wave decomposition of the single-site t matrix to evaluate the right-hand side of Eq. (3.18). This is given by, as in LEED theory,

$$(\underline{t}_{\bar{R}_{A}})_{LL'} = -\frac{\hbar^{2}}{2m} \left(\frac{\exp(2i\delta_{L}^{A}) - 1}{2ik_{0}}\right) \delta_{LL'}, \qquad (3.24)$$

where  $k_0 = [2m(E + V_0 + iV_i)/\hbar^2]^{1/2}$  is the complex wave vector of the electron in the crystal, with Ebeing the external energy, corrected inside for the inner potential  $(V_0)$  and inelastic damping  $(V_i)$ .

Once the electron-phonon coupling matrices  $Q_{G\|G\|}^{(A_G)^{\pm\pm}}$  are obtained for a given layer and mode, interlayer scatterings before and after phonon excitation can be obtained in a straightforward manner from the methods of LEED theory. In essence one must append interlayer scatterings onto the intralayer processes just examined, for both the incoming and outgoing electron legs. Thus, in a notation similar to the LEED problem, we encounter propagators of the form

$$P_{G_{\parallel}\bar{G}_{\parallel}}^{\pm}(\vec{k}) = \delta_{\bar{G}_{\parallel}\bar{G}_{\parallel}}^{\pm} \exp[\pm i\,\vec{a}\cdot\vec{k}_{\pm}(\vec{G}_{\parallel})]$$
(3.25)

defined for both the incoming electron (wave vector  $\vec{k}^{(I)}$ ) and outgoing electron (wave vector  $\vec{k}^{(F)}$ ), and  $\vec{a} = \vec{d}_{i+1} - \vec{d}_i$ , where  $\vec{d}_i$  and  $\vec{d}_{i+1}$  are directed to equivalent origins in layer *i* and layer *i*+1. Also, for propagation within layer *i* (different from the layer in which phonon excitation occurs), we encounter scattering matrices

$$M_{\tilde{G}_{\parallel}\tilde{G}_{\parallel}}^{\pm\pm}(\vec{k}) = \frac{16\pi^{2}mn_{s}}{i\hbar^{2}} \sum_{LL'} \frac{Y_{L}(\vec{k}_{\pm}(\vec{G}_{\parallel}))}{k_{\perp}(\vec{G}_{\parallel})} (\underline{1} - \underline{t}^{(i)}\underline{G}^{(i)})_{LL}^{-1},$$
$$\times t_{L}^{(i)}Y_{L}^{*}, (\vec{k}_{\pm}(\vec{G}_{\parallel})) \qquad (3.26)$$

evaluated for both the incoming and the outgoing electron.

With the "building blocks" described above, we

can now construct prescriptions for summing over all possible scattering paths by which the onephonon excitation process can occur. For this purpose, suppose the layer A in which the phonon excitation occurs is the outermost layer of nuclei, so all other layers including layer B lie below. Then we can break the multiple-scattering series down into four basic sets of processes, as illustrated in Fig. 2. We describe these processes, then write down the relevant scattering amplitudes.

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In the first process, the incoming electron first strikes layer A, multiply scatters always in layer A but excites a phonon before it exits to the vacuum. The contribution to the scattering amplitude for this process is just  $\underline{Q}^{(A\alpha)^{-+}}$ , where the amplitude  $\underline{Q}^{(A\alpha)^{-+}}$  is a matrix in the space of reciprocallattice vectors  $\vec{G}_{\parallel}$  and  $\vec{G}'_{\parallel}$ , as one sees from Eq. (3.18).

In the second basic process, the electron first multiply scatters off the combination of layer A, and layer B combined with the substrate, before exciting the phonon in layer A and exiting. For this process, we supplement the amplitude  $\underline{Q}^{(A,\alpha)^{-+}}$  by

$$\frac{Q_{2}^{(A,\alpha)} = Q^{(A,\alpha)^{-}} - \frac{P^{(AB)}_{\vec{k}}(1) \left(1 - \frac{R^{(BS)}_{\vec{k}} - \frac{P^{(BA)}_{\vec{k}}(1)}{\frac{P^{(A)}_{\vec{k}}(1)} - \frac{P^{(AB)}_{\vec{k}}(1)}{\frac{P^{(A)}_{\vec{k}}(1)} - \frac{P^{(A)}_{\vec{k}}(1)}{\frac{P^{(A)}_{\vec{k}}(1)} - \frac{P^{(A)}_{\vec{k}}(1)} - \frac{P^{(A)}_{\vec{k}}(1)}{\frac{P^{(A)}_{\vec{k}}(1)} - \frac{P^{(A)}_{\vec{k}}(1)} - \frac{P^{(A)}_{\vec{k}}(1)} - \frac{P^{(A)}_{\vec{k}}(1)} - \frac{P^{(A)}_{\vec{k}}(1)} - \frac{P^{(A)}_{\vec{k}}(1)} - \frac{P^{(A)}_{\vec{k}}(1)} - \frac{P^{(A)}_{\vec{k}}$$



FIG. 2. (a) Illustration of some of the factors which enter the final expression for the one-phonon excitation amplitude. The matrix  $\underline{R}^{(BS)}$  describes reflection of an electron from the combination (BS) of layer B and the substrate. Here  $\underline{P}^{BA}$  and  $\underline{P}^{AB}$  account for the damping and change in phase of the electron wave as it propagates from layer A to layer B or conversely. In part (b) through (e) of the figure, the four basic classes of paths are outlined. The open circle with wavy line attached denotes the point where excitation of the phonon occurs.

where  $\underline{R}_{k}^{(BS) \pm \pm}$ , a matrix in the space of reciprocal-lattice vectors, sums the amplitudes for multiple scattering within layer *B*, between layer *B* and the substrate, and within the substrate. Again  $\underline{P}_{k}^{(AB)}$  and  $\underline{P}_{k}^{(BA)}$  are the interlayer propagators defined in Eq. (3.25) and shown in Fig. 2.

In the third basic process, the electron encounters and scatters within layer A first, with excitation of the phonon, then multiply scatters off the combination of layer B and the substrate (and layer A) before exiting. Here for the scattering amplitude we have

$$\frac{Q_3^{(A\alpha)}}{\xi} = (\underline{1} + \underline{M}_{\overline{k}}^{(A)} - \underline{P}_{\overline{k}}^{(AB)}) \underline{P}_{\overline{k}}^{(AB)} \\
\times (\underline{1} - \underline{R}_{\overline{k}}^{(BS)} - \underline{P}_{\overline{k}}^{(BA)}) \underline{M}_{\overline{k}}^{(A)} - \underline{P}_{\overline{k}}^{(AB)})^{-1} \\
\times \underline{R}_{\overline{k}}^{(BS)} - \underline{P}_{\overline{k}}^{(BA)} \underline{Q}^{(A\alpha)++}.$$
(3.28)

Finally, for the fourth combination of processes, illustrated in Fig. 2(e), we have

$$\frac{Q_{4}^{(A\alpha)}}{k} = \left(\frac{1}{k} + \frac{M_{k}^{(A)}}{k} + \frac{M_{k}^{(A)}}{k} + \frac{M_{k}^{(B)}}{k} + \frac{1}{k} +$$

While the expressions above have a formidable appearance, once  $Q_{\overline{G}_{\parallel}\overline{G}_{\parallel}}^{(\underline{A}\underline{\alpha})^{\pm}\pm}$  is constructed through use of Eq. (3.18), the factors which appear in Eq. (3.27) through Eq. (3.29) are identical to those which enter LEED theories, and the theory of angle-resolved photoemission.

When all the factors introduced above are collected together, and the definition of  $[\partial f(\{\vec{R}\},\vec{G}_{\parallel})/\partial R_A^{\alpha}]_0$  is noted [Eq. (3.8)], we have

$$\frac{\left(\frac{\partial f\left(\left\{\vec{\mathbf{R}}\right\},\vec{\mathbf{G}}_{\parallel}\right)}{\partial R_{A}^{\alpha}}\right)_{0}}{=}\frac{P_{\vec{k}}^{(0,A)}(Q^{(A\alpha)^{-+}}+Q^{(A\alpha)}_{2}+\cdots+Q^{(A\alpha)}_{4})}{\times \frac{P_{\vec{k}}^{(A\alpha)}}{(1-\alpha)}},$$

$$(3.30)$$

where  $\underline{P}_{k}^{(A0)}$  and  $\underline{P}_{k}^{(0A)}$  are propagators that take the electron wave from the vacuum-solid interface, located above the layer A, into layer A and back. We have the explicit form

$$\underline{P}_{\vec{k}+\vec{G}_{\parallel}}^{(AO)} = \delta_{\vec{G}_{\parallel}\vec{G}_{\parallel}}^{*} \exp[i\vec{d}_{s}\cdot(\vec{k}+\vec{G}_{\parallel})]$$
(3.31a)

and

$$\underline{P}_{\vec{k}+\vec{G}_{\parallel}}^{(0A)} = \delta_{\vec{G}_{\parallel}\vec{G}_{\parallel}} \exp\left[-i\vec{d}_{s}\cdot(\vec{k}+\vec{G}_{\parallel})\right], \qquad (3.31b)$$

with  $\overline{d}_s$  the distance between the solid-vacuum interface and layer A.

In Eq. (3.30) and the discussion that preceeds it, we have outlined the method of constructing the

scattering amplitude derivative  $\left[\partial f(\{\vec{R}\}, \vec{G}_{\parallel}) / \partial R_{\perp}^{\alpha}\right)_{0}$ through explicit summation of the multiple-scattering series. As we have seen from the discussion of Sec. II, we must also construct  $[\partial f(\{\vec{R}\},$  $\overline{G}_{\parallel}$ )/ $\partial R_{B}^{\alpha}$ ]<sub>0</sub> by the same method. The derivation may be carried through in a straightforward manner, and for completeness we set down the explicit form of this quantity. First we must construct the matrix  $Q_{G_{i}}^{(\boldsymbol{B},\boldsymbol{\alpha}') \neq \pm}$  that describes phonon creation at a site in layer B, plus multiple scattering inside the layer as the electron approaches and exits from the site in the master unit cell where the phonon creation event occurs. For this we can use Eq. (3.18) directly, but with all quantities that enter indexed to refer to species B rather than species A. Then we sum over all possible scattering paths from layer B and the substrate below using precisely the same decomposition procedure as that given in Fig. 2. Of course, now it is only the substrate that is directly below layer B. We require the propagators  $P^{(SB)}$  and  $P^{(BS)}$  that take the electron from layer  $\overline{B}$  to the substrate, and from the substrate back to layer B, respectively. Also, we require a reflection matrix  $R^{(S)^{-+}}$  that describes reflection of the electron from the substrate. Then if we denote the analog of the sum  $Q^{(A\alpha)^{-+}} + \cdots$  $+ Q_4^{(A\alpha)}$  by  $Q_{TS}^{(B\alpha)}$ , we have the explicit form:

$$\frac{Q_{TS}^{(B\alpha)} = Q^{(B\alpha)^{-}} + Q^{(B\alpha)^{-}} - P_{k}^{(Bs)}(1 - R_{k}^{(S)^{-}} + P_{k}^{(SB)}M_{k}^{(Bt)} - P_{k}^{(Bs)})^{-1}R_{k}^{(S)^{-}} + P_{k}^{(SB)}(1 + M_{k}^{(B)^{+}}) + (1 + M_{k}^{(B)^{+}}) - P_{k}^{(Bs)})}{(1 - R_{k}^{(S)^{-}} + P_{k}^{(SB)}M_{k}^{(Bt)} - P_{k}^{(Bs)})^{-1}R_{k}^{(S)^{-}} + P_{k}^{(SB)}(1 + M_{k}^{(B)^{-}}) - P_{k}^{(Bs)})} \times (1 - R_{k}^{(S)^{-}} + P_{k}^{(SB)}M_{k}^{(Bt)^{-}} - P_{k}^{(Bs)})^{-1}R_{k}^{(S)^{-}} + Q_{k}^{(SB)}M_{k}^{(Bt)^{-}} + Q_{k}^{(SB)})^{-1}R_{k}^{(St)^{-}} + Q_{k}^{(SB)}(1 - R_{k}^{(S)^{-}} + P_{k}^{(SB)})^{-1}R_{k}^{(St)^{-}} + Q_{k}^{(SB)})^{-1}R_{k}^{(St)^{-}} + Q_{k}^{(SB)} + Q_{k}^{(Bt)^{-}} + Q_{k}^{(Bs)})^{-1}R_{k}^{(St)^{-}} + Q_{k}^{(SB)}(1 - R_{k}^{(S)^{-}} + P_{k}^{(SB)})^{-1}R_{k}^{(St)^{-}} + Q_{k}^{(SB)})^{-1}R_{k}^{(St)^{-}} + Q_{k}^{(SB)} + Q_{k}^{(Bt)^{-}} + Q_{k}^{(Bs)})^{-1}R_{k}^{(St)^{-}} + Q_{k}^{(SB)} + Q_{k}^{(SB)} + Q_{k}^{(Bt)^{-}} + Q_{k}^{(SB)})^{-1}R_{k}^{(St)^{-}} + Q_{k}^{(SB)} + Q_{k}^{(SB)} + Q_{k}^{(Bt)^{-}} + Q_{k}^{(SB)})^{-1}R_{k}^{(St)^{-}} + Q_{k}^{(SB)} + Q_{k}^{(SB)^{-}} + Q_{k}^{(SB)} + Q_{k}^{(SB)^{-}} + Q_{k}^{(SB)} + Q_{k}^{(SB)^{-}} + Q_{k}^{(SB)} + Q_{k}^{(SB)^{-}} + Q_$$

The sequence of scatterings incorporated into the amplitude displayed in Eq. (3.33) sums all processes which occur within layer *B*, or all paths that involve scatterings which originate first in the substrate or which have the electron first strike layer B, then move to the substrate (and possibly return to layer B). We must still incorporate events which involve scatterings from layer B up

to layer A and possibly back. We may include all such scatterings by sandwiching the amplitude  $Q_{TS}^{(B\alpha)}$  between two amplitudes  $A_{k}^{++}(I)$  and  $A_{k}^{--}(F)$ which describes the interaction of the electron with the outermost layer A as it enters and exits the crystal. If we introduce as a final step

$$\frac{A_{\bar{k}}^{++}}{(I)} = \underline{P}_{\bar{k}}^{(BA)} (\underline{1} - \underline{M}_{\bar{k}}^{(A)+} - \underline{P}_{\bar{k}}^{(AB)} \underline{R}_{\bar{k}}^{(BS)-} + \underline{P}_{\bar{k}}^{(BA)})^{-1} \times (\underline{1} + \underline{M}_{\bar{k}}^{(A)++}) \underline{P}_{\bar{k}}^{(A0)}, \qquad (3.33)$$

$$\underline{A}_{\bar{k}}^{--} \underline{P}_{\bar{k}}^{(OA)} (\underline{1} + \underline{M}_{\bar{k}}^{(A)-}) \underline{P}_{\bar{k}}^{(AB)}, \qquad (3.33)$$

$$\times (\underline{1 - R_{\overline{k}}^{(BS)^{-}} + P_{\overline{k}}^{(BA)} \underline{M}_{\overline{k}}^{(A)+} - P_{\overline{k}}^{(AB)})^{-1}}, \qquad (3.34)$$

then we may synthesize the scattering amplitude derivative as

$$\left(\frac{\partial f(\{\vec{\mathbf{R}}\},\vec{\mathbf{G}}_{\parallel})}{\partial R_{B}^{\alpha}}\right)_{0} = \underline{A}_{\vec{\mathbf{k}}}^{-} \overline{P} \underline{Q}_{TS}^{(B\alpha)-+} \underline{A}_{\vec{\mathbf{k}}}^{++} \underline{I}_{1}.$$
(3.35)

Thus we have constructed the explicit form of the two basic amplitudes  $[\partial f(\{\vec{R}\},\vec{G}_{\parallel})/\partial R^{\alpha}_{B_{0}}]_{0}$  and  $[\partial f(\{\vec{R}\},\vec{G}_{\parallel})/\partial R^{\alpha}_{B_{0}}]_{0}$  required to calculate the fundamental matrix element  $M(\vec{k}^{(I)},\vec{k}^{(F)};\vec{Q}_{\parallel}j)$  which appears in Eq. (2.13). (Remember that the Kronecker delta is absorbed in  $[\partial f(\{\vec{R}\},\vec{G}_{\parallel})/\partial R^{\alpha}_{A,B_{0}}]_{0}$ .) In a separate paper, we describe a series of numerical calculations carried out with the present formalism, for a  $c(2\times 2)$  overlayer of CO on a Ni(100) surface. In the present paper, we turn to brief concluding remarks of a general nature.

# **IV. CONCLUDING REMARKS**

We have outlined a method for calculating the energy and angle variation of the intensity for large-angle inelastic scattering of electrons from an adsorbed layer of diatomic molecules, in the approximation that substrate atoms fail to participate in the vibrational motion. While we report detailed calculations of the loss intensities elsewhere for scattering off vibrations of a  $c(2 \times 2)$ layer of CO on a Ni(100) surface, some general observations may prove useful.

We see from Eq. (2.13) that the loss cross section involves the square of the linear combination of the scattering amplitude for exciting the vibration by striking atom A and by striking atom B. It would be useful to be able to extract  $(\partial f / \partial R_A^{(i)})_0$  and  $(\partial f / \partial R_B^{(i)})_0$  directly from the data on scattering from the two vibrational modes associated with motion in the Cartesian direction  $\hat{x}_i$ . We see from Appendix A that  $\sin\theta_i^{(i)}$  and  $\cos\theta_i^{(i)}$  may be calculated once the frequencies of the two normal modes  $\omega_{\perp}$ and  $\omega_{-}$  are known. But unfortunately,  $(\partial f / \partial R_{A}^{(i)})_{0}$ and  $(\partial f / \partial R_B^{(i)})_0$  are both complex numbers with a modulus and phase. Thus the cross section depends on three parameters, the modulus of each quantity, and the relative phase. Thus two pieces of experimental information are insufficient to enable each scattering amplitude derivative to be extracted from the data.

The expression in Eq. (3.9) expresses the wave function of the emerging electron in a form useful to contemplate. The approach of the electron to a particular site where phonon excitation occurs is controlled by  $|\psi_{\text{LEED}}\rangle$ , precisely the same wave function as encountered in LEED theory. Similarly, the exit process is precisely that in angle-resolved photoemission.

By choosing the energy of the incoming electron in the appropriate fashion, and also the incident and scattered angles, it should be possible to enhance the magnitude of the inelastic scattering cross section. The LEED intensity, considered as a function of energy for fixed angle, contains strong structure with maxima produced by Bragg reflections (kinematical features) or multiplescattering resonances of the electron from the surface structure. An appropriate choice of incident energy and angle should allow one, in principle, to enhance the amplitude of the incoming electron wave function in the adsorbed layer, and thus enhance the inelastic scattering cross section. At the same time, once the scattering event occurs, the exit probability will be enhanced in those directions where one finds prominent resonances in the angle-resolved photoemission intensity. Thus it should be possible to choose an appropriate combination of incident electron energy and scattering geometry to take advantage of multiple-scattering resonances in both the incoming and outgoing scattered waves.

We note that in light-scattering studies of excitations on surfaces and in thin films, this method has been proposed<sup>19</sup> and subsequently utilized with considerable success.<sup>20</sup> Here one places a dielectric prism above a substrate with an air gap between. At certain angles and in the appropriate spectral regime, one obtains large enhancements of the electric field of a light wave in the air gap and near the substrate; this occurs when the phase-matching condition is satisfied for excitation of surface polaritons on the vacuum-substrate system. Recent light-scattering studies utilize a prism structure and geometry in which both the incident and scattered light lie in an angular range where one finds resonant enhancement of both light fields. The result is an increase in the scattering cross section of one to two orders of magnitude. The expression in Eq. (3.9) leads one to form an analogy between these light-scattering studies carried out in a three-layer geometry and the problem addressed in the present paper.

We also wish to make a general remark on the presentation of data obtained in large-angle EELS studies. In the study of small-angle, dipole-dominated scattering, it has proved very useful to form the ratio  $r(E) = I_{\text{EELS}} / I_{\text{LEED}}$ . That is, one measures the energy variation  $I_{\rm LEED}$  for elastic scattering along the specular direction and the energy variation  $I_{\text{EELS}}$  of the inelastic-electron-scattering cross section and then forms the stated ratio. The theory<sup>9</sup> shows that the details of the electron-substrate interaction drops out of the ratio. One is left with a function that displays a smooth energy variation and contains information about only the dipole excitation process. The energy variation of r(E) provided by the theory has been checked in considerable detail,<sup>21</sup> and the form provided by the dipole-scattering theory allows numerical values for the dynamic effective charge (or polarizability derivative) of the adsorbed molecule to be extracted from the data.<sup>10</sup>

It is important to recognize that formation of the ratio r(E) is useful *only* in the small-angle regime, under conditions where dipole scattering dominates. In this situation, the inelastic scattering event occurs while the electron is well into the vacuum *above* the crystal,<sup>9</sup> by virtue of the long-range character of the dipole potential. It suffers a very small-angle deflection there, as it either approaches or exits from the crystal. It never deviates far from the specular direction, and suffers a small change in energy. Only under these rather special conditions, as outlined in early papers,<sup>9</sup> is the cross section expressible as the product of  $I_{\text{LEED}}$  and a prefactor that describes the dipole excitation process.

We see clearly from the structure of Eq. (3.9) that in the large-angle-scattering regime, formation of the ratio r(E) is not a physically meaningful manner of presenting EELS data. The quantity of interest is simply  $I_{EELS}$  itself; by dividing by  $I_{LEED}$ , one may add spurious structure into the ratio r(E), and this confuses rather than aids the interpretation. Thus, while formation of r(E) is a useful procedure that aids quantitative interpretation of the small-angle data, more gnerally it is  $I_{EELS}$ itself that is of interest.

It would be useful to formulate the theory of EELS in a manner that allows direct contact with the earlier, small-angle dipole-excitation theories. It is not possible to do this from the approach used here. The approximation that prohibits such explicit comparison is the use of the muffin-tin procedure to calculate the derivative  $(\partial V(\{\vec{R}\})/\partial R_A^{\alpha})_0$ . In Eq. (3.14), the right-hand side vanishes identically when  $\rho_A$  lies outside the sphere within which the potential is nonzero.

The physical picture implied by this procedure is the following. Consider a particular unit cell which surrounds an equilibrium position in the lattice, and for simplicity suppose the unit cell is

electrically neutral (this will not be the case near the surface, but we only make a qualitative point here). Now displace the nucleus in this unit cell from the equilibrium position  $\vec{R}^{(0)}$  to  $\vec{R}$ , with  $\vec{u} = \vec{R}$  $-\vec{R}^{(0)}$  the magnitude of the displacement. If the electron charge cloud remains rigid and unchanged in shape, and follows the nucleus, then our procedure is quite correct. Actually, displacement of the nucleus relative to other nuclei in the material will distort the electron charge cloud so its geometrical center no longer coincides with the position of the displaced nucleus. The unit cell thus acquires an electric dipole moment, which produces a long-range electrostatic potential that extends well outside the muffin-tin sphere. Also, charge transfer between unit cells will occur at the same time, to produce a net dipole moment in the surface region. These effects must be incorporated into the theory before one can contemplate direct contact with the early dipole-scattering theories. This is a formidable task; the calculation of the Born effective charge in the bulk of insulating crystals is a topic that has received only limited attention, and the extension of such calculations to the surface is a major modification.<sup>22</sup> It is possible, however, to use a phenomenological approach which grafts the dipole-scattering amplitude onto the amplitude produced by the impactscattering approach developed in the present paper. This is a question we hope to address in future work.

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#### APPENDIX A: NORMAL-MODE EXPANSION FOR A DIATOMIC MOLECULE BOUND TO A MASSIVE SUBSTRATE

The purpose of this Appendix is to provide explicit expressions for the quantities  $\cos\theta_j^{(i)}$  and  $\sin\theta_j^{(i)}$ . The geometry we employ is illustrated in Fig. 3. We consider a molecule which "stands on its head," on a substrate regarded as fabricated from infinitely heavy masses. If the bonding site has symmetry sufficiently high that the geometry is invariant under reflection in the xz plane and the yz plane, then the vibrational Hamiltonian in the harmonic approximation is diagonal in the Cartesian components of the displacements of the atoms. The vibrational Hamiltonian thus decomposes into three terms, one of which involves mo-



FIG. 3. Illustration of the simple picture that forms the basis for our description of the adsorbate vibrations.

tion in the z direction, one in the y direction, and one in the x direction. Each is identical in formal structure, and has the form

$$H = \frac{P_A^2}{2M_A} + \frac{P_B^2}{2M_B} + \frac{1}{2}k_0(u_A - u_B)^2 + \frac{1}{2}k_s u_B^2, \quad (A1)$$

where  $M_A$  and  $M_B$  are the masses of the two atoms, and  $k_0$  and  $k_s$  are the spring constants illustrated in Fig. 3.

The eigenfrequencies are readily determined by elementary methods and are given by

$$\omega_{\pm}^{2} = \frac{1}{2}k_{0}\left(\frac{1}{M_{A}} + \frac{1}{M_{B}}\right) + \frac{1}{2}\frac{k_{s}}{M_{B}}$$
$$\pm \frac{1}{2}\left[k_{0}^{2}\left(\frac{1}{M_{A}} + \frac{1}{M_{B}}\right)^{2} + \frac{2k_{0}k_{s}}{M_{B}}\left(\frac{1}{M_{B}} - \frac{1}{M_{A}}\right) + \frac{k_{s}^{2}}{M_{B}^{2}}\right]^{1/2}.$$
(A2)

If we set  $k_s$  to zero, then  $\omega_+^2 = k_0/\mu$ , with  $\mu$  the reduced mass. This is the "A-B stretch" mode of the gas phase. At the same time,  $\omega_-^2$  sinks to zero to become the center-of-mass translation mode.

The quantities

$$\sin\theta_{\pm} = \frac{k_0}{(M_A M_B)^{1/2}} \left[ \frac{k_0^2}{M_A M_B} + \left( \omega_{\pm}^2 - \frac{k_0}{M_A} \right)^2 \right]^{-1/2}$$
(A3)

and

$$\cos\theta_{\pm} = \left(\frac{k_0}{M_A} - \omega_{\pm}^2\right) \left[\frac{k_0^2}{M_A M_B} + \left(\omega_{\pm}^2 - \frac{k_0}{M_A}\right)^2\right]^{-1/2}$$
(A4)

are the objects  $\cos\theta_j^{(i)}$  and  $\sin\theta_j^{(i)}$  which enter Eqs. (2.12a) and (2.12b) of the text. In the text, the superscript is appended to the angle to designate the Cartesian direction associated with mode j, and the formulas in the text are cast in phonon language, with a phonon spectrum constructed from the oscillator amplitudes associated with the array of vibrating molecules. While the use of the phonon language may seem superflurous at the present stage of development of our lattice-dynamical model, it will prove useful to have the theory formulated in this language for later applications.

After a bit of algebra, one may demonstrate that  $\cos\theta_{\pm}$ ,  $\sin\theta_{\pm}$  satisfy the orthonormality relations

$$\cos^2\theta_+ + \sin^2\theta_+ = 1 \tag{A5}$$

$$\cos\theta_{+}\cos\theta_{-} + \sin\theta_{+}\sin\theta_{-} = 0. \qquad (A6)$$

### APPENDIX B: THE SCATTERING AMPLITUDE FOR PHONON EXCITATION AND MULTIPLE SCATTERING WITHIN A LAYER

The purpose of this Appendix is to summarize the details of the derivation of the scattering amplitudes  $Q_{\overline{G}_{\parallel}\overline{G}_{\parallel}}^{(A\alpha)^{\pm z}}$  that describe multiple scattering combined with phonon excitation within a layer of atoms. This amplitude plays a critical role in the analysis of Sec. III of the text.

We begin with  $|\psi_{\text{EELS}}\rangle$  defined in Sec. III and for the moment examine only the factors that describe the interaction of the electron with the particular site where the phonon-excitation event occurs, ignoring all multiple scattering from other sites. We call this portion of the wave function  $|\psi_{\text{EELS}}^{(D)}\rangle$ , where the superscript (D) denotes the portion of the wave that propagates directly to the phononexcitation site and then on to the detector. We have (again using  $\vec{R}_A$  to represent the equilibrium site vector)

$$\langle \vec{\mathbf{r}} | \psi_{\text{EELS}}^{(D)} \rangle = \frac{m}{4\pi^3 \hbar^2} \frac{1}{N_s} \sum_{D} \exp[i \vec{\mathbf{s}}_{\nu} \cdot (\vec{\mathbf{k}}^{(I)} - \vec{\mathbf{Q}}_{\text{I}})]$$

$$\times \int \frac{d^3 r'' d^3 k \exp[i \vec{\mathbf{k}} \cdot (\vec{\mathbf{r}} - \vec{\mathbf{r}}')]}{[2mE/\hbar^2 - k^2 - (2m/\hbar^2)\Sigma(E)]} \left( \delta(\vec{\mathbf{r}}' - \vec{\mathbf{r}}''') + \int d^3 r'' t_{\vec{\mathbf{R}}_A} (\vec{\mathbf{r}}' - \vec{\mathbf{R}}_A, \vec{\mathbf{r}}'' - \vec{\mathbf{R}}_A) G(\vec{\mathbf{r}}'' - \vec{\mathbf{r}}''') \right) \left( \frac{\partial v_A (\vec{\mathbf{r}}'' - \vec{\mathbf{R}}_A)}{\partial R_A^{\alpha}} \right)_{C} \left( \delta(\vec{\mathbf{r}}'' - \vec{\mathbf{r}}'') + \int d^3 r'' t_{\vec{\mathbf{R}}_A} (\vec{\mathbf{r}}' - \vec{\mathbf{R}}_A, \vec{\mathbf{r}}'' - \vec{\mathbf{R}}_A) G(\vec{\mathbf{r}}'' - \vec{\mathbf{r}}''') \right) \left( \frac{\partial v_A (\vec{\mathbf{r}}'' - \vec{\mathbf{R}}_A)}{\partial R_A^{\alpha}} \right)_{C} \left( \delta(\vec{\mathbf{r}}'' - \vec{\mathbf{r}}'') + \int d^3 r'' G(\vec{\mathbf{r}}''' - \vec{\mathbf{r}}'') t_{\vec{\mathbf{R}}_A} (\vec{\mathbf{r}}'' - \vec{\mathbf{R}}_A, \vec{\mathbf{r}}'' - \vec{\mathbf{R}}_A) \right) \frac{\exp(i \vec{\mathbf{k}} (l) \cdot \vec{\mathbf{r}}')}{\sqrt{\mathbf{v}}} \exp(i \vec{\mathbf{k}} \cdot \vec{\mathbf{S}}_{\nu}) .$$

$$(B1)$$

We can expand various factors in Eq. (B1) in spherical-harmonic expansions, beginning with the well-known plane-wave expansion

$$\exp(i\vec{k}\cdot\vec{r}) = 4\pi \sum_{L} (i)^{l} j_{l}(kr) Y_{L}^{*}(\vec{k}) Y_{L}(\vec{r}), \qquad (B2)$$

where L stands for the pair of indices (l,m) appended to the spherical harmonics. We also have

$$G(\vec{\mathbf{r}} - \vec{\mathbf{r}}') = \sum_{L} G_{l}(\mathbf{r}, \mathbf{r}') Y_{L}(\vec{\mathbf{r}}) Y_{L}^{*}(\vec{\mathbf{r}}'), \qquad (B3)$$

and, with  $\vec{\rho}_A = \vec{r} - \vec{R}_A$ ,

$$t_{\overline{\mathsf{R}}_{A}}(\vec{\rho}_{A},\vec{\rho}_{A}') = \sum_{L} t_{\overline{\mathsf{R}}_{A}i}(\rho_{A},\rho_{A}')Y_{L}(\vec{\rho}_{A})Y_{L}^{*}(\vec{\rho}_{A}').$$
(B4)

When these identities are combined with the definition  $D(k,E) = 2m[E - \hbar^2 k^2/2m - \Sigma(E)]/\hbar^2$ , then we have

$$\langle \mathbf{\tilde{r}} | \psi_{\text{EELS}}^{(D)} \rangle = \frac{m}{4\pi^{3}\hbar^{2}\sqrt{V}} \int \frac{d^{3}k \exp[i\,\mathbf{\tilde{k}}\cdot(\mathbf{\tilde{r}}-\mathbf{\vec{R}}_{A})]}{D(k,E)}$$

$$\times \int d^{3}\rho_{A}^{'''} \sum_{LL'} \left[ 4\pi i^{-1}Y_{L}(\mathbf{k}) \left( j_{l}(k\rho_{A}^{'''}) + \int d\rho_{A}^{\prime}d\rho_{A}^{''}(\rho_{A}^{\prime'})^{2}(\rho_{A}^{''})^{2} j_{l}(k\rho_{A}^{\prime})t_{Al}(\rho_{A}^{\prime},\rho_{A}^{\prime''})G_{l}(\rho_{A}^{\prime''},\rho_{A}^{'''}) \right) Y_{L}^{*}(\bar{\rho}_{A}^{'''})$$

$$\times \left( \frac{\partial v_{A}(\bar{\rho}_{A}^{'''})}{\partial R_{A}^{\prime}} \right)_{LL'} 4\pi i^{l'}Y_{L'}^{*}(\mathbf{\tilde{k}}^{(l)}) \exp(i\,\mathbf{\tilde{k}}^{(l)}\cdot\mathbf{\vec{R}}_{A})$$

$$\times \left( j_{l'}(k\rho_{A}^{''''}) + \int d\rho_{A}^{iv}d\rho_{A}^{v}(\rho_{A}^{iv})^{2}(\rho_{A}^{v})^{2}G_{l'}(\rho_{A}^{'''},\rho_{A}^{iv})t_{Al'}(\rho_{A}^{iv},\rho_{A}^{v})j_{l'}(\rho_{A}^{v}) \right)$$

$$\times Y_{L'}(\bar{\rho}_{A}^{'''}) \right] \delta_{\mathbf{\tilde{k}}_{ll}}; \mathbf{\tilde{k}}_{ll}^{\prime L} \mathbf{\tilde{c}}_{ll}^{*+} \mathbf{\tilde{c}}_{ll} \quad .$$

$$(B5)$$

Now if  $R_1(\rho)$  is the full solution to the radial portion of the Schrödinger equation, within the sphere where the muffin-tin potential associated with atom A is located, we have an identity that couples the single-site t matrix with the scattering phase shift and  $R_1(\rho)$ . It reads

$$\exp(i\delta_{I})R_{I}(\rho) = j_{I}(k\rho) + \int d\rho_{1}d\rho_{2}\rho_{1}^{2}\rho_{2}^{2}j_{I}(k\rho_{1})t_{I}(\rho_{1},\rho_{2})G_{I}(\rho_{2},\rho)$$
(B6)

and with this identity the form in Eq. (B6) can be compacted to read

$$\langle \vec{\mathbf{r}} | \psi_{\text{EELS}}^{(D)} \rangle = -\frac{4m}{\pi\hbar^2 \sqrt{V}} \sum_{LL'} \int \frac{d^3k \exp(i\vec{\mathbf{k}}\cdot\vec{\mathbf{r}})}{D(k,E)} \exp[i(\vec{\mathbf{k}}^{(I)}-\vec{\mathbf{k}})\cdot\vec{\mathbf{R}}_A] Y_L(\vec{\mathbf{k}})(F_A^{\alpha})_{LL}, Y_L^*, (\vec{\mathbf{k}}^{(I)})\delta_{\vec{\mathbf{k}}_{\parallel}}; \vec{\mathbf{k}}_{\parallel}^{\alpha}) - \tilde{\mathbf{Q}}_{\parallel} + \tilde{\mathbf{G}}_{\parallel}, \quad (B7)$$

where  $(F_A^{\alpha})_{LL}$ , is the matrix displayed explicitly in Eq. (3.21) of the text. Upon performing the integration over  $\vec{k}$ , following the methods of LEED theory, we are led to an explicit expression for the outgoing wave:

$$\langle \mathbf{\tilde{r}} | \psi_{\text{EELS}}^{(D)} \rangle = \frac{16\pi^2 m i}{S\hbar^2 \sqrt{V}} \sum_{LL'} \frac{Y_L(\mathbf{\tilde{k}}^{(F)}(\mathbf{\tilde{G}}_{\parallel}))}{k_{\perp}^{(F)}(\mathbf{\tilde{G}}_{\parallel})} (F_A^{\alpha})_{LL'} Y_L^* \langle \mathbf{\tilde{k}}^{(I)} \rangle \exp[i \, \mathbf{\tilde{k}}^{(F)}(\mathbf{\tilde{G}}_{\parallel}) \cdot \mathbf{\tilde{r}}] \exp\{i [\mathbf{\tilde{k}}^{(I)} - \mathbf{\tilde{k}}^{(F)}(\mathbf{\tilde{G}}_{\parallel})] \cdot \mathbf{\tilde{R}}_A\}. \tag{B8}$$

To construct the matrix  $Q_{G_{\parallel}C_{\parallel}}^{(4\alpha)^{\pm\pm}}$ , we must append to the single-site calculation that leads to Eq. (B8), the incoming and outgoing "legs" that appear in Eq. (3.17) of the text. Here we proceed by decomposing the Green's function that describes intersite propagation by the methods used in the LEED problem. Recall that

$$G(\vec{p}_{A} - \vec{p}_{A'} + \vec{R}_{A} - \vec{R}_{A'}) = \frac{8\pi mk}{i\hbar^{2}} \sum_{L_{1}L_{2}L_{3}} h_{l_{3}}^{(1)}(k|\vec{R}_{A} - \vec{R}_{A'}|) i^{l_{1}+l_{3}-l_{2}} a(L_{1}L_{2}L_{3}) j_{l_{1}}(k\rho_{A}) j_{l_{2}}(k\rho_{A}) Y_{L_{1}}(\vec{p}_{A}) Y_{L_{2}}^{*}(\vec{p}_{A'}) Y_{L_{3}} \times (\vec{R}_{A} - \vec{R}_{A'}),$$
(B9)

where  $\vec{R}_A \neq \vec{R}_A$  is a site in layer A. Through use of this decomposition combined with a bit of formal matrix algebra, we have for the total outgoing amplitude, after multiple scattering from sites in layer A as the site of phonon emission is approached, and as the electron exits,

$$\langle \vec{\mathbf{r}} | \psi_{\text{EELS}} \rangle = \frac{16\pi^2 m i}{S\hbar^2} \exp\{ i \vec{\mathbf{R}}_A \cdot [\vec{\mathbf{k}}^{(I)} - \vec{\mathbf{k}}^{(F)} (\vec{\mathbf{G}}_{\parallel})] \} \sum_{LL'} \sum_{L_1 L_2} \frac{Y_L (\vec{\mathbf{k}}^{(F)} (\vec{\mathbf{G}}_{\parallel}))}{k_1^{(F)} (\vec{\mathbf{G}}_{\parallel})} (\underline{1} - \underline{t}_{\vec{\mathbf{R}}_A} \underline{G}_{\vec{\mathbf{k}}^{(F)}}^{AA})_{L_1 L_2} (\underline{1} - \underline{G}_{\vec{\mathbf{k}}}^{AA} (\underline{t}_{\vec{\mathbf{R}}_A})_{L_2 L_2}^{-1} (\mathbf{I}_{\vec{\mathbf{R}}_A})_{L_2 L$$

We note that  $\mathbf{R}_{A}$  is a site vector to an atom in the 0 unit cell.

This form leads to the definition of the layer matrices

$$Q_{\tilde{G}_{\parallel}\tilde{G}_{\parallel}}^{(A,\alpha)^{\pm\pm}} = \frac{16\pi^{2}mi}{S\hbar^{2}} \sum_{L_{1}L_{2}} \sum_{L_{3}L_{4}} \frac{Y_{L_{1}}(k_{\pm}^{(F)}(\bar{G}_{\parallel}))}{k_{\perp}^{(F)}(\bar{G}_{\parallel})} (\underline{1} - \underline{t}_{\bar{R}_{A}} \underline{G}_{\bar{k}}^{AA}(F))_{L_{1}L_{2}}^{-1} (F_{A}^{\alpha})_{L_{2}L_{3}} (\underline{1} - \underline{G}_{\bar{k}}^{AA}(F) \underline{t}_{\bar{R}_{A}})_{L_{3}L_{4}}^{-1} Y_{L_{4}}^{*}(\bar{k}_{\perp}^{(I)}(\bar{G}_{\parallel}))$$
(B11)

for incident electron directions with parallel components  $\vec{k}_{\parallel}^{(I)} + \vec{G}_{\parallel}$  to final electron directions with parallel components  $\vec{k}_{\parallel}^{(F)} + \vec{G}_{\parallel}$ .

- <sup>1</sup>See the discussions in the following references: L. H. Little, *Infrared Spectra of Adsorbed Species* (Academic, New York, 1966); M. L. Hair, *Infrared Spectroscopy in Surface Chemistry* (Dekker, New York, 1967).
- <sup>2</sup>See M. Fleischmann, P. J. Hendra, and A. J. Mc-Quillan, Chem. Phys. Lett. <u>26</u>, 163 (1974); D J. Jeanmaire and R. P. Van Duyne, J. Electroanal. Chem. <u>66</u>, 235 (1975); M. G. Albrecht and J. A. Creighton, J. Am. Chem. Soc. <u>99</u>, 5215 (1977); B. Pettinger and V. Wenning, Chem. Phys. Lett. <u>56</u>, 253 (1978); T. H. Wood and M. V. Klein, J. Vac. Sci. Technol. (to be published). A large number of papers on this topic have appeared recently, and only a few representative samples are cited above.
- <sup>3</sup>As far as we know, all experiments that report "giant signals," except for the recent experiment by Wood and Klein cited in Ref. 2, have examined molecules adsorbed on electrodes immersed in electrolytic solution; the electrodes have been subjected to a number of electrochemical cycles and are quite rough. While it is of great interest to acquire the ability of probing adsorbates in electrochemical cells, it is unclear to us at this writing whether the enhancement of the Raman signal has its origin in some feature of the electrochemically produced environment (roughness?), or is an intrinsic effect of a molecule bound to a metallic substrate.
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