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Dynamical theory of low-energy-electron diffraction from disordered overlayers. I. Quasicrystalline analysis

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A dynamical theory is developed for the elastic diffraction of low-energy electrons from disordered monolayers adsorbed on ordered substrates. The quasicrystalline approximation is adapted to treat multiple scattering from the adsorbate. Multiple scattering within the periodic substrate is analyzed without approximation in the context of the inelastic-collision model. Multiple scattering between adsorbate and substrate is considered in two distinct manners, namely in (a) a renormalization of the quasicrystalline description and (b) a more restricted version of this renormalization. Expressions for the cross sections, suitable for numerical evaluation, are calculated for an isotropic-scatterer model of the elastic electron–ion-core interaction. These expressions are functionals of only two statistical quantities: the adsorbate coverage and the pair correlations between adatoms. A lattice-gas model is used to describe the thermodynamic properties of the overlayer thus providing an adequate basis for the consideration of effects on electron scattering associated with the degree of both short- and long-range order in the adsorbate. The expressions for the cross-sections predict characteristic dynamical structure in the intensity and beam profiles associated with the degree of order in the overlayer.

I. INTRODUCTION

In recent years, the theory of elastic low-energy-electron diffraction (ELEED) from solids has been developed in two complementary directions. On the one hand, consideration of the combined consequences of ("dynamical") multiple-elastic scattering[1] and inelastic-electron-electron-interaction–induced processes[2] has led to a generally satisfactory description of ELEED from low-index single-crystal surfaces,[3–9] as well as from ordered overlayers adsorbed on such surfaces.[10–19] On the other hand, studies of defects and disorder at clean surfaces and within adsorbed overlayers have been pursued using single-scattering (i.e., kinematical) models.[20–25] Only one calculation[26] of LEED intensities from an empirical distribution of steps has so far been based on a semidynamical analysis. In this paper we proceed one step further by developing a dynamical theory of electron diffraction from disordered overlayers and by combining this theory with a microscopic model of the degree of order within the adsorbed layer.

A field of extensive activity which exhibits a close conceptual relationship to our analysis is that of the electronic structure of liquids and substitutional solid-state alloys.[27] Indeed, our treatment of multiple-scattering processes within the adsorbed overlayer is directly analogous to the quasicrystalline (or "geometric"[28]) approximation (QCA)[27,29] in the theory of liquids and to the average-t-matrix approximation[27] in the theory of substitutional binary alloys. An essentially new complexity in our analysis, however, lies in the occurrence of dynamical scattering between the periodic substrate and the disordered adsorbate. This aspect of the present problem is taken into consideration in two distinct manners. First, the presence of the substrate is incorporated by utilizing new intra-adsorbate electron propagators which are renormalized to account for intermediate dynamical substrate scattering. This procedure formally reduces the problem of multiple scattering from the entire adsorbate-substrate system to that of multiple scattering from the disordered overlayer alone. While the propagator renormalization requires, in practice, an approximate treatment of intermediate dynamical substrate-scattering events, the renormalized quasicrystalline approximation (RQCA) of the substrate-adsorbate interference terms is adequate in the entire temperature region, i.e., in the presence of both short- and long-range order within the overlayer. Moreover, the RQCA reduces to the exact zero-temperature limit of the expressions for the scattering cross sections. An immediate and highly useful consequence of this result[30] is the description of dynamical scattering from ordered superlattices adsorbed on periodic substrates entirely in terms of *layer*, rather than *sublattice*[14] scattering matrices.

Second, an additional approximation is imposed on the RQCA to the effect that multiple-scattering processes between overlayer sites are replaced by their infinite-temperature limits whenever intermediate substrate-scattering events occur. This restricted RQCA exhibits the attractive analytical feature that it leads to an exactly summable multiple-scattering series for the cross section which is directly accessible to a numerical analysis. Because of the underlying assumptions, however, this approximation results in a satisfactory incorporation of adsorbate-substrate interference terms only in the high-temperature region.

An improvement of the present analysis in analogy to the self-consistent versions of the QCA does not appear essential for three reasons. First, a distinction between the quasicrystalline approximation and its self-consistent extensions does not occur until third order in a perturbation-theory description of the diffraction process. Second, the strong inelastic-collision damping reduces considerably the relative importance of multiple-elastic-scattering processes.[4,31,32] Thus, self-energy corrections due to self-consistency requirements will be small. Third, "realistic" model atomic potentials[3–9] lead to no sharp electron-scattering resonances in the energy region of interest in LEED. Therefore, we expect that the failure of our analysis to be self-consistent leads to far less serious consequences than in the case of calculations of the electronic structure of binary alloys.[27,33]

In the approximate multiple-diffraction theory developed in this paper, only two manifestations of the site-occupation probabilities ultimately are required: the adsorbate coverage and the pair correlation between occupied sites. It is of no consequence in the multiple-scattering analysis whether the correlations are obtained empirically (a statistical model) or via an assumed interaction between adatoms (a statistical-mechanical model). In order to devise a microscopic model whose consequences could be evaluated with as few approximations as possible, however, we consider in our numerical work a lattice-gas model[34] characteristic of an adsorbate coverage of one-half and repulsive nearest-neighbor interactions. It should be emphasized that this choice of a statistical-mechanical system is based on considerations of conceptual simplicity rather than of analytical necessity or of physical "realism."

The problem of evaluating ELEED intensities from overlayers described by a lattice-gas model closely resembles that of describing x-ray diffraction from solid-state alloys. Indeed, kinematical analyses of ELEED associated with order-disorder transitions in adsorbed overlayers[20–25] are essentially identical to those of x-ray diffraction from disordered solids.[35] An important qualitative result which emerges from these analyses is a classification scheme for models of lattice disorder. Disorder of the first kind is characterized by the preservation of long-range correlations, i.e., by deviations from a periodic "average lattice." These deviations can be either displacements (as in lattice-vibration-induced disorder) or substitutions (as in homogeneous-solid binary alloys). Disorder of the second kind is characterized by the loss of long-range correlations. Liquids, gases, and sputter-damaged surface layers[36] are examples of this type of disorder. Houston and Park's concept[20] of disorder of the third kind, characteristic of lattice-gas domain models of adsorbed overlayers, is a special case of substitutional disorder of the first kind, as defined in the literature of x-ray crystallography.

It is evident from the above discussion that our use of a lattice-gas model to describe the adsorbed overlayer restricts our analysis, *a priori*, to one of disorder of the first kind. Thus, if surface melting[37] is regarded as a two-dimensional solid-liquid phase transformation, it is excluded from our consideration. In this context, however, three facts are noteworthy. First, lattice-gas models exhibit both long- and short-range order. Therefore, our model can provide a suitable basis for the study of the consequences of order-disorder transformations on ELEED intensities. Second, the asymptotic long-range behavior of the autocorrelation function is irrelevant in the analysis of LEED. The range of correlations parallel to the surface probed by this technique is limited at best to about 100 Å by the coherence of the incident-electron beam.[20] Moreover, the corresponding range normal to the surface for single-scattering processes (and in all directions for multiple-scattering processes) is limited by the inelastic-collision mean free path, $2\lambda_{ee}$, of the incident electrons. For the energies of interest in LEED, we find[2] $2 \leq \lambda_{ee} \leq 10$ Å. Consequently, we see that the ELEED intensities are sensitive to atomic correlations on the scale of two to five lattice spacings normal to the surface and perhaps of as many as 50 spacings parallel to the surface. Third, surface melting has been defined operationally[37] as an abrupt loss of intensity with increasing temperature of the additional overlayer beam characteristic of an adsorbate structure of lower symmetry than the substrate. Since the substrate beams still exist[23,37–39] at temperatures above those at which surface melting occurs in the sense defined above, the lattice-gas model remains conceptually plausible above the "melting" temperature of the overlayer. The combined effects of this plausibility and the restricted range of correlations measured by LEED lead us to the conclusion that a definitive distinction between a solid-liquid and order-disorder transformation for an adsorbed overlayer cannot be made at the present time. Consequently, there is little incentive to generalize our model to describe disorder of the second kind.

Having noted the relationship of our analysis both to existing experimental ELEED data and to related x-ray and substitutional-alloy calculations, we proceed by describing in Sec. II our model Hamiltonian. The development of the multiple-scattering theory is outlined in Sec. III. In Sec. III A we describe a general diagrammatic version of the perturbation series for the cross sections, while in III B we discuss modifications of this series expansion due to the use of the RQCA and the restricted RQCA. Section IV deals exclusively with the evaluation of the cross sections. It is organized so that approximations and complications are introduced sequentially. Section IV A contains a review of the explicit summation of the exact perturbation series in the case of multiple scattering only from the substrate. In IV B, the approximate series is evaluated for the adsorbate alone. In Secs. IV C 1 and IV C 2, the summation is performed for the substrate-overlayer system in the RQCA and in the restricted RQCA, respectively. Finally, in Sec. V, we present a critical assessment of the accuracy and limitations of the quasicrystalline approximation within the framework of which numerical calculations may be carried out.

Since we anticipate that the formal structure of our theory may be of direct interest only to a modest audience, we have performed such numerical calculations, based on a one-dimensional lattice-gas model, which illustrate some of the main consequences of the theory. These are presented in the following paper. The application of the theory to three-dimensional systems (two-dimensional adsorbates) will be considered in the third paper of this series. A synopsis of our major qualitative results is given in the following paper, to which those readers interested in the predictions but not the mathematical structure of the theory are referred.

II. MODEL HAMILTONIAN

The most general situation described by our model analysis is that of ELEED from an overlayer adsorbed on a vibrating but otherwise periodic single-crystal substrate. The sites occupied by the adsorbate atoms are determined by the symmetry of the substrate. If one of these sites is occupied, however, the adsorbate may vibrate harmonically about its equilibrium position.

Five types of parameters are contained in such a model Hamiltonian. The substrate is characterized by parameters specifying its geometry, those describing the electron-ion-core potential in a rigid lattice, those defining the electron-electron-interaction-induced "optical" potential, and those specifying the thermal motions of the ion cores. The adsorbed overlayer is described in terms of the statistical probability that the various possible adsorbate sites are occupied and the scattering of the electron from the occupied sites. The specification of the geometry of the lattice enters our theory through the definition of certain electron propagators and the performance of sums over atomic scattering amplitudes. We discuss it further only within the context of evaluating these quantities. In this section we proceed by describing first the scattering of the electron from the sub-strate and adsorbate ion cores. We then examine the specification of the adsorbate site-occupancy statistics.

The electron–ion-core interaction in a rigid lattice is described by a one-electron muffin-tin potential. Specifically, we consider a model consisting of spherically symmetric ion-core potentials within individual layers of the solid parallel to the surface.[40–42] For such potentials, the scattering of the electrons from an individual ion core is specified by a sequence of phase shifts, $\{\delta_l(E)\}$, which depend on the angular momentum $L = l\hbar$ and energy E of the incident electron relative to the scatterer. The periodic substrate is described in terms of an array of atomic "subplanes" parallel to the surface of the solid. All of the scatterers in each subplane are taken to be identical. For a monatomic solid, these subplanes become the atomic layers parallel to the surface, in each of which the individual reduced electron–ion-core-scattering vertex is given by

$$t_\nu(\vec{\mathrm{k}}', \vec{\mathrm{k}}) = \frac{4\pi^2 i\hbar^2}{mk(E)} \sum_{l,m} (e^{2i\delta_l^\nu(E)} - 1) Y^*_{lm}(\hat{k}') Y_{lm}(\hat{k}) \quad , \tag{1}$$

$$k^2(E) = 2m\,[E - \Sigma(E)]/\hbar^2 \quad . \tag{2}$$

The index ν labels the layer parallel to the surface in which the ion core is found. The quantity $\Sigma(E)$ is the one-electron optical potential which, by definition, is taken to be uniform inside the solid. The wave vectors, $\vec{\mathrm{k}}$ inside the solid are expressed in terms of the incident electron's energy E and angle θ, with the exterior surface normal via conservation of energy and momentum parallel to the surface. Indicating the components of the momentum perpendicular and parallel to the surface by the corresponding subscripts, we obtain

$$k_\perp^2(\vec{\mathrm{g}}, E) = 2m\,[E - \Sigma(E)]/\hbar^2 - (\vec{\mathrm{k}}_\parallel + \vec{\mathrm{g}})^2 \quad , \tag{3a}$$

$$\vec{\mathrm{k}}_\parallel^2 = 2mE \sin^2\theta/\hbar^2 \quad . \tag{3b}$$

The unit vectors $\hat{k}'$ and $\hat{k}$ in Eq. (1) are defined by Eqs. (3), in which the symbols $\vec{\mathrm{g}}$ designate the reciprocal-lattice vectors of the atomic-scattering subplanes.[40–42] Finally, the single-ion scattering phase shifts $\delta_l^\nu(E)$ depend on the subplane index ν as well as the electron energy E. This dependence is obviously important if the adsorbate ($\nu = 1$) and substrate ($\nu \geq 2$) are different materials. More significantly, however, the presence of an adsorbate at a given site alters the scattering potentials and hence phase shifts of the neighboring substrate (and adsorbate) scatterers. This effect has been examined for both clean surfaces[43] and chemisorbed monolayers.[44] Although the changes in potential can be appreciable, the corresponding alterations of the ELEED intensities usually are small. Therefore, we neglect this effect by presuming both substrate and overlayer scatterers to be characterized by $\delta_l^\nu(E)$, which are independent of the occupancy or lack thereof of neighboring adsorbate sites.

We next turn to our discussion of the parameters associated with the electron-electron-interaction-induced optical potential. As in Refs. 2, 8, and 41–44, they are specified by taking the single-electron proper self-energy to assume the form

$$\Sigma(E) = -V_0 - i\hbar\,[2m\,(E+V_0)]^{1/2}/m\lambda_{ee} \quad , \tag{4}$$

in which V_0 is the real "inner potential" and λ_{ee} is the inelastic-collision damping length. For typical solids in the energy range of interest in ELEED, the damping length assumes the values $2 \lesssim \lambda_{ee} \lesssim 10$ Å.

The final atomic electron–ion-core-scattering parameters which we must specify are those associated with the vibrational motion of the scatterers. This motion is incorporated into the calculation of the ELEED intensities by a renormalization of the rigid-lattice electron–ion-core vertex.[41,42] This is accomplished, in an approximate way,[41] by the multiplication of the rigid-lattice t vertices by the associated Debye-Waller factor. Using the spherical Debye model of the lattice vibration spectra, we get.

$$b_\nu(\vec{k}', \vec{k}) = t_\nu(\vec{k}', \vec{k}) \exp\left[-(\vec{k}' - \vec{k})^2 W_\nu(T)\right] , \tag{5a}$$

$$W_\nu(T) = \frac{3\hbar^2}{2M_\nu \kappa \Theta_D^\nu}\left[\frac{1}{4} + \left(\frac{T}{\Theta_D^\nu}\right)^2 \int_0^{(\Theta_D^\nu/T)} dx\, \frac{x}{e^x - 1}\right] , \tag{5b}$$

in which M_ν is the mass of the atoms in the layer labeled by ν, Θ_D^ν is the Debye temperature describing the motion of the atoms in this layer, T is the temperature, and κ is Boltzmann's constant. The quantity $b_\nu(\vec{k}', \vec{k})$ is the renormalized electron–ion-core vertex, which is expanded into partial-wave components in calculations of ELEED intensities. The temperature dependence of these intensities created by the use of Eqs. (5) occurs in addition to that associated with order-disorder transitions in the adsorbate overlayer. Consequently, both phenomena must be incorporated into an adequate model description of experimental observations.[23,24,37–39] Our general analysis in Secs. III and IV includes both. In our numerical estimates presented in the following paper, however, we examine the case in which the vibrational motion of both substrate and adsorbate atoms is neglected. This permits us to isolate those features of the results which depend solely on the combined effects of multiple electron–ion-core scattering and the disordering of the adsorbed overlayer. Calculations which include the consequences of both lattice vibrations and thermally induced overlayer disorder are underway.[45]

The model-Hamiltonian and multiple-scattering theory, based on the considerations given above and appropriate for the periodic substrate, is given in Refs. 41 and 42. We adopt the notation and Hamiltonian defined in these papers without further discussion. In addition, however, we must specify the occupation statistics for the adsorbate atoms. We conclude the present section with the discussion of this topic.

A fundamental assumption of the multiple-scattering analysis of ELEED is that the (rigid-lattice) electron–ion-core interaction can be written as a sum of spherical, "atomic" potentials.[8] The new feature of our model lies in the fact that the sites in the surface layer which *can* be occupied by overlayer atoms *need not* be so occupied. This aspect of the analysis is incorporated into the Hamiltonian by writing the electron-ion-core potential as

$$V(\vec{r}) = \sum_{\vec{R}} e_{\vec{R}} V_{\vec{R}}(\vec{r} - \vec{R}) \quad , \tag{6}$$

in which $e_{\vec{R}}$ is a site-occupancy number whose value is unity if the site at $\vec{R}$ is occupied, and zero otherwise. We will apply this notation to both adsorbate and substrate with the assumption that all substrate occupation numbers are unity. The multiple-scattering analysis proceeds by first calculating the ELEED cross sections as functionals of the $e_{\vec{R}}$ and subsequently evaluating the thermodynamic equilibrium average of the resulting expressions to give the observed cross sections. Therefore the quantities of interest in this theory are thermodynamic averages of products of the $e_{\vec{R}}$ numbers, i.e., $\langle e_{\vec{R}_1} \cdots e_{\vec{R}_n} \rangle_T$.

The multiple-scattering theory is developed in the following sections. In this theory, however, we introduce the quasicrystalline approximation[27,29] by decomposing the thermodynamic average of a general product of n site-occupancy numbers into products of thermodynamic averages of one and two such numbers. Consequently, the fundamental statistical quantities entering the final approximate theory are the average site-occupancy function

$$f_0(\vec{R}, T) \equiv \langle e_{\vec{R}} \rangle_T \tag{7a}$$

and the site-occupancy pair-correlation function

$$f_1(\vec{R}, \vec{R}', T) \equiv \langle e_{\vec{R}} e_{\vec{R}+\vec{R}'} \rangle_T \quad . \tag{7b}$$

The Fourier transform of the two-site autocorrelation function of the adsorbate is defined by

$$\Phi(\vec{k}) \equiv \sum_{\vec{R}\,\vec{R}'} \langle e_{\vec{R}} e_{\vec{R}'} \rangle_T \, e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} \quad , \tag{8}$$

where the sum is restricted to adsorbate lattice sites.

As indicated in the Introduction, it is irrelevant for our multiple-scattering analysis whether f_0 and f_1 are prescribed (statistical models) or are derived from microscopic models of interactions of the adsorbates with each other and the substrate (statistical-mechanical models). All the multiple-scattering theory requires is that f_0 and f_1 be independent of $\vec{R}$ (i.e., lateral homogeneity along the surface). To illustrate the main features of our theory, however, we use a lattice-gas model[34] for the overlayer to evaluate these statistical quantities.

The Hamiltonian describing the interactions between the adsorbates in this model overlayer is given by

$$H_0 = -\sum_{\vec{R}} v_a e_{\vec{R}} - \sum_{\vec{R}\,\vec{R}'} W e_{\vec{R}} e_{\vec{R}'} \quad , \tag{9a}$$

where the second sum runs over all pairs of neighboring lattice sites in the adsorbate. The quantity v_a is the single-atom adsorption energy, whereas W is the interaction energy between nearest-neighbor adsorbates. The grand partition function of the lattice gas may be written as

$$Z = e^{\mu N_A/\kappa T} \sum_{e_{\vec{R}_1}} \cdots \sum_{e_{\vec{R}_N}} e^{-H_0/\kappa T} \quad , \tag{9b}$$

and the thermodynamical ensemble average of a quantity A is defined as

$$\langle A \rangle_T \equiv Z^{-1} e^{\mu N_A/\kappa T} \sum_{e_{\vec{R}_1}} \cdots \sum_{e_{\vec{R}_N}} A \, e^{-H_0/\kappa T} \quad . \tag{9c}$$

The quantity μ is the chemical potential of a gas phase in equilibrium with the lattice gas and N is the total number of sites available for adsorption. The total number of adsorbed species is given by

$$N_A = \sum_{\vec{R}} e_{\vec{R}} \quad . \tag{10}$$

Accordingly, the fractional coverage γ is given by

$$\gamma = \langle N_A \rangle_T / N \quad . \tag{11}$$

Using the above-specified Hamiltonian, the grand partition function and the site-occupancy functions can be evaluated analytically for one-dimensional systems (i.e., adsorption along a line). These results are used in the following paper in a numerical analysis of the multiple-scattering theory developed in Sec. III. For two-dimensional lattice-gases, series expansions of the pair-correlation function are available.[34] These are utilized in the third paper of this series, in which we present an application of our dynamical theory to the case of three-dimensional systems (two-dimensional adsorbates). Although the lattice-gas description is only one possible selection of a model to calculate the statistical probabilities of the adsorbate, it suffices to illustrate many of the consequences of surface disorder on the dynamical theory of ELEED intensities.

III. MULTIPLE-SCATTERING ANALYSIS

Having given a description of our microscopic statistical model for the adsorbed monolayer, we now turn to the development of a multiple-scattering theory for the system consisting of the ordered substrate and the thermally disordered adsorbate. We first give in A an exact expression for the thermodynamic cross section in the form of a perturbation series. We then describe in B how the terms of this series have to be approximated in order to become suitable for numerical evaluation. This leads us to a quasicrystalline approximation. The summation of the approximate series is performed in Sec. IV.

A. Perturbation-theory expansion for the cross section

We employ a diagrammatic multiple-scattering formalism[42] which embodies a partial-wave-expansion technique. As already indicated in Sec. II, the lattice of the adsorbed monolayer is taken to have the same geometry as the layers of the underlying substrate. The adsorbed atoms are all of the same species, constituting a single layer of an unspecified coverage. The electronic and thermodynamic properties of the target are allowed to vary normal to the plane of the surface, i.e., from layer to layer, but not within a given layer. With these restrictions, the elastic-electron-solid-scattering amplitude is specified by the following multiple-scattering series[42]:

$$R(\vec{k}_f, \vec{k}_i, E) = \sum_{j=0}^{\infty} R_j(\vec{k}_f, \vec{k}_i, E) \quad , \tag{12}$$

$$\begin{aligned} R_j(\vec{k}_f, \vec{k}_i, E) = \sum_{LL'} \Bigg(Y^*(\hat{k}_f) \sum_{\vec{R}_0 \neq \cdots \neq \vec{R}_j} & \times e^{i(\vec{k}_i\cdot\vec{R}_0 - \vec{k}_f\cdot\vec{R}_j)} b_{\vec{R}_j}(k(E)) \\ & \times G(\vec{R}_{j-1} - \vec{R}_j, E) b_{\vec{R}_{j-1}}(k(E)) \cdots b_{\vec{R}_1}(k(E)) \\ & \times G(\vec{R}_0 - \vec{R}_1, E) b_{\vec{R}_0}(k(E)) Y(\hat{k}_i) \Bigg)_{LL'} \quad . \end{aligned} \tag{13}$$

For $j=0$, the site-dependent part of the summand in Eq. (13) simply reduces to $\exp[i(\vec{k}_i - \vec{k}_f)\cdot\vec{R}_0]$

$\times b_{\vec{R}_0}(k(E))$. The quantities $Y(\hat{k})$, $b_{\vec{R}}(k(E))$, and $G(\vec{R}, E)$ are matrices whose elements are labeled by the angular momentum quantum numbers L:

$$Y(\hat{k}) \equiv \| Y_L(\hat{k})\, \delta_{LL'} \| \quad , \tag{14}$$

$$b_{\vec{R}}(k(E)) \equiv \| b_{\vec{R}}^{LL'}(k(E),\, k(E),\, E\,) \| \quad , \tag{15}$$

$$G(\vec{R}, E) \equiv \| G_{LL'}(\vec{R}, E) \| \quad . \tag{16}$$

The $Y_L(\hat{k})$ are spherical harmonics[41,46] and the $b_{\vec{R}}^{LL'}(k', k, E)$ are the partial-wave components of the reduced ion-core-scattering vertices given by Eq. (5a), i.e.,

$$b_{\vec{R}}(\vec{k}', \vec{k}, E) = \sum_{LL'} b_{\vec{R}}^{LL'}(k', k, E)\, Y_L^*(\hat{k}')\, Y_{L'}(\hat{k}) \quad . \tag{17}$$

The partial-wave components of the electron propagator are defined by

$$G_{LL'}(\vec{R}, E) = \frac{-im\,k(E)}{2\pi\hbar^2} \sum_{L_2} (-i)^{l_2} I(L, L', L_2) \times h_{l_2}^{(1)}(k(E)\,|\vec{R}|)\, Y_{L_2}(\hat{R}) \quad , \tag{18}$$

in which $h_l^{(1)}$ are the spherical Hankel functions and

$$I(L, L', L_2) \equiv \int d\Omega_{k_1} Y_L(\hat{k}_1)\, Y_{L'}^*(\hat{k}_1)\, Y_{L_2}^*(\hat{k}_1) \quad . \tag{19}$$

The quantity $k(E)$ in Eqs. (13), (15), and (18) represents the complex momentum of the electronic wave inside the solid as defined by Eq. (2). The sums over the lattice site vectors $\vec{R}$ in Eq. (13) include the sites in the substrate as well as the (occupied or vacant) sites in the adsorbed monolayer. We write $\vec{R} \equiv \vec{P} + \vec{d}_\nu$, where $\vec{d}_\nu$ designates the position of the vector $\vec{P} \equiv 0$ of the layer with the index ν (the adsorbed layer has the index $\nu = 1$) and $\vec{P}$ specifies the sites within this layer. We take into consideration the existence of vacant lattice sites in the adsorbed layer by incorporating into each ion-core-scattering vertex the appropriate occupation number, i.e.,

$$b_{\vec{R}=\vec{P}+\vec{d}_\nu}(k(E)) = e_{\vec{R}}\, b_\nu(k(E)) \,, \quad \nu \geq 1 \quad , \tag{20a}$$

with

$$\begin{aligned} e_{\vec{R}=\vec{P}+\vec{d}_\nu} &\equiv e_{\vec{P}} \quad (\nu = 1) \\ &\equiv 1 \quad (\nu \geq 2) \quad . \end{aligned} \tag{20b}$$

Because of the lack of translational invariance in the adsorbed layer, the sums over the lattice sites in the expression for the multiple scattering amplitude, Eq. (13), can no longer be performed as in the case of a perfectly ordered bulk. For a particular statistical configuration, $\{e_{\vec{P}}\}$, of the adsorbed atoms, the elastic-scattering cross section is given by

$$\frac{d\sigma}{d\Omega}(\vec{k}_f, \vec{k}_i, E) = \left(\frac{m}{2\pi\hbar^2}\right)^2 |R(\vec{k}_j, \vec{k}_i, E)|^2 \quad . \tag{21}$$

In electron-scattering experiments, however, the thermal-equilibrium average of the cross section is measured. It is therefore necessary to average the cross section, Eq. (21), over all possible statistical configurations of the adsorbate lattice gas:

$$\left\langle \frac{d\sigma}{d\Omega}(\vec{k}_f, \vec{k}_i, E) \right\rangle_T \equiv \left(\frac{m}{2\pi\hbar^2}\right)^2 \langle |R(\vec{k}_f, \vec{k}_i, E)|^2 \rangle_T \quad , \tag{22}$$

in which $\langle \cdots \rangle_T$ designates the thermodynamical average of the occupation numbers in the lattice-gas model, as described in Sec. II. Usings Eqs. (12), (13), and (22), we construct the following expansion of the equilibrium cross section in terms of powers of the reduced ion-core-scattering vertices:

$$\left\langle \frac{d\sigma}{d\Omega}(\vec{k}_f, \vec{k}_i, E) \right\rangle_T \equiv \sum_{n=0}^{\infty} \left\langle \frac{d\sigma^{(n)}}{d\Omega}(\vec{k}_f, \vec{k}_i, E) \right\rangle_T \quad , \tag{23}$$

with

$$\left\langle \frac{d\sigma^{(n)}}{d\Omega}(\vec{k}_f, \vec{k}_i, E) \right\rangle_T \equiv \left(\frac{m}{2\pi\hbar^2}\right)^2 \sum_{l=0}^{n} \langle R_{n-l}^*(\vec{k}_f, \vec{k}_i, E)\, R_l(\vec{k}_f, \vec{k}_i, E) \rangle_T \quad . \tag{24}$$

The first term in this expansion represents the familiar kinematical (Born) approximation to the cross section:

$$\left\langle \frac{d\sigma^{(0)}}{d\Omega}(\vec{k}_f, \vec{k}_i, E) \right\rangle_T = \left(\frac{m}{2\pi\hbar^2}\right)^2 \left\langle \left| \sum_{\vec{R}} e^{-i\vec{q}\cdot\vec{R}} \sum_{LL'} [Y^*(\hat{k}_f)\, b_{\vec{R}}(k(E)) \times Y(\hat{k}_i)]_{LL'} \right|^2 \right\rangle_T \quad , \tag{25}$$

in which $\vec{q} \equiv \vec{k}_f - \vec{k}_i$ denotes the momentum transfer. Using Eqs. (20) and writing $\vec{R} = \vec{P} + \vec{d}_\nu$ we obtain for Eq. (25)

$$\begin{aligned} \left\langle \frac{d\sigma^{(0)}}{d\Omega}(\vec{k}_f, \vec{k}_i, E) \right\rangle_T = \left(\frac{m}{2\pi\hbar^2}\right)^2 N_\parallel \sum_{\vec{g}} \delta(\vec{q} - \vec{g}) \Bigg\{ & \left| \sum_{\nu \geq 2} e^{-i\vec{q}\cdot\vec{d}_\nu} \sum_{LL'} [Y^*(\hat{k}_f)\, b_\nu(k(E))\, Y(\hat{k}_i)]_{LL'} \right|^2 \\ & + 2\gamma \mathrm{Re} \left[\sum_{\nu \geq 2} \left(e^{i\vec{q}\cdot\vec{d}_\nu} \sum_{LL'} [Y^*(\hat{k}_f)\, b_\nu(k(E))\, Y(\hat{k}_i)]_{LL'} \right)^* e^{-i\vec{q}\cdot\vec{d}_1} \sum_{LL'} [Y^*(\hat{k}_f)\, b_1(k(E))\, Y(\hat{k}_i)]_{LL'} \right] \Bigg\} \\ & + \left(\frac{m}{2\pi\hbar^2}\right)^2 \Phi(\vec{q}) \left| \sum_{LL'} [Y^*(\hat{k}_f)\, b_1(k(E))\, Y(\hat{k}_i)]_{LL'} \right|^2 \quad . \end{aligned} \tag{26}$$

In Eq. (26) $N_{\parallel}$ designates the number of cells per unit area in a subplane and $\vec{g}$ denotes the reciprocal-lattice vectors of the Bravais net of each plane. $\Phi(\vec{q})$ is the autocorrelation function of the adsorbate, as defined in Eq. (8). The first term in Eq. (26) represents the cross section due to single scattering from the ordered substrate and contains conservation of the momentum component parallel to the surface plane. The second term gives the interference between single scattering from the bulk and from the adsorbate. It also leads to momentum conservation. The last term represents the kinematical cross section for scattering from the disordered monolayer. We notice that, in the Born approximation, the effect of disorder in the adsorbate is entirely described by the autocorrelation function $\Phi(\vec{q})$.

The terms beyond the kinematical approximation of the thermal cross section [Eqs. (3) and (4)] contain as the fundamental statistical quantities thermal averages over products of occupation numbers of the form

$$\langle e_{\vec{R}_1} \cdots e_{\vec{R}_n} \rangle_T, \quad 1 \le n \le \infty \quad . \tag{27}$$

The inclusion of terms in Eq. (23) that depend on these higher-order correlation functions constitutes the new feature of our analysis. Our main task is to develop a procedure which allows the incorporation of these correlations in an approximate way such that the individual terms of the series [Eq. (23)] can be evaluated.

In order to accomplish this goal, it is convenient to express the perturbation-theory expansion for the thermally averaged cross section in terms of its diagrammatic representation. To obtain all possible terms of nth order in the reduced ion-core interaction we use the following prescription.

(a) Draw two vertical lines, the one on the left being directed upward and the one on the right being directed downward. On these lines distribute n dots with the only restriction being that at least one dot must be on each line. Label each dot with a lattice-site index.

(b) Connect the highest dot on the right side with the highest on the left side with a wavy line. Similarly, connect the lowest on the right with the lowest on the left. Furthermore, connect neighboring dots on each side with a wavy line.

(c) Completely interior line segments in this drawing (those connecting two dots) represent electron propagators. The four exterior line segments label the initial and final scattering states of the incident electron. Label the incoming line segments with momentum $\vec{k}_i$, and the outgoing line segments with momentum $\vec{k}_f$.

(d) Construct all topologically distinct diagrams using the preceding instructions.

(e) With each dot on the right-hand line, associate a site-renormalized interaction vertex $b_{\vec{R}}(k(E))$ defined by Eq. (15), where $\vec{R}$ denotes the label of the dot. With a corresponding dot on the left-hand line associate $b^*_{\vec{R}}(k(E))$.

(f) With each interior line segment on the right-hand line, associate the electron propagator $G(\vec{R}-\vec{R}', E)$ defined in Eq. (16), where $\vec{R}$ and $\vec{R}'$ designate the upper and lower of the two dots between which the line is drawn. With each interior line segment on the left-hand line associate the propagator $G^*(\vec{R}-\vec{R}', E)$, where $\vec{R}(\vec{R}')$ is now the lower (upper) of the two dots between which the line is drawn.

(g) On the right-hand side of the diagram, associate the phase factor $e^{i\vec{k}_i \cdot \vec{R}}$ with the ingoing line and $e^{-i\vec{k}_f \cdot \vec{R}'}$ with the outgoing line, where $\vec{R}$ and $\vec{R}'$ are the labels of the dots connected to the corresponding line. Use the complex-conjugate phase factors on the left-hand side.

(h) For each side of each diagram, form the matrix product of all quantities associated with the lines and dots by using the same sequence as in the diagram, the dot next to the ingoing line being at the right end, the dot next to the outgoing line at the left end of the product. On the right- (left-) hand side of a diagram, multiply the product with the matrix $Y(\hat{k}_i)$ $[Y^*(\hat{k}_i)]$ from the right and with $Y^*(\hat{k}_f)$ $[Y(\hat{k}_f)]$ from the left. Sum the resulting product matrices over all matrix elements and then multiply the two sums by each other.

(i) With the entire wavy line, associate the correlation function $\langle e_{\vec{R}_1} \cdots e_{\vec{R}_n} \rangle_T$, where the $\vec{R}_i$ denote the labels of the dots.

(j) Sum over all site indices, labeling the dots with the restriction that no two neighboring sites be equal.

(k) Multiply each diagram by the factor $(m/2\pi\hbar^2)^2$.

To illustrate this prescription let us consider the diagrams shown in Fig. 1. Figure 1(a) represents the kinematical (Born) approximation. The corresponding thermally averaged cross section is given by Eqs. (25) and (26). Figure 1(b) represents the two contributions to the second term in the expansion of the cross section, i.e.,

$$\left\langle \frac{d\sigma^{(1)}}{d\Omega}(\vec{k}_f, \vec{k}_i, E) \right\rangle_T = \left(\frac{m}{2\pi\hbar^2}\right)^2 \left\langle \sum_{LL'} \left(Y^*(\hat{k}_f) \sum_{\vec{R}_0'} e^{-i\vec{q}\cdot\vec{R}_0'} b_{\vec{R}_0'}(k(E))\, Y(\hat{k}_i) \right)^*_{LL'} \right.$$
$$\left. \times \sum_{LL'} \left(Y^*(\hat{k}_f) \sum_{\vec{R}_0 \neq \vec{R}_1} e^{i(\vec{k}_i \cdot \vec{R}_0 - \vec{k}_f \cdot \vec{R}_1)} b_{\vec{R}_1}(k(E))\, G(\vec{R}_0 - \vec{R}_1, E)\, b_{\vec{R}_0}(k(E))\, Y(\hat{k}_i) \right)_{LL'} \right\rangle_T + \text{c.c.} \tag{28}$$

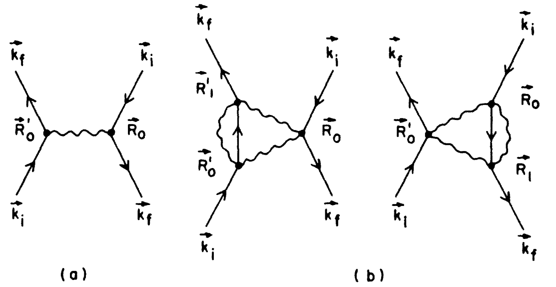

FIG. 1. Diagrams representing contributions to the perturbation series expansion [Eq. (23)] of the exact equilibrium-scattering cross section. Panel (a) illustrates the lowest-order contribution, i.e., the kinematical (Born) approximation, and is given by Eq. (25). Panel (b) represents the two first-order contributions and is given by Eq. (28). Site-renormalized vertices are designated by solid dots. Wavy lines connecting the dots indicate correlations between the sites that are symbolized by the dots. The labels of the dots refer to adsorbate as well as substrate sites.

In contrast to the Born approximation, which depends only on the coverage and the pair-correlation function, the term given by Eq. (28) involves a three-point correlation function. This is indicated in Fig. 1(b) by the fact that the three dots are connected by wavy lines. In general, the nth term in the expansion of the cross section, Eq. (24), is a linear functional of the n-point function,

$$\left\langle \frac{d\sigma^{(n)}}{d\Omega} (\vec{k}_f, \vec{k}_i, E) \right\rangle_T \equiv F\{\langle e_{\vec{R}_1} \cdots e_{\vec{R}_n} \rangle_T\} \quad . \tag{29}$$

Because of the presence of the higher correlation functions, the sums over the lattice sites in the expressions for the terms of the thermal cross section [Eqs. (23) and (24)] cannot be performed even if the correlation functions were known. The difficulty resides in the fact that the correlations are not simply functions of the distances between two consecutive sites appearing in them. In addition, the thermal cross section cannot be written as the square of the absolute value of the thermally averaged scattering amplitude, since the squaring and the thermal averaging do not commute.

B. Approximate expressions for cross section

An approximation for the exact expression of the thermally averaged cross section [Eqs. (23) and (24)] is particularly suitable for numerical analysis if the sums over lattice sites implicitly involved in Eq. (24) can be performed analytically. A convenient and conceptually plausible way to achieve this goal in the case of scattering from the disordered adsorbate alone is to factorize all higher correlations into products of two-point functions in such a way that the latter depend on the same arguments as the electron propagators entering the expression for the scattering amplitude. Since by using this procedure only pair correlations between consecutive scattering sites are taken into consideration, this factorization is referred to as the "geometric"[28] or "quasicrystalline"[29] approximation (QCA) in the theory of liquids and substitutional alloys.[27] The presence of the substrate is incorporated by summing over all intermediate scattering processes which take place in the substrate between scattering events in the overlayer. This summation leads to the definition of new intra-adsorbate electron propagators which are renormalized for intermediate dynamical scattering from the substrate. Thus we will refer to this approximation as renormalized quasicrystalline approximation (RQCA).

The utilization of renormalized intra-adsorbate propagators renders the analysis of multiple scattering from the substrate-overlayer system formally analogous to that of scattering from the adsorbate alone. We will show in Sec. IV C 1 that the thermal-equilibrium cross section in the renormalized QCA can be written in the following simple form:

$$\left\langle \frac{d\sigma}{d\Omega} (\vec{k}_f, \vec{k}_i, E) \right\rangle_T^{\mathrm{RQCA}}$$

$$= \left(\frac{m}{2\pi\hbar^2}\right)^2 \left\langle \left| \sum_{\vec{p}} e^{-i\vec{q}\cdot\vec{p}} \times [A(\vec{k}_f, \vec{k}_i, E) + e_{\vec{p}} B(\vec{k}_f, \vec{k}_i, E)] \right|^2 \right\rangle_T \quad . \tag{30}$$

The quantities $A(\vec{k}_f, \vec{k}_i, E)$ and $B(\vec{k}_f, \vec{k}_i, E)$ do not depend explicitly on the occupation numbers and are functionals only of the coverage, $\gamma = \langle e_{\vec{p}} \rangle_T$, and the pair-correlation function, $\langle e_{\vec{p}} e_{\vec{p}'} \rangle_T$.

The form of Eq. (30) indicates that the RQCA introduces a partial thermodynamical average of the scattering amplitude which depends explicitly only on a single occupation number. This is the original formulation of the QCA and geometric approximation, since the partially averaged scattering amplitude can be directly related to the local density of states.[27,28] Because we are dealing with a nonuniform system exhibiting both short- and long-range order, however, the procedure for obtaining a partial average of the scattering amplitude is rather more subtle than in the case of a randomly ordered system. The derivation of this procedure is the topic of Sec. IV. The RQCA exhibits the attractive feature, in that it represents an appropriate description of short- and long-range-order effects in the overlayer on dynamical scattering processes that involve both substrate and adsorbate. Unfortunately, the summation over intermediate substrate-scattering processes that is required for the propagator renormalization cannot be performed exactly.

If the adsorbate-substrate interference contributions to the cross section [Eq. (30)] are, however, further approximated such that pair correlations between overlayer sites are replaced by their random (i.e., infinite-temperature) limits whenever intermediate substrate scattering events take place, the renormalization described above can be performed analytically. This restricted RQCA is useful because the resulting expressions for the cross section are directly accessible to a numerical evaluation. Due to its inherent assumptions, however, this approximation leads only in the high-temperature region to a satisfactory description of multiple-scattering processes that involve both the overlayer and the bulk.

It is well known that the quasicrystalline approximation (as well as its renormalized version) does not deal correctly with cases in which several lattice sites coincide in the summation in Eq. (13). Only the autocorrelations of the sites (repeated scattering from a single site) are treated exactly via the introduction of reduced ion-core vertices [Eq. (5a)]. We consider this problem in Sec. V and indicate how the approximation should be improved.

IV. SUMMATION OF PERTURBATION SERIES

This section is devoted to the explicit evaluation of the multiple-scattering series that have been defined in Sec. III. It is organized so that approximations and complications are introduced sequentially. In A we briefly review the case of multiple scattering from the substrate alone, in order to introduce the various substrate-scattering matrices and electron propagators. Subsection B contains the summation of the approximate series in the case of scattering only from the adsorbate. In C 1 and C 2 the multiple-scattering series is performed for the substrate-overlayer system in the RQCA and in the restricted RQCA, respectively.

A. Review of multiple scattering from substrate

In the case in which the multiple electron scattering occurs exclusively in the bulk, all sums over lattice sites in the scattering amplitude are restricted to the substrate lattice. Consequently, all occupation numbers are unity and can be omitted. The scattering amplitude [Eq. (13)] is then given by

$$\begin{aligned} R^{\mathrm{B}}(\vec{\mathrm{k}}_f, \vec{\mathrm{k}}_i, E) = \sum_{LL'} \Big(& Y^*(\hat{k}_f) \sum_{j=0}^{\infty} \sum_{\nu_0 \cdots \nu_j} \sum_{\vec{\mathrm{P}}_0 \cdots \vec{\mathrm{P}}_j}{}' \exp[-i\vec{\mathrm{q}} \cdot (\vec{\mathrm{P}}_j + \vec{\mathrm{d}}_{\nu_j})] \, b_{\nu_j}(k(E)) \exp[i\vec{\mathrm{k}}_i \cdot (\vec{\mathrm{P}}_{j-1} + \vec{\mathrm{d}}_{\nu_{j-1}} - \vec{\mathrm{P}}_j - \vec{\mathrm{d}}_{\nu_j})] \\ & \times G(\vec{\mathrm{P}}_{j-1} + \vec{\mathrm{d}}_{\nu_{j-1}} - \vec{\mathrm{P}}_j - \vec{\mathrm{d}}_{\nu_j}, E) \, b_{\nu_{j-1}}(k(E)) \cdots b_{\nu_1}(k(E)) \exp[i\vec{\mathrm{k}}_i \cdot (\vec{\mathrm{P}}_0 + \vec{\mathrm{d}}_{\nu_0} - \vec{\mathrm{P}}_1 - \vec{\mathrm{d}}_{\nu_1})] \\ & \times G(\vec{\mathrm{P}}_0 + \vec{\mathrm{d}}_{\nu_0} - \vec{\mathrm{P}}_1 - \vec{\mathrm{d}}_{\nu_1}, E) \, b_{\nu_0}(k(E)) \, Y(\hat{k}_i) \Big)_{LL'} \quad . \end{aligned} \tag{31}$$

The summation over the $\vec{\mathrm{P}}_i$ is restricted by the condition $\vec{\mathrm{P}}_i \neq \vec{\mathrm{P}}_{i+1}$ whenever $\nu_i = \nu_{i+1}$, a restriction which is designated by a prime on the summation symbol. The above expression can be reduced by summing first over $\vec{\mathrm{P}}_0$, then over $\vec{\mathrm{P}}_1$, and so forth. This procedure leads us to define the following inter- and intralayer electron propagators:

$$G_{\nu_1\nu_0}(\vec{\mathrm{k}}, E) \equiv \sum_{\vec{\mathrm{P}}} \exp[i\vec{\mathrm{k}} \cdot (\vec{\mathrm{P}} + \vec{\mathrm{d}}_{\nu_0} - \vec{\mathrm{d}}_{\nu_1})] G(\vec{\mathrm{P}} + \vec{\mathrm{d}}_{\nu_0} - \vec{\mathrm{d}}_{\nu_1}, E) \qquad (\nu_0 \neq \nu_1; \;\; \nu_0, \nu_1 \geq 2) \tag{32a}$$

$$\equiv \sum_{\vec{\mathrm{P}} \neq 0} e^{i\vec{\mathrm{k}} \cdot \vec{\mathrm{P}}} G(\vec{\mathrm{P}}, E) \equiv G^{\mathrm{sp}}_{\nu_0}(\vec{\mathrm{k}}, E) \quad (\nu_0 = \nu_1 \geq 2) \quad . \tag{32b}$$

These propagators are matrices in the partial-wave representation just like the quantities $G(\vec{\mathrm{P}}, E)$ defined by Eq. (16). The summations in these equations are to be applied for each matrix element. Defining $\vec{\mathrm{P}} \equiv \vec{\mathrm{P}}_j$, $\nu \equiv \nu_j$, we obtain from Eq. (31)

$$\begin{aligned} R^B(\vec{\mathrm{k}}_j, \vec{\mathrm{k}}_i, E) = \sum_{\vec{\mathrm{P}}} e^{-i\vec{\mathrm{q}} \cdot \vec{\mathrm{P}}} \sum_{\nu \geq 2} e^{-i\vec{\mathrm{q}} \cdot \vec{\mathrm{d}}_\nu} \sum_{LL'} \Big(& Y^*(\hat{k}_f) \\ & \times \sum_{j=0}^{\infty} \sum_{\nu_0 \cdots \nu_{j-1}} b_\nu(k(E)) G_{\nu\nu_{j-1}}(\vec{\mathrm{k}}_i, E) \\ & \times b_{\nu_{j-1}}(k(E)) \cdots b_{\nu_1}(k(E)) \\ & \times G_{\nu_1\nu_0}(\vec{\mathrm{k}}_i, E) \, b_{\nu_0}(k(E)) \, Y(\hat{k}_i) \Big)_{LL'} \end{aligned} \tag{33}$$

The terms inside the large parentheses in Eq. (33) can be rearranged as follows

$$\sum_{j=0}^{\infty} \sum_{\nu_0 \cdots \nu_{j-1}} b_\nu G_{\nu\nu_{j-1}} b_{\nu_{j-1}} \cdots b_{\nu_1} G_{\nu_1\nu_0} b_{\nu_0}$$

$$= \tau_\nu + \sum_{\mu \neq \nu} \tau_\nu G_{\nu\mu} \tau_\mu + \sum_{\mu \neq \lambda \neq \nu} \tau_\nu G_{\nu\lambda} \tau_\lambda G_{\lambda\mu} \tau_\mu + \cdots \tag{34a}$$

$$= \sum_{\mu \geq 2} T_{\nu\mu}(\vec{\mathrm{k}}_i, E) \quad . \tag{34b}$$

The matrices $\tau_\nu(\vec{\mathrm{k}}, E)$ in Eq. (34b) are the subplane scattering matrices defined by

$$\tau_\nu(\vec{\mathrm{k}}, E) = b_\nu(k(E)) + b_\nu(k(E)) G_{\nu\nu}(\vec{\mathrm{k}}, E) \tau_\nu(\vec{\mathrm{k}}, E), \qquad \nu \geq 2 \quad . \tag{35}$$

The matrices $T_{\nu\mu}(\vec{\mathrm{k}}, E)$ are the interlayer scattering matrices of the bulk representing all scattering events which start in layer μ and end in layer ν. They are given by the following set of algebraic equations:

$$T_{\nu\mu}(\vec{k},E)=\tau_\nu(\vec{k},E)\,\delta_{\nu\mu}+\sum_{\lambda\neq\nu}\tau_\nu(\vec{k},E)\,G_{\nu\lambda}(\vec{k},E)\times T_{\lambda\mu}(\vec{k},E),\quad \nu,\mu,\lambda\geq 2\ . \tag{36}$$

The interlayer scattering matrices $T_\nu(\vec{k},E)$ used in the previous literature are obtained from the ones given by Eq. (36) simply by summing over the index μ which denotes the layer in which the scattering process starts: $T_\nu(\vec{k},E)\equiv\sum_{\mu\geq 2}T_{\nu\mu}(\vec{k},E)$. The motivation for introducing the more general matrices $T_{\nu\mu}(\vec{k},E)$ becomes clear in the case of multiple scattering between substrate and disordered adsorbate (see IV C). We then need to explicitly distinguish various classes of scattering processes according to the layers in which they start and end. Such a classification is not required for scattering from ordered systems consisting of identical sublattices.

Using Eqs. (33) and (34), we obtain for the scattering amplitude

$$R^B(\vec{k}_f,\vec{k}_i,E)=\sum_{\vec{P}}e^{-i\vec{q}\cdot\vec{P}}\sum_{\nu\mu\geq 2}e^{-i\vec{q}\cdot\vec{d}_\nu}\times\sum_{LL'}[Y^*(\hat{k}_f)\,T_{\nu\mu}(\vec{k}_i,E)\,Y(\hat{k}_i)]_{LL'}\ . \tag{37}$$

The scattering cross section is given by the expression[42]

$$\frac{d\sigma^{(B)}}{d\Omega}(\vec{k}_f,\vec{k}_i,E)=\left(\frac{m}{2\pi\hbar^2}\right)^2|R^B(\vec{k}_f,\vec{k}_i,E)|^2$$
$$=\left(\frac{m}{2\pi\hbar^2}\right)^2N_{\parallel}\sum_{\vec{g}}\delta(\vec{q}-\vec{g})\left|\sum_{LL'}\left(Y^*(\hat{k}_f)\times\sum_{\nu\mu\geq 2}e^{-i\vec{q}\cdot\vec{d}_\nu}T_{\nu\mu}(\vec{k}_i,E)\,Y(\hat{k}_i)\right)_{LL'}\right|^2\ . \tag{38}$$

The diagrammatic representation of the scattering cross section for the bulk i.e., Eq. (38), can be obtained easily using the rules given in Sec. III A. The only modification occurs in rule (a), in that the labels of the dots are restricted exclusively to the sites of the substrate lattice. Because of the fact that all of the correlation functions are unity, the wavy lines can be omitted and the cross section can be written as proportional to the square of the absolute value of the scattering amplitude. The diagrammatic expression for the substrate-scattering cross section is indicated in Fig. 2. The fact that the multiple-scattering series of the bulk scattering amplitude [Eq. (31)] can be expressed as a sum over interlayer scattering matrices, $T_{\nu\mu}(\vec{k},E)$, suggests the use of a renormalized vertex diagram which represents the multiple scattering from all substrate sites, as defined in Fig. 3(a) for the right-hand side of a cross-section diagram. The cross section can be related to this vertex diagram in a simple way, as shown in Fig. 3(b). The diagram in Fig. 3(a) is not equivalent to the scattering amplitude because of the absence of external lines. Also, since it is to be understood as the interior part of a full diagram, no sums over lattice-site labels are associated with it.

B. Multiple scattering from adsorbate

In this subsection we examine multiple scattering from the adsorbed monolayer, disregarding, for the moment, the presence of the substrate. This special case serves to illustrate the application of the quasicrystalline approximation. Since the RQCA and the restricted RQCA introduced in Sec. III differ only with regard to scattering processes that involve both substrate and adsorbate, they need not be considered separately in this case.

This subsection also provides a convenient introduction to an essentially new complexity in the theory of multiple scattering from a disordered (rather than periodic) lattice: the preservation of time-reversal invariance of the cross sections. For scattering from an ordered system, the translational symmetry parallel to the surface guarantees that $\vec{k}_{f,\parallel}=\vec{k}_{i,\parallel}+\vec{g}$, if $\vec{g}$ is a reciprocal-lattice vector of the Bravais net for translations parallel to the surface. In the presence of disorder, however, we must consider all values of $\vec{k}_{f,\parallel}$ without regard to this parallel momentum-conservation law. This fact has the consequence that we must use certain symmetrized forms in our expressions for the correlation functions $\langle e_{\vec{P}_1}\cdots e_{\vec{P}_n}\rangle_T$ introduced in Sec. III A, and that $G_\nu^{sp}(\vec{k}_i,E)$ does not necessarily equal $G_\nu^{sp}(\vec{k}_f,E)$. These new features of the theory are introduced in this subsection.

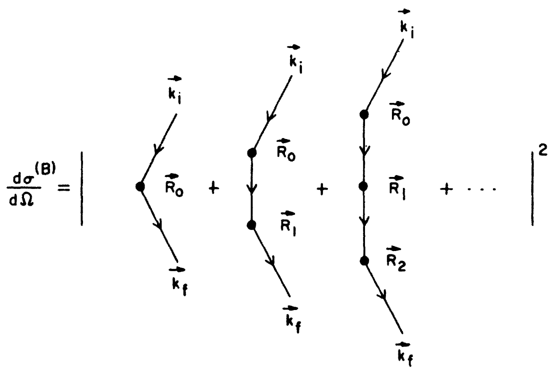

FIG. 2. Exact diagrammatic series for the cross section in the case of multiple scattering from the substrate, as given by Eq. (38). The labels of the dots denote substrate lattice sites exclusively.

In C we extend our analysis to the more complicated case of the combined system of adsorbate and underlying substrate. As shown in Eq. (20), the reduced ion-core scattering vertex of a given site $\vec{P}$ in the adsorbed monolayer is proportional to its occupation number $e_{\vec{P}}$. By restricting all sums over lattice sites to the plane of the adsorbate, we obtain from Eqs. (20), (22), and (23) the following expression for the cross section for the adsorbate:

$$\begin{aligned}\left\langle\frac{d\sigma^{(A)}}{d\Omega}(\vec{k}_f,\vec{k}_i,E)\right\rangle_T = \left(\frac{m}{2\pi\hbar^2}\right)^2 \Bigg\langle \sum_{LL'} \Bigg(Y^*(\hat{k}_f)\sum_{i=0}^{\infty}\ \sum_{\vec{P}'_0\cdots\vec{P}'_i}{}' e_{\vec{P}'_i}\cdots e_{\vec{P}'_0}\exp[i(\vec{k}_i\cdot\vec{P}'_0-\vec{k}_f\circ\vec{P}'_i)] \\ \times b_1(k(E))G(\vec{P}'_{i-1}-\vec{P}'_i,E)b_1(k(E))\circ\cdots b_1(k(E))G(\vec{P}'_0-\vec{P}'_1,E)b_1(k(E))Y(\hat{k}_i)\Bigg)^*_{LL'} \\ \times\sum_{LL'}\Bigg(Y^*(\hat{k}_f)\sum_{j=0}^{\infty}\ \sum_{\vec{P}_0\cdots\vec{P}_j}{}' e_{\vec{P}_j}\cdots e_{\vec{P}_0}\exp[i(\vec{k}_i\cdot\vec{P}_0-\vec{k}_f\cdot\vec{P}_j)]b_1(k(E))G(\vec{P}_{j-1}-\vec{P}_j,E) \\ \times b_1(k(E))\cdots b_1(k(E))G(\vec{P}_0-\vec{P}_1,E)b_1(k(E))Y(\hat{k}_i)\Bigg)_{LL'}\Bigg\rangle_T \ . \qquad (39)\end{aligned}$$

The sums over lattice sites are again restricted by the condition $\vec{P}_n \neq \vec{P}_{n+1}$, $\vec{P}'_n \neq \vec{P}'_{n+1}$, as indicated by the primes on the summation symbols. A typical correlation function appearing in the above expression is of the form

$$\langle e_{\vec{P}'_i}\cdots e_{\vec{P}'_0}\,e_{\vec{P}_j}\circ\circ\circ\, e_{\vec{P}_0}\rangle_T \ . \qquad (40)$$

As indicated in Sec. III A, it is necessary to factorize these correlations in order to be able to perform the sums over lattice sites. This factorization is performed in such a way that only pair correlations between consecutive scattering sites remain; i.e., the correlation function given by Eq. (40) is approximated by terms of the form

$$\begin{aligned}&\langle e_{\vec{P}'_i}\,e_{\vec{P}'_{i-1}}\rangle_T\gamma^{-1}\langle e_{\vec{P}'_{i-1}}\,e_{\vec{P}'_{i-2}}\rangle_T\gamma^{-1}\cdots\gamma^{-1}\\ &\times\langle e_{\vec{P}'_1}\,e_{\vec{P}'_0}\rangle_T\gamma^{-1}\langle e_{\vec{P}'_0}\,e_{\vec{P}_j}\rangle_T\gamma^{-1}\\ &\times\langle e_{\vec{P}_j}\,e_{\vec{P}_{j-1}}\rangle_T\gamma^{-1}\cdots\gamma^{-1}\langle e_{\vec{P}_1}\,e_{\vec{P}_0}\rangle_T \ . \qquad (41)\end{aligned}$$

This factorization is exact if we are dealing with a one-dimensional lattice and all sites are arranged in a sequential order. In expression (41), the two sets of lattice vectors, $\{\vec{P}_0\cdot\circ\cdot\vec{P}_j\}$ and $\{\vec{P}'_0\circ\cdot\circ\vec{P}'_i\}$, are linked by a single two-point correlation, $\langle e_{\vec{P}'_0}e_{\vec{P}_j}\rangle_T$.

The selection of the two sites, $\vec{P}'_0$ and $\vec{P}_j$, to be linked together is entirely arbitrary, since all sums range over all available sites within the plane of the adsorbed layer. In order to give all possible selections the same weight, we choose as an appropriate approximation for the correlation function the mean value of all possible selections. To illustrate this procedure, let us consider a particular term in Eq. (39) which contains j adsorbate lattice sites in the scattering amplitude at the right-hand side and i sites in the one at the left. Obviously, each of the j sites at the right can be linked to each of the i sites at the left, the total number of selections being $i\times j$. We approximate the correlation function (40) by the sum of all these possible combinations divided by $i\times j$. The resulting expression for the cross section can be written in the following form:

$$\left\langle\frac{d\sigma^{(A)}}{d\Omega}(\vec{k}_f,\vec{k}_i,E)\right\rangle_T^{\mathrm{QCA}} = \left(\frac{m}{2\pi\hbar^2}\right)^2 \times\langle\,|R^A(\vec{k}_f,\vec{k}_i,E)_{\mathrm{av}}|^2\rangle_T \ , \qquad (42)$$

where $R^A(\vec{k}_f,\vec{k}_i,E)_{\mathrm{av}}$ represents a *partial* thermodynamical average over the scattering amplitude $R^A(\vec{k}_f,\vec{k}_i,E)$ obtained through the above-outlined procedure of taking the mean value of all possible averages. The first few terms of $R^A(\vec{k}_f,\vec{k}_i,E)_{\mathrm{av}}$ are given by

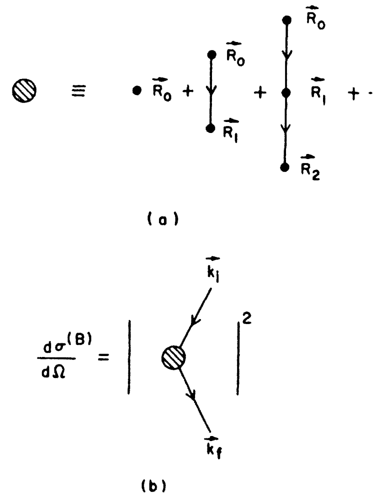

FIG. 3. (a) Diagrammatic definition of a renormalized vertex representing multiple scattering from the substrate. The vertex is to be understood as an interior part of a full diagram. The labels of the dots denote only substrate sites. (b) The scattering cross section, Eq. (38) and Fig. 2, for the substrate expressed in terms of the renormalized-vertex diagram defined in (a).

$$
\begin{aligned}
R^A(\vec{k}_f,\vec{k}_i,E)_{\rm av}=\sum_{LL'}\Big[&Y^*(\hat{k}_f)e^{-i\vec{q}\cdot\vec{d}_1}\sum_{\vec{P}}e_{\vec{P}}e^{-i\vec{q}\cdot\vec{P}}\Big(b_1(k(E))+\frac{1}{2}\sum_{\vec{P}_0}{}'\,b_1(k(E))\,[e^{i\vec{k}_i\cdot(\vec{P}_0-\vec{P})}\gamma^{-1}\langle e_{\vec{P}}e_{\vec{P}_0}\rangle_T G(\vec{P}_0-P,E)\\
&+e^{i\vec{k}_f\cdot(\vec{P}-\vec{P}_0)}\gamma^{-1}\langle e_{\vec{P}_0}e_{\vec{P}}\rangle_T G(\vec{P}-\vec{P}_0,E)]\,b_1(k(E))+\frac{1}{3}\sum_{\vec{P}_0\vec{P}_1}b_1(k(E))\,[e^{i\vec{k}_i\cdot(\vec{P}_1-\vec{P})}\gamma^{-1}\langle e_{\vec{P}}e_{\vec{P}_1}\rangle_T\\
&\times G(\vec{P}_1-\vec{P},E)\,b_1(k(E))\,e^{i\vec{k}_i\cdot(\vec{P}_0-\vec{P}_1)}\gamma^{-1}\langle e_{\vec{P}_1}e_{\vec{P}_0}\rangle_T G(\vec{P}_0-\vec{P}_1,E)+e^{i\vec{k}_f\cdot(\vec{P}-\vec{P}_1)}\gamma^{-1}\\
&\times\langle e_{\vec{P}_1}e_{\vec{P}}\rangle_T G(\vec{P}-\vec{P}_1,E)\,b_1(k(E))\,e^{i\vec{k}_i\cdot(\vec{P}_0-\vec{P})}\gamma^{-1}\langle e_{\vec{P}}e_{\vec{P}_1}\rangle_T G(\vec{P}_0-\vec{P},E)+e^{i\vec{k}_f\cdot(\vec{P}_0-\vec{P}_1)}\gamma^{-1}\\
&\times\langle e_{\vec{P}_1}e_{\vec{P}_0}\rangle_T G(\vec{P}_0-\vec{P}_1,E)\,b_1(k(E))\,e^{i\vec{k}_f\cdot(\vec{P}-\vec{P}_0)}\gamma^{-1}\langle e_{\vec{P}_0}e_{\vec{P}}\rangle_T G(\vec{P}-\vec{P}_0,E)]\\
&\times b_1(k(E))+\cdots\Big)\,Y(\hat{k}_i)\Big]_{LL'}\quad .
\end{aligned}
\tag{43}
$$

The use of this symmetrized approximation procedure is demanded by the requirement that the partially averaged scattering amplitude, $R^A(\vec{k}_f, \vec{k}_i, E)_{\rm av}$, exhibit time-reversal symmetry.

The sums over adsorbate lattice sites in the expression for $R^A(\vec{k}_f, \vec{k}_i, E)_{\rm av}$ now can be performed. This leads us to the following definition of the intralayer electron propagators of the adsorbate:

$$
G_{11}(\vec{k},E)\equiv G_1^{\rm sp}(\vec{k},E)\equiv\sum_{\vec{P}\neq 0}e^{i\vec{k}\cdot\vec{P}}\gamma^{-1}\times\langle e_{\vec{P}'}e_{\vec{P}'+\vec{P}}\rangle_T G(\vec{P},E)\quad . \tag{44}
$$

$G_{11}(\vec{k}, E)$ is a matrix in the partial-wave representation similar to the propagators defined in Eq. (32). The comparison between the intrasubplane propagators of the adsorbate [Eq. (44)] and of the bulk [Eq. (32b)] shows that the thermal disorder among the adatoms causes damping of the electronic wave, in addition to that already existing in both substrate and adsorbate due to electron-electron interactions. Using the definition [Eq. (44)], the series for the scattering amplitude [Eq. (43)] can be written as

$$
\begin{aligned}
R^A(\vec{k}_f,\vec{k}_i,E)_{\rm av}=\sum_{\vec{P}}e_{\vec{P}}e^{-i\vec{q}\cdot\vec{P}}\,e^{-i\vec{q}\cdot\vec{d}_1}\sum_{LL'}\big(&Y^*(\hat{k}_f)\{b_1(k(E))+\tfrac{1}{2}b_1(k(E))\,[G_{11}(\vec{k}_i,E)+G_{11}(\vec{k}_f,E)]\,b_1(k(E))\\
&+\tfrac{1}{3}b_1(k(E))\,[G_{11}(\vec{k}_i,E)\,b_1(k(E))\,G_{11}(\vec{k}_i,E)+G_{11}(\vec{k}_f,E)\,b_1(k(E))\,G_{11}(\vec{k}_i,E)\\
&+G_{11}(\vec{k}_f,E)\,b_1(k(E))\,G_{11}(\vec{k}_f,E)]\,b_1(k(E))+\ldots\}Y(k_i)\big)_{LL'}\quad .
\end{aligned}
\tag{45}
$$

All factors γ^{-1} in Eq. (43) are absorbed in the intralayer propagators defined in Eq. (44). For values of $\vec{k}_f$ associated with substrate beams, $\vec{k}_f$ and $\vec{k}_i$ are related by conservation of momentum parallel to the surface, i.e., $\vec{k}_{f\parallel}=\vec{k}_{i\parallel}+\vec{g}$. In this case, $G_{11}(\vec{k}_i, E)=G_{11}(\vec{k}_f, E)$, so that the sums in Eq. (45) assume a particularly simple form. Scattering from the disordered overlayer is not subject to this conservation law, however, so we also must examine the general case in which $\vec{k}_{f\parallel}\neq\vec{k}_{i\parallel}+\vec{g}$. The summation of the logarithmic series in Eq. (45) is performed in Appendix A. The result is given by the expression

$$
R^A(\vec{k}_f,\vec{k}_i,E)_{\rm av}=\sum_{\vec{P}}e_{\vec{P}}\,e^{-i\vec{q}\cdot\vec{P}}e^{-i\vec{q}\cdot\vec{d}_1}\times\sum_{LL'}[Y^*(\hat{k}_f)\,Q^A(\vec{k}_f,\vec{k}_i,E)\,Y(\hat{k}_i)]_{LL'} \tag{46a}
$$

where

$$
Q^A(\vec{k}_f,\vec{k}_{\rm i},E)\equiv\tau_1(\vec{k}_i,E)=\tau_1(\vec{k}_f,E)\quad(\vec{k}_{f\parallel}=\vec{k}_{i\parallel}+\vec{g}) \tag{46b}
$$

$$
\begin{aligned}
&\equiv b_1(k(E))\,[Q_0^A(\vec{k}_f,\vec{k}_i,E)\ln(\phi_1(\vec{k}_f,E))\\
&-\ln(\phi_1(\vec{k}_i,E))\,Q_0^A(\vec{k}_f,\vec{k}_i,E)]\quad(\vec{k}_{f\parallel}\neq\vec{k}_{i\parallel}+\vec{g})
\end{aligned}
\tag{46c}
$$

and

$$
Q_0^A(\vec{k}_f,\vec{k}_i,E)\equiv\sum_{n=0}^{\infty}[G_{11}(\vec{k}_f,E)\,b_1(k(E))]^n\times[G_{11}(\vec{k}_i,E)\,b_1(k(E))]^{-n-1}\quad , \tag{46d}
$$

or

$$
Q_0^A(\vec{k}_f,\vec{k}_i,E)\equiv-\sum_{n=0}^{\infty}[G_{11}(\vec{k}_f,E)\,b_1(k(E))]^{-n-1}\times[G_{11}(\vec{k}_i,E)\,b_1(k(E))]^n\quad , \tag{46e}
$$

depending on which series converges.[47] In the s-wave model, the series in Eqs. (46d) and (46e) can be summed and $Q^A(\vec{k}_j, \vec{k}_i, E)$ reduces to

$$
Q^A(\vec{k}_f,\vec{k}_i,E)=[G_{11}(\vec{k}_i,E)-G_{11}(\vec{k}_f,E)]^{-1}\times\ln\left(\frac{\phi_1(\vec{k}_i,E)}{\phi_1(\vec{k}_f,E)}\right)\quad(s\text{-wave model}). \tag{46f}
$$

The quantity $\tau_1(\vec{k}, E)$ in Eqs. (46c) and (46f) is the subplane scattering matrix of the adsorbate and is defined analogously to the subplane scattering matrices of the substrate [Eq. (35)]:

$$\tau_1(\vec{k}, E) \equiv b_1(k(E)) + b_1(k(E))\, G_{11}(\vec{k}, E)\, \tau_1(\vec{k}, E) \quad . \tag{47}$$

$\phi_1(\vec{k}, E)$ is the effective field of the monolayer defined by

$$\phi_1(\vec{k}, E) \equiv [1 - b_1(k(E))\, G_{11}(\vec{k}, E)]^{-1} = b_1^{-1}(k(E))\, \tau_1(\vec{k}, E) \quad . \tag{48}$$

It is apparent that $\tau_1(\vec{k}, E)$ may differ considerably from the corresponding subplane scattering matrices, $\tau_\nu(\vec{k}, E)$, $\nu \geq 2$, of the bulk due to the incorporation of the modified intra-adsorbate electron propagator [Eq. (44)]. In fact, as we will see in our numerical analysis in the following paper, $\tau_1(\vec{k}, E)$ exhibits the characteristic features caused by the thermal disorder among the adatoms.

Using Eqs. (42) and (46), we obtain the dynamical scattering cross section for the adsorbate in the QCA:

$$\left\langle \frac{d\sigma^{(A)}}{d\Omega}(\vec{k}_f, \vec{k}_i, E) \right\rangle_T^{\text{QCA}} = \left(\frac{m}{2\pi\hbar^2}\right)^2 \Phi(\vec{q}) \left| \sum_{LL'} [Y^*(\hat{k}_f) \times Q^A(\vec{k}_f, \vec{k}_i, E)\, Y(\hat{k}_i)]_{LL'} \right|^2 \quad . \tag{49a}$$

In the s-wave model this matrix expression reduces to the simple algebraic form

$$\left\langle \frac{d\sigma^{(A)}}{d\Omega}(\vec{k}_f, \vec{k}_i, E) \right\rangle_T^{\text{QCA}} = \left(\frac{m}{2\pi\hbar^2}\right)^2 \frac{\Phi(\vec{q})}{(4\pi)^2} \left| \tau_1(\vec{k}_i, E) \right|^2 \quad (\vec{k}_{f\parallel} = \vec{k}_{i\parallel} + \vec{g}) \tag{49b}$$

$$= \left(\frac{m}{2\pi\hbar^2}\right)^2 \frac{\Phi(\vec{q})}{(4\pi)^2} \times \left| \frac{\ln[\phi_1(\vec{k}_i, E)/\phi_1(\vec{k}_f, E)]}{G_{11}(\vec{k}_i, E) - G_{11}(\vec{k}_f, E)} \right|^2 \quad (\text{otherwise}) \quad . \tag{49c}$$

By expanding the logarithm in Eq. (49c) and using the definitions [Eqs. (47) and (48)], it is easily shown that the expression (49c) leads to the correct limit [(49b)] as $\vec{k}_{f\parallel}$ approaches $\vec{k}_{i\parallel} + \vec{g}$. Furthermore, the general expression [Eq. (49a) reduces to the correct form in the kinematical limit [see the last term of Eq. (26)]:

$$\left\langle \frac{d\sigma^{(A)\prime}}{d\Omega}(\vec{k}_f, \vec{k}_i, E) \right\rangle_T^{\text{Born}} = \left(\frac{m}{2\pi\hbar^2}\right)^2 \Phi(\vec{q}) \times \left| \sum_{LL'} \{Y^*(\hat{k}_f)\, b_1(k(E)) \times Y(\hat{k}_i)\}_{LL'} \right|^2 \quad . \tag{50}$$

In comparing these two expressions, we notice an important feature of the QCA: The dynamical equilibrium cross section of the adsorbate is, in the QCA, proportional to the autocorrelation function of the lattice gas, just as in the kinematical limit. The effect of multiple electron scattering is therefore to introduce a renormalization of the scattering vertex $b_1(k(E))$, as shown in Eqs. (49). This renormalization is described by the subplane scattering matrix of the adsorbate, $\tau_1(\vec{k}, E)$. It is compatible with the requirement that the partially averaged scattering amplitudes [Eq. (46)] and, consequently, the scattering cross sections conserve time-reversal symmetry. We will show in C that the partially averaged scattering amplitude for the adsorbate-substrate system is invariant under time reversal. Since this more general amplitude contains the adsorbate amplitude, it follows that the latter also is invariant.

We conclude this subsection by presenting a diagrammatic representation of the thermal-scattering cross section in the QCA. We indicate the fact that all higher correlation functions are factorized into two-point functions by changing rules (b) and (i) in Sec. III A in the following way.

(b′) Connect any dot on the right-hand side with any dot on the left-hand side by a dashed line. Connect, on both sides, neighboring dots by a dashed line. Associate with each diagram the factor $(i \times j)^{-1}$, where $j(i)$ is the number of dots on the right- (left-) hand side.

(i′) Associate with each dashed line the two-point correlation $\langle e_{\vec{R}} e_{\vec{R}'} \rangle_T$, where $\vec{R}$ and $\vec{R}'$ are the labels of the dots connected by this line. Associate with each dashed line except the one connecting both sides the factor $1/\gamma$. In addition, of course, the labels of the dots are now restricted to adsorbate lattice sites, since at the moment we are ignoring the presence of the substrate. In Fig. 4 we give the diagrammatic representation of the contributions to the cross sections that are of third order in the interaction. These diagrams illustrate the approximation to the corresponding exact

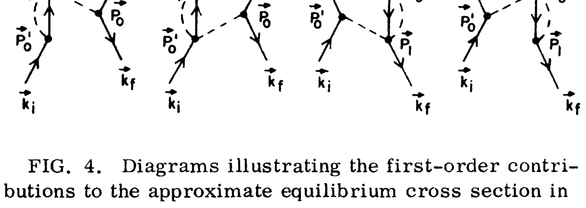

FIG. 4. Diagrams illustrating the first-order contributions to the approximate equilibrium cross section in the case of scattering from the disordered adsorbate. The diagrams represent the quasicrystalline approximation of the corresponding exact diagrams shown in Fig. 1 (b). Dashed lines connecting two dots designate two-point correlations between the sites that are represented by the dots. The labels of the dots denote only adsorbate sites.

diagrams shown in Fig. 1(b).

Finally, the form of the expression for the cross section [Eq. (42)] indicates that the partially averaged adsorbate scattering amplitude $R^A(\vec{k}_f, \vec{k}_i, E)_{av}$ [Eqs. (43) and (46)] can be represented directly by a diagrammatic series (i.e., we need not use the diagrams for the cross section once the QCA has been imposed). The definition of the individual terms of this series follows from the rules given above and in A. The first few contributions to $R^A(\vec{k}_f, \vec{k}_i, E)_{av}$ are shown in Fig. 5.

C. Multiple scattering from adsorbate-substrate system

1. Renormalized quasicrystalline approximation

In this subsection we determine the equilibrium cross section for multiple electron scattering from the combined adsorbate-substrate system by applying the renormalized quasicrystalline approximation as outlined in Sec. III B. The motivation for introducing the RQCA lies in the fact that the renormalization permits an adequate description of short- and long-range-order effects on scattering processes involving both substrate and adsorbate. A less generally valid version of the RQCA is described in C 2. We proceed in four steps. First, we decompose the scattering amplitude, $R(\vec{k}_f, \vec{k}_i, E)$ [Eqs. (12) and (13)] into five contributions, each of which describes a certain class of scattering events. Second, we perform in these terms all sums over intermediate scattering processes that take place in the substrate between two scattering events in the overlayer. This summation leads to the definition of a renormalized intra-adsorbate electron propagator. Using these propagators in the third step, we cast the various contributions to the unaveraged scattering amplitude into such a form that the formalism developed in Sec. IV B can be applied directly to obtain the corresponding partially averaged contributions. We conclude by deriving the expressions for the partially averaged scattering amplitude and for the equilibrium cross section.

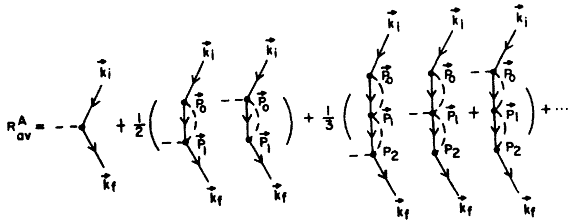

FIG. 5. Diagrammatic series for the proper partially averaged scattering amplitude R^A_{av} defined by Eq. (46) of the adsorbate. The factors that are associated with each diagram because of the arithmetic averaging procedure described in Sec. IV B are indicated explicitly.

It is useful to separate the contributions to the unaveraged scattering amplitude [Eqs. (12) and (13)] of the adsorbate-substrate system into five classes of scattering processes. These are defined as follows:

$R^B(\vec{k}_f, \vec{k}_i, E)$: scattering only from substrate, (51a)

$S_1(\vec{k}_f, \vec{k}_i, E)$: scattering starts and ends in adsorbate, (51b)

$S_2(\vec{k}_f, \vec{k}_i, E)$: scattering starts in adsorbate and ends in substrate, (51c)

$S_3(\vec{k}_f, \vec{k}_i, E)$: scattering starts in substrate and ends in adsorbate, (51d)

$S_4(\vec{k}_f, \vec{k}_i, E)$: scattering starts and ends in substrate involving intermediate scattering sites in the adsorbate. (51e)

The first of these terms represents the amplitude for dynamical scattering from the bulk. It is given by Eq. (37). According to the above definitions, Eq. (12) may be written as

$$R(\vec{k}_f, \vec{k}_i, E) = R^B(\vec{k}_f, \vec{k}_i, E) + \sum_{i=1}^{4} S_i(\vec{k}_f, \vec{k}_i, E) \quad . \tag{52}$$

Let us next consider those contributions to the quantity $S_1(\vec{k}_f, \vec{k}_i, E)$ which involve only two sites in the absorbate. It is easily seen that these are given by the expression

$$\sum_{LL'} \Big(Y^*(\hat{k}_f) \exp(-i\vec{q} \cdot \vec{d}_1) \sum_{\vec{P}_0 \vec{P}_1} \exp[i(\vec{k}_i \cdot \vec{P}_0 - \vec{k}_f \cdot \vec{P}_1) \\ \times e_{\vec{P}_1} b_1(k(E)) \overline{G}(\vec{P}_0 - \vec{P}_1, E) e_{\vec{P}_0} b_1(k(E)) \\ \times Y(\hat{k}_i) \Big)_{LL'} \quad . \tag{53}$$

Here we have used Eqs. (20), and $\vec{P}_0$, $\vec{P}_1$ denote lattice sites in the adsorbate. The propagator $\overline{G}(\vec{P}_0 - \vec{P}_1, E)$ describes the propagation of the electronic wave between the two overlayer sites $\vec{P}_0$ and $\vec{P}_1$, either directly or via multiple scattering from the substrate. It is defined as

$$\vec{G}(\vec{P}_0 - \vec{P}_1, E) \equiv (1 - \delta_{\vec{P}_0 \vec{P}_1}) G(\vec{P}_0 - \vec{P}_1, E) \\ + g(\vec{P}_0 - \vec{P}_1, E) \quad , \tag{54a}$$

$$g(\vec{P}_0 - \vec{P}_1, E) \equiv \sum_{\vec{R}_0} G(\vec{R}_0 - \vec{P}_1, E) b_{\vec{R}_0}(k(E)) G(\vec{P}_0 - \vec{R}_0, E) \\ + \sum_{\vec{R}_0 \vec{R}_1}{}' G(\vec{R}_1 - \vec{P}_1, E) b_{\vec{R}_1}(k(E)) \\ \times G(\vec{R}_0 - \vec{R}_1, E) b_{\vec{R}_0}(k(E)) \\ \times G(\vec{P}_0 - \vec{R}_0, E) + \dots \quad . \tag{54b}$$

The $\vec{R}_i$ denote lattice sites in the substrate.

The utilization of the propagator $\overline{G}(\vec{P}_0 - \vec{P}_1, E)$ constitutes the essential feature of the renormalized quasicrystalline approximation. Formally, it reduces the problem of dynamical scattering from the entire adsorbate-substrate system to that of multiple scattering from the adsorbed overlayer alone. Therefore, this reduction represents a significant conceptual simplification of the multiple-scattering analysis.

The infinite series designated by $g(\vec{P}_0-\vec{P}_1,E)$ [Eq. (54b)] can be summed by performing a two-dimensional Fourier transformation:

$$\begin{aligned} g(\vec{k},E) &= \sum_{\vec{P}_0} \exp[i\vec{k}\cdot(\vec{P}_0-\vec{P}_1)]\,g(\vec{P}_0-\vec{P}_1,E) \\ &= \sum_{\nu\neq 1} G_{1\nu}(\vec{k},E)\,b_\nu(k(E))\,G_{\nu 1}(\vec{k},E) + \sum_{\nu,\mu\neq 1} G_{1\nu}(\vec{k},E) \\ &\quad\times b_\nu(k(E))\,G_{\nu\mu}(\vec{k},E)\,b_\mu(k(E))\,G_{\mu 1}(\vec{k},E) + \ldots, \end{aligned} \tag{55}$$

in which

$$G_{\nu\mu}(\vec{k},E) \equiv \sum_{\vec{P}} \exp[i\vec{k}\cdot(\vec{P}+\vec{d}_\mu-\vec{d}_\nu)]\,G(\vec{P}+\vec{d}_\mu-\vec{d}_\nu) \quad \left\{\begin{matrix} \nu=1, & \mu\geq 2 \\ & \text{or} \\ \nu\geq 2, & \mu=1 \end{matrix}\right\}, \tag{56}$$

and the $G_{\nu\mu}(\vec{k},E)$, $\nu\mu\geq 2$, are defined in Eq. (32). Using now the definitions of the subplane scattering matrices, $\tau_\nu(\vec{k},E)$ [Eq. (35)], and of the interlayer scattering matrices, $T_{\nu\mu}(\vec{k},E)$ [Eq. (36)], for the substrate, we obtain for the series in Eq. (55) the following simple expression:

$$g(\vec{k},E) = \sum_{\nu\mu\geq 2} G_{1\nu}(\vec{k},E)\,T_{\nu\mu}(\vec{k},E)\,G_{\mu 1}(\vec{k},E) \quad . \tag{57}$$

By Fourier inverting this equation, we arrive at an alternative expression for the quantity $g(\vec{P},E)$ in terms of real-space coordinates:

$$\begin{aligned} g(\vec{P},E) &= \frac{1}{(2\pi)^2}\int_{-\pi}^{\pi} d^2k\, e^{-i\vec{k}\cdot\vec{P}} \sum_{\nu\mu\geq 2} G_{1\nu}(\vec{k},E) \\ &\quad\times T_{\nu\mu}(\vec{k},E)\,G_{\mu 1}(\vec{k},E) \quad . \end{aligned} \tag{58}$$

This Fourier integral may be simplified by utilizing the symmetry properties for the propagators and scattering matrices which are derived in Appendix B. Thus the renormalized intra-adsorbate propagator $\overline{G}(\vec{P}_0-\vec{P}_1,E)$ [Eq. (54)] can be evaluated by using either the series expansion, Eq. (54b), or the integral representation, Eq. (58), for the quantity $g(\vec{P}_0-\vec{P}_1,E)$.

If we now bring the contributions to $S_1(\vec{k}_f,\vec{k}_i,E)$ that involve three, four, etc., overlayer sites into a form analogous to the one given in (53), we obtain the following series:

$$\begin{aligned} S_1(\vec{k}_f,\vec{k}_i,E) &= \sum_{LL'}\Bigg(Y^*(\hat{k}_f)\exp(-i\vec{q}\cdot\vec{d}_1)\sum_{j=0}^{\infty} \\ &\quad\times\sum_{\vec{P}_0\cdots\vec{P}_j}\exp[i(\vec{k}_i\cdot\vec{P}_0-\vec{k}_f\cdot\vec{P}_j)] \\ &\quad\times e_{\vec{P}_j}\cdots e_{\vec{P}_0}\,b_1(k(E))\,\overline{G}(\vec{P}_{j-1}-\vec{P}_j,E)\cdots \\ &\quad\times b_1(k(E))\,\overline{G}(\vec{P}_0-\vec{P}_1,E)\,b_1(k(E))\,Y(\hat{k}_i)\Bigg)_{LL'} \quad . \end{aligned} \tag{59}$$

This expression is formally identical to that for the unaveraged scattering amplitude of the adsorbate, except that the intra-adsorbate propagators $G(\vec{P}_0-\vec{P}_1,E)$ are replaced by their renormalized counterparts, $\overline{G}(\vec{P}_0-\vec{P}_1,E)$. [The unaveraged adsorbate amplitude may be obtained from Eqs. (12) and (13) by restricting all site summations to the overlayer.] This similarity allows us to take advantage of the entire formalism developed in Sec. IV B for the quasicrystalline approximation of dynamical scattering from the disordered overlayer. Thus, in analogy to the partial averaging of the adsorbate scattering amplitude, the above expression (59) is replaced by a partial average which we denote by $S_1(\vec{k}_f,\vec{k}_i,E)_{\text{av}}$. Using the results given in Sec. IV B [Eqs. (46)] we obtain for this average the following expressions:

$$\begin{aligned} S_1(\vec{k}_f,\vec{k}_i,E)_{\text{av}} &\equiv \sum_{\vec{P}} e_{\vec{P}}\, e^{-i\vec{q}\cdot\vec{P}}\, e^{-i\vec{q}\cdot\vec{d}_1} \\ &\quad\times\sum_{LL'}[Y^*(\hat{k}_f)\,\overline{Q}(\vec{k}_f,\vec{k}_i,E)\,Y(\hat{k}_i)]_{LL'} \quad , \end{aligned} \tag{60a}$$

in which

$$\overline{Q}(\vec{k}_f,\vec{k}_i,E) \equiv \overline{\tau}_1(\vec{k}_i,E) = \overline{\tau}_1(\vec{k}_f,E) \quad (\vec{k}_{f,\parallel}=\vec{k}_{i,\parallel}+\vec{g}) \tag{60b}$$

$$\begin{aligned} &\equiv b_1(k(E))\,[\overline{Q}_0(\vec{k}_f,\vec{k}_i,E)\ln(\phi_1(\vec{k}_i,E)) \\ &\quad-\ln(\phi_1(\vec{k}_f,E))\,\overline{Q}_0(\vec{k}_f,\vec{k}_i,E)] \\ &\quad(\vec{k}_{f,\parallel}\neq\vec{k}_{i,\parallel}+\vec{g}) \end{aligned} \tag{60c}$$

$$\equiv [\overline{G}(\vec{k}_f,E)-\overline{G}(\vec{k}_i,E)]^{-1}\ln\left(\frac{\overline{\phi}_1(\vec{k}_f,E)}{\overline{\phi}_1(\vec{k}_i,E)}\right) \quad , \quad (s\text{-wave model}) \tag{60d}$$

and

$$\begin{aligned} \overline{Q}_0(\vec{k}_f,\vec{k}_i,E) &\equiv \sum_{n=0}^{\infty}[\overline{G}(\vec{k}_f,E)\,b_1(k(E))]^n \\ &\quad\times[\overline{G}(\vec{k}_i,E)\,b_1(k(E))]^{-n-1} \end{aligned} \tag{60e}$$

or

$$\begin{aligned} \overline{Q}_0(\vec{k}_f,\vec{k}_i,E) &\equiv -\sum_{n=0}^{\infty}[\overline{G}(\vec{k}_f,E)\,b_1(k(E))]^{-n-1} \\ &\quad\times[\overline{G}(\vec{k}_i,E)\,b_1(k(E))]^n \quad , \end{aligned} \tag{60f}$$

depending on which series converges.[47]

The propagator $\overline{G}(\vec{k},E)$ is defined in analogy to Eq. (44) as

$$\overline{G}(\vec{k},E) \equiv \sum_{\vec{P}} e^{i\vec{k}\cdot\vec{P}}\,\gamma^{-1}\langle e_{\vec{P}'}, e_{\vec{P}'+\vec{P}}\rangle_T\,\overline{G}(\vec{P},E) \quad . \tag{61}$$

The quantity $\overline{\tau}_1(\vec{k},E)$ represents the renormalized subplane scattering matrix of the adsorbate and is defined similarly to Eq. (47):

$$\overline{\tau}_1(\vec{k},E) \equiv b_1(k(E)) + b_1(k(E))\,\overline{G}(\vec{k},E)\,\overline{\tau}_1(\vec{k},E) \,. \tag{62}$$

Finally, the renormalized effective field of the overlayer is given by [see Eq. (48)]

$$\overline{\phi}_1(\vec{k},E)\equiv b_1^{-1}(k(E))\,\overline{\tau}_1(\vec{k},E) \quad . \tag{63}$$

The formal similarity between $R^A(\vec{k}_f,\vec{k}_i,E)_{\mathrm{av}}$ [Eqs. (46)] and $S_1(\vec{k}_f,\vec{k}_i,E)_{\mathrm{av}}$ [Eqs. (60)] allows us to use the prescription given in Sec. IV B to construct a diagrammatic representation for the latter quantity. This prescription is altered only in that the renormalized intra-adsorbate propagators, $\overline{G}(\vec{P}_0-\vec{P}_1,E)$, rather than unmodified propagators, $G(\vec{P}_0-\vec{P}_1,E)$, are used to construct $S_1(\vec{k}_f,\vec{k}_i,E)_{\mathrm{av}}$. Figure 6(a) shows the diagrammatic series representing $S_1(\vec{k}_f,\vec{k}_i,E)_{\mathrm{av}}$. The internal double line symbolizes the renormalized intra-adsorbate propagator [Eq. (54)], which is defined diagrammatically in panel (b) of Fig. 6. The series in panel (a) is formally identical to that shown in Fig. 5 for the partially averaged overlayer scattering amplitude.

We next discuss briefly how the partial averages of the remaining terms $S_i(\vec{k}_f,\vec{k}_i,E)$, $i=2,\ldots,4$ in Eq. (52) can be derived from the results for $S_1(\vec{k}_f,\vec{k}_i,E)_{\mathrm{av}}$ obtained above. According to the definition (51c), the quantity $S_2(\vec{k}_f,\vec{k}_i,E)_{\mathrm{av}}$ describes all scattering processes that start in the adsorbate and end in the substrate. These scattering processes consist of three stages: multiple scattering between adsorbate sites, either directly or via multiple scattering from the bulk, then propagation from adsorbate to substrate; and, finally, multiple scattering from the bulk. Using the diagrams shown in Figs. 3(a) and (6), we obtain for $S_2(\vec{k}_f,\vec{k}_i,E)_{\mathrm{av}}$ the diagram shown in Fig. 7(a). Its contribution to the partial average, $R(\vec{k}_f,\vec{k}_i,E)_{\mathrm{av}}$, of the total scattering amplitude [Eq. (52)] is given by

$$S_2(\vec{k}_f,\vec{k}_i,E)_{\mathrm{av}}=\sum_{\vec{P}}e_{\vec{P}}\,e^{-i\vec{q}\cdot\vec{P}}\,e^{-i\vec{q}\cdot\vec{d}_1}\sum_{LL'}\Big(Y^*(\hat{k}_f)\times\sum_{\nu\mu\geq 2}T_{\nu\mu}(\vec{k}_f,E)\,G_{\mu 1}(\vec{k}_f,E)\,\overline{Q}(\vec{k}_f,\vec{k}_i,E)\times Y(\hat{k}_i)\Big)_{LL'} \quad , \tag{64a}$$

in which $\overline{Q}(\vec{k}_f,\vec{k}_i,E)$ is defined in Eq. (60b). The quantity $S_3(\vec{k}_f,\vec{k}_i,E)_{\mathrm{av}}$ is obtained in an analogous fashion. Its diagrammatic representation is shown in Fig. 7(b) and its contribution to $R(\vec{k}_f,\vec{k}_i,E)_{\mathrm{av}}$ is given by

$$S_3(\vec{k}_f,\vec{k}_i,E)_{\mathrm{av}}=\sum_{\vec{P}}e_{\vec{P}}\,e^{-i\vec{q}\cdot\vec{P}}\,e^{-i\vec{q}\cdot\vec{d}_1}\sum_{LL'}\Big(Y^*(\hat{k}_f)\times\overline{Q}(\vec{k}_f,\vec{k}_i,E)\sum_{\nu\mu\geq 2}G_{1\nu}(\vec{k}_i,E)\,T_{\nu\mu}(\vec{k}_i,E)\times Y(\hat{k}_i)\Big)_{LL'} \quad . \tag{64b}$$

According to the definition (51d), the scattering processes described by $S_4(\vec{k}_f,\vec{k}_i,E)_{\mathrm{av}}$ consist of five stages: multiple scattering in the bulk, propagation from bulk to adsorbate; multiple scattering from adsorbate to adsorbate, either directly or via multiple scattering from the bulk; then propagation from adsorbate to substrate; and, finally, multiple scattering within the bulk. The diagrammatic representation of this term is shown in Fig. 7(c). Its contribution to $R(\vec{k}_f,\vec{k}_i,E)_{\mathrm{av}}$ is given by

$$S_4(\vec{k}_f,\vec{k}_i,E)_{\mathrm{av}}=\sum_{\vec{P}}e_{\vec{P}}\,e^{-i\vec{q}\cdot\vec{P}}\,e^{-i\vec{q}\cdot\vec{d}_1}\sum_{LL'}\Big(Y^*(\hat{k}_f)\times\sum_{\nu\mu\geq 2}T_{\nu\mu}(\vec{k}_f,E)\,G_{\mu 1}(\vec{k}_f,E)\,\overline{Q}(\vec{k}_f,\vec{k}_i,E)\times\sum_{\nu'\mu'\geq 2}G_{1\nu'}(\vec{k}_i,E)\,T_{\nu'\mu'}(\vec{k}_i,E)\times Y(\hat{k}_i)\Big)_{LL'} \quad . \tag{64c}$$

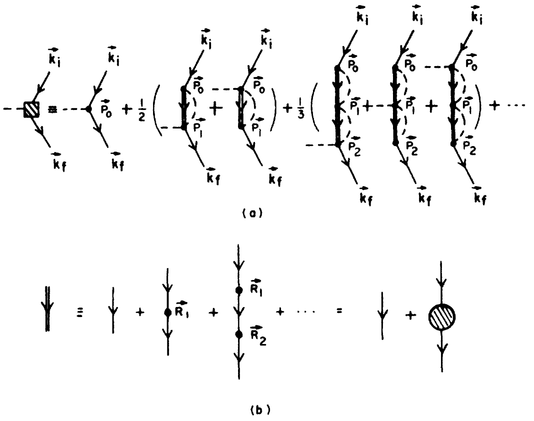

FIG. 6. (a) Diagrammatic equation for the quantity $S_1(\vec{k}_f,\vec{k}_i,E)_{\mathrm{av}}$ as specified by Eqs. (60) in the text. The labels of the dots denote adsorbate sites. The factors resulting from the averaging procedure are shown explicitly. The double line symbolizes the intra-adsorbate electron propagator, which is renormalized to account for intermediate dynamical scattering from the substrate. It is defined in panel (b).

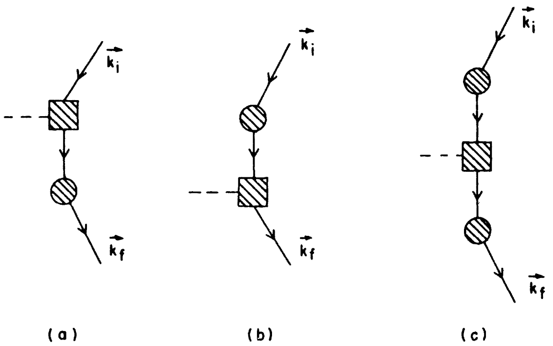

FIG. 7. Diagrammatic representation of various contributions to the partially averaged scattering amplitude [Eqs. (65)]. Panel (a) illustrates the quantity $S_2(\vec{k}_f,\vec{k}_i,E)_{\mathrm{av}}$, Eq. (64a). Panel (b) illustrates the quantity $S_3(\vec{k}_f,\vec{k}_i,E)_{\mathrm{av}}$, Eq. (64b). Panel (c) represents the quantity $S_4(\vec{k}_f,\vec{k}_i,E)_{\mathrm{av}}$, Eq. (64c). The circular vertex is defined in Fig. 3 and the rectangular vertex is obtained from Fig. 6(a) by omitting the two solid external lines.

Using Eqs. (37), (52), (60), and (64), we obtain the following expression for the partially averaged scattering amplitude for the combined absorbate-substrate system:

$$R(\vec{k}_f, \vec{k}_i, E)_{\text{av}} = R^B(\vec{k}_f, \vec{k}_i, E) + \sum_{i=1}^{4} S_1(\vec{k}_f, \vec{k}_i, E)_{\text{av}} \tag{65a}$$

$$= \sum_{\vec{p}} e^{-i\vec{q}\cdot\vec{p}} [A(\vec{k}_f, \vec{k}_i, E) + e_{\vec{p}} B(\vec{k}_f, \vec{k}_i, E)] \quad , \tag{65b}$$

where

$$A(\vec{k}_f, \vec{k}_i, E) \equiv \sum_{LL'} \left(Y^*(\hat{k}_f) \sum_{\nu\mu \geq 2} e^{-i\vec{q}\cdot\vec{d}_\nu} T_{\nu\mu}(\vec{k}_i, E) \times Y(\hat{k}_i) \right)_{LL'} \quad , \tag{66}$$

$$B(\vec{k}_f, \vec{k}_i, E) \equiv \sum_{LL'} \left[Y^*(\hat{k}_f) e^{-i\vec{q}\cdot\vec{d}_1} \left(1 + \sum_{\nu\mu \geq 2} T_{\nu\mu}(\vec{k}_f, E) \times G_{\mu 1}(\vec{k}_f, E) \right) \overline{Q}(\vec{k}_f, \vec{k}_i, E) \left(1 + \sum_{\nu\mu \geq 2} G_{1\nu}(\vec{k}_i, E) \times T_{\nu\mu}(\vec{k}_i, E) \right) Y(\hat{k}_i) \right]_{LL'} \quad , \tag{67}$$

and $\overline{Q}(\vec{k}_f, \vec{k}_i, E)$ is defined in Eq. (60b). The derivation of Eqs. (65)–(67) completes our discussion of the scattering amplitude. That it is indeed invariant under time reversal is shown in Appendix B. We note, however, that $R(\vec{k}_f, \vec{k}_i, E)_{\text{av}}$ depends explicitly on both the initial- and final-state wave vectors in a more complex fashion than the substrate-scattering amplitude $R^B(\vec{k}_f, \vec{k}_i, E)$ [Eq. (37)] [i.e., the first term in Eq. (65)].

The dynamical scattering cross section in the RQCA for the complete adsorbate-substrate system may now be written in the following way:

$$\left\langle \frac{d\sigma}{d\Omega}(\vec{k}_f, \vec{k}_i, E) \right\rangle_T^{\text{RQCA}} = \left(\frac{m}{2\pi\hbar^2} \right)^2 \langle | R(\vec{k}_f, \vec{k}_i, E)_{\text{av}} |^2 \rangle_T \tag{68a}$$

$$= \left(\frac{m}{2\pi\hbar^2} \right)^2 \left\langle \left| \sum_{\vec{p}} e^{-i\vec{q}\cdot\vec{p}} [A(\vec{k}_f, \vec{k}_i, E) + e_{\vec{p}} B(\vec{k}_f, \vec{k}_i, E)] \right|^2 \right\rangle_T \quad . \tag{68b}$$

The diagrammatic representation of the cross section in the RQCA is shown in Fig. 8.

Equations (68) specify our results for the renormalized quasicrystalline approximation of the dynamical scattering cross section for the complete system consisting of the disordered adsorbate and the underlying periodic substrate. In Eqs. (68) the only statistical quantities describing the thermodynamic features of the adsorbed monolayer are the coverage γ and the two-point correlations, $\langle e_{\vec{p}} e_{\vec{p}'} \rangle_T$. For the derivation of our final results presented in Eqs. (68), it is immaterial how these two statistical quantities are determined. We have taken in Sec. II a microscopic (i.e., statistical-mechanical) approach by applying the lattice-gas model to the disordered adsorbate in order to evaluate these quantities. Our theoretical analysis of the multiple-electron-diffraction problem presented in this section is also valid, however, in the context of a statistical approach in which the coverage and the two-point functions are determined phenomenologically.

The RQCA described above exhibits the important feature that it represents an appropriate description of the effects of short- and long-range order within the overlayer on contributions to the cross section due to dynamical scattering not only from the adsorbate, but also between substrate and adsorbate. In particular, as demonstrated in Appendix C, the RQCA leads to the correct $T = 0$ limit of the expressions for the dynamical scattering cross sections. This result is specifically significant since it permits an exact multiple-scattering analysis for ordered superlattices adsorbed on periodic substrates entirely in terms of intra- and inter*layer scattering matrices*,[30] thereby

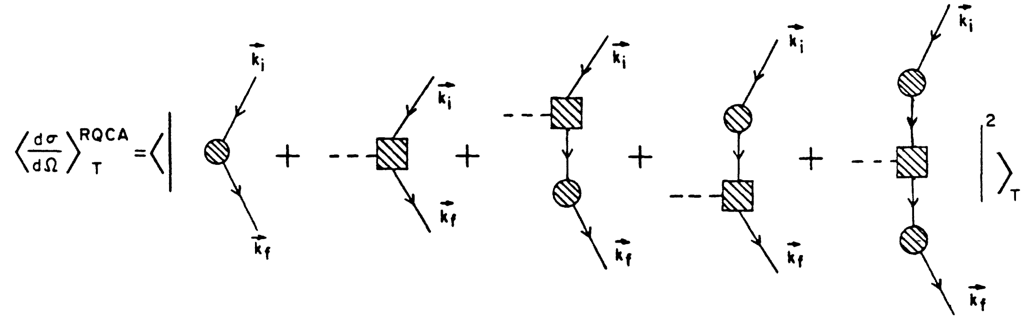

FIG. 8. Figure shows, for the adsorbate-substrate system, the dynamical equilibrium-scattering cross section [Eqs. 68] in the renormalized quasicrystalline approximation RQCA. The circular vertex denotes multiple scattering from the ordered substrate. It is defined in Fig. 3. The rectangular vertex symbolizes scattering processes that start and end in the disordered adsorbate but may involve intermediate scattering events in the substrate. It is defined in Fig. 6.

avoiding the more complex *sublattice* formalism[14] employed in the present literature.

At finite temperatures, the renormalization procedure outlined above requires the explicit knowledge of the propagator $g(\vec{P}, E)$, which describes the indirect electron propagation via the substrate between two overlayer sites separated by the vector $\vec{P}$. The numerical evaluation of the quantity of $g(\vec{P}, E)$ through either the series expansion [Eq. (54b)] or the integral representation [Eq. (58)] will, in practice, imply an approximate treatment of contributions to the cross section due to dynamical scattering between adsorbate and substrate. Recently proposed perturbation schemes in dynamical theories of ELEED such as the renormalized forward-scattering technique,[48] however, might allow an accurate and practical approximate procedure for performing the renormalization. The explicit determination of the propagator $g(\vec{P}, E)$ can be avoided if an additional approximation is imposed on the RQCA. This approximation is the subject of C 2.

2. *Restricted renormalized quasicrystalline approximation*

Let us write down the two contributions to the renormalized electron propagator $\overline{G}(\vec{k}, E)$ [Eq. (61)] by using Eqs. (44) and (54a),

$$\overline{G}(\vec{k}, E) = G_1^{sp}(\vec{k}, E) + \sum_{\vec{P}} e^{i\vec{k}\cdot\vec{P}}\gamma^{-1}\langle e_{\vec{P}'} e_{\vec{P}'+\vec{P}}\rangle_T\, g(\vec{P}, E) \quad . \tag{69}$$

If we approximate the second term in this equation by replacing the pair correlation $\langle e_{\vec{P}'} e_{\vec{P}'+\vec{P}}\rangle_T$ by its random limit γ^2, the summation over the lattice sites $\vec{P}$ can be performed [see Eq. (57)]:

$$\overline{G}'(\vec{k}, E) \equiv G_1^{sp}(\vec{k}, E) + \gamma g(\vec{k}, E) \tag{70a}$$

$$= G_1^{sp}(\vec{k}, E) + \gamma \sum_{\nu\mu \geq 2} G_{1\nu}(\vec{k}, E)\, T_{\nu\mu}(\vec{k}, E) \times G_{\mu 1}(\vec{k}, E) \ . \tag{70b}$$

The above approximation implies that pair correlations between overlayer sites are replaced by their random limits whenever intermediate scattering from the substrate occurs.

The expressions for the scattering cross section in this restricted version of the RQCA are identical to the ones derived in C 1 for the RQCA, except that the renormalized electron propagator $\overline{G}(\vec{k}, E)$ is replaced by the corresponding approximate propagator, $\overline{G}'(\vec{k}, E)$. The fact that this latter quantity can be written entirely in terms of the known substrate-layer scattering matrices, $T_{\nu\mu}(\vec{k}, E)$, constitutes a specifically useful aspect of this approximation. The substitution of the random (i.e., infinite-temperature) limit for the correlation in Eq. (69) indicates, however, that the restricted RQCA is applicable only in the high-temperature region.

We conclude by pointing out how the diagrammatic representation of the cross sections given in C 1 has to be modified in the present case. Since the distinction between the two approximations lies entirely in the treatment of the pair correlation in the second term in Eq. (69), we only need to change in all diagrams the dashed line that accompanies each renormalized propagator $\overline{G}(\vec{P}, E)$, as indicated in Fig. 9. The factor γ in front of the second contribution to the diagram in this figure is analogous to the one in the second term of Eqs. (70).

Having presented a detailed analysis of the RQCA and the restricted RQCA, we proceed in Sec. V to a discussion of the limitations that are inherent in both approximations.

V. ASSESSMENT OF QUASICRYSTALLINE APPROXIMATION

In Sec. IV we derived detailed expressions for the electron-solid scattering cross section in the renormalized quasicrystalline approximation (RQCA) and in a more restricted version of this approximation. The only statistical correlations incorporated in the multiple-scattering theory are those between pairs of sites involved in consecutive scattering events. Moreover, with some effort we were able to cast the approximations into a form consistent with the known conservation laws obeyed by the scattering process (neglecting specifically spin-dependent interactions). Therefore, we have constructed a sensible, historically motivated if approximate theory of multiple scattering from an overlayer exhibiting both long- and short-range order on a periodic substrate. We give in this section a critique of both approximations by assessing which aspects of the present problem are not dealt with correctly because of the application of the quasicrystalline description. We begin by considering the case of multiple scattering from the disordered adsorbate for which both approximations are identical.

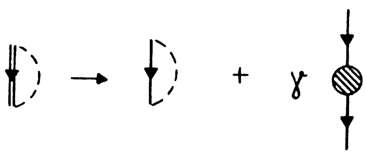

FIG. 9. How the renormalized propagator defined in Fig. 6 (b) and the pair correlation that accompanies it have to be modified in the case of the restricted RQCA. In the first term, representing propagation within the overlayer, the pair correlation is unchanged. In the second term, which accounts for indirect propagation between overlayer sites via the substrate, however, the correlation $\gamma^{-1}\langle e_{\vec{P}} e_{\vec{P}'}\rangle_T$ is replaced by its random limit γ. [See Eqs. (69) and (70).]

Any theory of short-range order must incorporate two characteristic features of a disordered system: the possibility of repeated scattering within a finite cluster of atoms and the finite range of the pair-distribution function. The quasicrystalline approximation describes both features in an approximate manner. The effects of short-range order and clustering are most easily demonstrated in the contribution to the equilibrium cross section which is of third order in the reduced interaction. (The term of second order represents the Born approximation and is treated exactly in the QCA.) This contribution is obtained from Eq. (28) by restricting all summations to adsorbate sites. Indicating only the relevant site dependent quantities, Eq. (28) can be written as

$$\left\langle \frac{d\sigma^{(A)}}{d\Omega}(\vec{k}_f,\vec{k}_i,E)\right\rangle_T = \sum_{\vec{P}_0'\neq\vec{P}_0\neq\vec{P}_1\neq\vec{P}_0'} e^{i\vec{q}\cdot\vec{P}_0'}\, e^{i(\vec{k}_i\cdot\vec{P}_0-\vec{k}_f\cdot\vec{P}_1)} \times\langle e_{\vec{P}_0'}e_{\vec{P}_1}e_{\vec{P}_0}\rangle_T\cdots + \sum_{\vec{P}_0\neq\vec{P}_1} e^{i\vec{k}_f\cdot(\vec{P}_0-\vec{P}_1)}\langle e_{\vec{P}_0}e_{\vec{P}_1}\rangle_T\cdots + \sum_{\vec{P}_0\neq\vec{P}_1} e^{i\vec{k}_i\cdot(\vec{P}_0-\vec{P}_1)}\langle e_{\vec{P}_0}e_{\vec{P}_1}\rangle_T\cdots+\text{c.c.}\,, \qquad (71)$$

where the dots refer to all remaining quantities appearing in Eq. (28). In the first term in the above equation, all three sites are distinct. The second and third term are obtained by setting $\vec{P}_0'=\vec{P}_0$ and $\vec{P}_1'=\vec{P}_1$, respectively. These two terms represent the interference between double scattering from the two sites $\vec{P}_0$ and $\vec{P}_1$ and single scattering from site $\vec{P}_0$ or $\vec{P}_1$, respectively. To obtain an estimate of the accuracy of the QCA, let us compare the above exact expression with its approximate form. According to the description outlined in Sec. IV B, this is given by

$$\begin{aligned}\left\langle \frac{d\sigma^{(A)}}{d\Omega}(\vec{k}_f,\vec{k}_i,E)\right\rangle_T^{\text{QCA}} &= \sum_{P_0'}\sum_{P_0\neq P_1} e^{i\vec{q}\cdot\vec{P}_0'}e^{i(\vec{k}_i\cdot\vec{P}_0-\vec{k}_f\cdot\vec{P}_1)}\,\tfrac{1}{2}\left(\langle e_{\vec{P}_0'}e_{\vec{P}_1}\rangle_T\gamma^{-1}\langle e_{\vec{P}_1}e_{\vec{P}_0}\rangle_T+\langle e_{\vec{P}_0'}e_{\vec{P}_0}\rangle_T\gamma^{-1}\langle e_{\vec{P}_0}e_{\vec{P}_1}\rangle_T\right)\cdots+\text{c.c.}\\ &= \sum_{\vec{P}_0'\neq\vec{P}_0\neq\vec{P}_1\neq\vec{P}_0'} e^{i\vec{q}\cdot\vec{P}_0'}e^{i(\vec{k}_i\cdot\vec{P}_0-\vec{k}_f\cdot\vec{P}_1)}\,\tfrac{1}{2}\left(\langle e_{\vec{P}_0'}e_{\vec{P}_1}\rangle_T\gamma^{-1}\langle e_{\vec{P}_1}e_{\vec{P}_0}\rangle_T+\langle e_{\vec{P}_0'}e_{\vec{P}_0}\rangle_T\gamma^{-1}\langle e_{\vec{P}_0}e_{\vec{P}_1}\rangle_T\right)\cdots\\ &\quad+\sum_{\vec{P}_0\neq\vec{P}_1} e^{i\vec{k}_f\cdot(\vec{P}_0-\vec{P}_1)}\,\tfrac{1}{2}\left(\gamma^{-1}\langle e_{\vec{P}_0}e_{\vec{P}_1}\rangle_T^2+\langle e_{\vec{P}_0}e_{\vec{P}_1}\rangle_T\right)\cdots+\sum_{\vec{P}_0\neq\vec{P}_1} e^{i\vec{k}_i\cdot(\vec{P}_0-\vec{P}_1)}\,\tfrac{1}{2}\left(\langle e_{\vec{P}_0}e_{\vec{P}_1}\rangle_T\right.\\ &\quad\left.+\gamma^{-1}\langle e_{\vec{P}_0}e_{\vec{P}_1}\rangle_T^2\right)\cdots+\text{c.c.}\end{aligned} \qquad (72)$$

The dots represent the remaining terms of Eq. (28). Using the fact that $\langle e_{\vec{P}_0}e_{\vec{P}_1}\rangle_T\leq\gamma$, we find

$$1\geq\tfrac{1}{2}\left(1+\gamma^{-1}\langle e_{\vec{P}_0}e_{\vec{P}_1}\rangle_T\right)\geq\tfrac{1}{2}\,. \qquad (73)$$

This relation implies that the clustering terms in Eq. (71) (i.e., the second and third term) are underestimated in the application of the QCA [Eq. (72)]. The two clustering terms of Eqs. (71) and (72) represent the contributions to the cross section of the adsorbate which are of third order in the interaction and of second order in the atomic density of the adsorbate. In a similar way it is possible to separate in all higher-order contributions to the exact as well as the approximate cross section the terms that are of second order in the adatom coverage. It is easily verified that all approximate terms are smaller than the corresponding exact contributions. If we carry out an analogous procedure for the terms of the cross section that are of higher order in the adatom density, it is in principle possible to construct a new perturbation series for the cross section in which the nth correction is given by the difference between the exact and the approximate contributions of order γ^n. The quasicrystalline approximation represents then the first term in this series since it is correct to first order in γ. (This is a consequence of the fact that we use reduced ion-core vertices rather than bare interactions.) In an entirely analogous fashion it is also possible to construct a similar perturbation series for the cross section of the combined substrate-adsorbate system.

At the present moment, all theories of multiple scattering from disordered systems include the contributions to the cross section that contain correlations of higher than second order in γ which are approximated by expressing them in terms of two-site correlations. The factorization of all higher correlation functions is required in order to be able to perform the summations over lattice sites analytically.

The clustering terms, however, appear to be described more accurately by self-consistent theories of multiple scattering from disorder systems than by their non-self-consistent counterparts.[27,49] Improvements of the present approximation by introducing self-consistency are presently underway. Because of the strong inelastic-collision damping, however, we do not expect the self-consistency requirement to be of the same importance as in theories of the electronic structure of binary alloys.[27,33] Moreover, "realistic" models for atomic potentials[3–9] do not result in strong electron-scattering resonances in the energy region that is characteristic for studies of LEED.

In order to incorporate the presence of the substrate in an appropriate fashion, we introduced in Sec. IV C 1 the RQCA. In this description, it is necessary to sum in the multiple-scattering series over all terms representing intermediate dynamical scattering from the substrate. The summation led us to the definition of new intra-adsorbate electron propagators which are renormalized to account for multiple intermediate substrate scattering. The RQCA as applied to the substrate-adsorbate system represents a description of short- and long-range order in the overlayer which is equivalent to that of the QCA applied only to the adsorbate. Thus the RQCA is appropriate also in the low-temperature region. In particular, it reproduces the exact zero-temperature limit of the scattering cross section, as shown in Appendix C.

By further approximating the substrate-overlayer interference terms, we were able to cast the renormalization into a particularly attractive form. In this restricted version of the RQCA, the final expressions for the cross sections are entirely specified in terms of the known substrate-layer-scattering matrices. In contrast to the RQCA, the explicit evaluation of the propagator $g(\vec{P}, E)$ [Eqs. (54b) and (58)] is in this approximation eliminated. Because of the underlying assumptions, however, the restricted RQCA is useful only in the high-temperature region.

Given the fact that the consequences of self-consistency requirements are likely to be minor, it appears that the renormalized quasicrystalline approximation provides an adequate basis for multiple-scattering models of LEED from disordered overlayers. Due to the circumstance that substrate-adsorbate interference contributions to the cross section are of fourth or higher order in the interaction, and because of the absence of long-range order in one-dimensional systems, it appears furthermore that the restricted RQCA suffices for the study of dynamical scattering from one-dimensional overlayers adsorbed on two-dimensional substrates. The numerical consequences of this analysis are examined in the following paper.[50]

ACKNOWLEDGMENTS

The authors are indebted to Dr. R. Bass, Dr. U. Landman, and Dr. Adams for useful discussions.

APPENDIX A: MONOLAYER MULTIPLE-SCATTERING SUMS

In this section we perform the summation of the logarithmic series in the expression for the partially averaged adsorbate scattering amplitude $R^A(\vec{k}_f, \vec{k}_i, E)_{\text{av}}$, given by Eq. (45).

For convenience we define the following abbreviations:

$$a \equiv G_{11}(\vec{k}_f, E)\, b_1(k(E)) \quad , \tag{A1}$$

$$b \equiv G_{11}(\vec{k}_i, E)\, b_1(k(E)) \quad , \tag{A2}$$

$$c \equiv b_1(k(E)) \quad . \tag{A3}$$

$R^A(\vec{k}_f, \vec{k}_i, E)_{\text{av}}$ can then be written as

$$R^A(\vec{k}_f, \vec{k}_i, E)_{\text{av}} = \sum_{\vec{P}} e_{\vec{P}}\, e^{-i\vec{q}\cdot\vec{P}} e^{-i\vec{q}\cdot\vec{d}_1} \times \sum_{LL'} [Y^*(\hat{k}_f)\, Q^A(\vec{k}_f, \vec{k}_i, E)\, Y(\hat{k}_i)]_{LL'} \quad , \tag{A4}$$

with

$$Q^A(\vec{k}_f, \vec{k}_i, E) \equiv c\, [1 + \tfrac{1}{2}(a+b) + \tfrac{1}{3}(a^2+ab+b^2) + \tfrac{1}{4}(a^3+a^2b+ab^2+b^3) + \ldots\,] \quad . \tag{A5}$$

We note first that $a=b$ if $G_{11}(\vec{k}_f, E) = G_{11}(\vec{k}_i, E)$. This is the situation for the substrate beams. In this case, the right-hand side of Eq. (A5) then becomes a geometric series with the result

$$Q^A(\vec{k}_f, \vec{k}_i, E) = \tau_1(\vec{k}_i, E) = \tau_1(\vec{k}_f, E), \quad \vec{k}_{f,\parallel} = \vec{k}_{i,\parallel} + \vec{g} \quad . \tag{A6}$$

In Eq. (A6), $\tau_1(\vec{k}, E)$ is the subplane scattering matrix of the adsorbate. It is defined in analogy to the subplane scattering matrices of the bulk:

$$\tau_1(\vec{k}, E) = b_1(k(E)) + b_1(k(E))\, G_{11}(\vec{k}, E)\, \tau_1(\vec{k}, E) \quad . \tag{A7}$$

For $\vec{k}_{f,\parallel} \neq \vec{k}_{i,\parallel} + \vec{g}$, we rearrange the terms in Eq. (A5) in the following way:

$$\begin{aligned} Q^A(\vec{k}_f, \vec{k}_i, E) &= c(1 + \tfrac{1}{2}a + \tfrac{1}{3}a^2 + \tfrac{1}{4}a^3 + \ldots) + c(\tfrac{1}{2} + \tfrac{1}{3}a + \tfrac{1}{4}a^2 + \ldots) + c(\tfrac{1}{3} + \tfrac{1}{4}a + \ldots) + \ldots \\ &= c\ln(1-a)^{-1}a^{-1} + c\ln(1-a)^{-1}a^{-2}b - ca^{-1}b + c\ln(1-a)^{-1}a^{-3}b^2 - c\,a^{-2}b^2 - \tfrac{1}{2}c\,a^{-1}b^2 + \cdots \\ &= c\ln(1-a)^{-1}\sum_{n=0}^{\infty} a^{-n-1}b^n - c\sum_{n=0}^{\infty} a^{-n-1}b^n \ln(1-b)^{-1} \quad . \end{aligned} \tag{A8a}$$

Instead of grouping together all powers of a, however, we can form a logarithmic series in b. This leads to the result

$$Q^A(\vec{k}_f, \vec{k}_i, E) = c \sum_{n=0}^{\infty} a^n b^{-n-1} \ln(1-b)^{-1}$$
$$- c \ln(1-a)^{-1} \sum_{n=0}^{\infty} a^n b^{-n-1} \quad . \qquad \text{(A8b)}$$

It is evident that only one of the infinite series in Eqs. (A8) is converging.[47] The criterion of convergence determines the choice of either (A8a) or (A8b) as expression for $Q^A(\vec{k}_f, \vec{k}_i, E)$. Substituting the definitions (A1)–(A3) into Eqs. (A8) we obtain

$$Q^A(\vec{k}_f, \vec{k}_i, E) = b_1(k(E)) \{ Q_0^A(\vec{k}_f, \vec{k}_i, E) \ln[b_1^{-1}(k(E))$$
$$\times \tau_1(\vec{k}_i, E)] - \ln[b_1^{-1}(k(E))\tau_1(\vec{k}_f, E)]$$
$$\times Q_0^A(\vec{k}_f, \vec{k}_i, E)\} \quad , \qquad \text{(A9a)}$$

with

$$Q_0^A(\vec{k}_f, \vec{k}_i, E) \equiv \sum_{n=0} [G_{11}(\vec{k}_f, E)\, b_1(k(E))]^n$$
$$\times [G_{11}(\vec{k}_i, E)\, b_1(k(E))]^{-n-1} \qquad \text{(A9b)}$$

or

$$Q_0^A(\vec{k}_f, \vec{k}_i, E) = -\sum_{n=0}^{\infty} [G_{11}(\vec{k}_f, E)\, b_1(k(E))]^{-n-1}$$
$$\times [G_{11}(\vec{k}_i, E)\, b(k(E))]^n \quad , \qquad \text{(A9c)}$$

depending on which series converges. In the s-wave model, the sums in Eqs. (A9b) and (A9c) can be performed because the summands in the series commute. We obtain the simple and suggestive result

$$Q^A(\vec{k}_f, \vec{k}_i, E) = [G_{11}(\vec{k}_i, E) - G_{11}(\vec{k}_f, E)]^{-1}$$
$$\times \ln\left(\frac{\tau_1(\vec{k}_i, E)}{\tau_1(\vec{k}_f, E)}\right) \quad . \qquad \text{(A10)}$$

Equations (A6), (A7), and (A9) specify our general results for the adsorbate scattering amplitude $R^A(\vec{k}_f, \vec{k}_i, E)_{av}$.

APPENDIX B: SATISFACTION OF TIME-REVERSAL INVARIANCE BY SYMMETRIZED APPROXIMATIONS FOR CORRELATION FUNCTIONS

In this Appendix we prove the time-reversal invariance of the partially averaged scattering amplitude, $R(\vec{k}_f, \vec{k}_i, E)_{av}$, given by Eq. (65). In particular, we show that the quantities $A(\vec{k}_f, \vec{k}_i, E)$ and $B(\vec{k}_f, \vec{k}_i, E)$, defined in Eqs. (66) and (67) conserve time-reversal symmetry.

It is useful first to derive some symmetry properties for the electron propagators and the scattering matrices. Using the definitions of the propagators [Eqs. (32), (44), and (56)] together with Eqs. (16) and (18), we easily find the relation

$$G_{\nu\mu}(\vec{k}, E) = G_{\nu\mu}(-\vec{k}, E), \quad \nu, \mu \geq 1 \quad . \qquad \text{(B1)}$$

This implies for the subplane scattering matrices [Eqs. (35) and (47)] the identity

$$\tau_\nu(\vec{k}, E) = \tau_\nu(-\vec{k}, E), \quad \nu \geq 1 \quad . \qquad \text{(B2)}$$

Let us now define the following matrices ($\nu, \mu \geq 2$):

$$T(\vec{k}, E) \equiv \| T_{\nu\mu}(\vec{k}, E) \| \quad , \qquad \text{(B3)}$$

$$\tau(\vec{k}, E) \equiv \| \tau_\nu(\vec{k}, E)\, \delta_{\nu\mu} \| \quad , \qquad \text{(B4)}$$

$$G(\vec{k}, E) \equiv \| G_{\nu\mu}(\vec{k}, E)\, (1 - \delta_{\nu\mu}) \| \quad . \qquad \text{(B5)}$$

The $T_{\nu\mu}(\vec{k}, E)$ are the scattering matrices given by Eq. (36). Denoting the transpose of a matrix by the superscript t and using the relations (B1) and (B2), we can derive a symmetry property for $T(\vec{k}, E)$:

$$T(\vec{k}, E) = [\tau^{-1}(\vec{k}, E) - G(\vec{k}, E)]^{-1}$$
$$= [(\tau^{-1}(\vec{k}, E) - G(-\vec{k}, E))^t]^{-1}$$
$$= T^t(-\vec{k}, E) \quad , \qquad \text{(B6)}$$

i.e.,

$$T_{\nu\mu}(\vec{k}, E) = T_{\nu\mu}(-\vec{k}, E) \quad . \qquad \text{(B7)}$$

We show now the invariance of the quantity $A(\vec{k}_f, \vec{k}_i, E)$. Instead of evaluating the substrate scattering amplitude [Eq. (31)] by summing first over $\vec{P}_0$, then $\vec{P}_1$, etc., it can also be reduced by first summing over $\vec{P}_j$, then $\vec{P}_{j-1}$, and so forth. In this way we derive the relation

$$\sum_{\nu\mu\geq 2} e^{-i\vec{q}\cdot\vec{d}_\nu}\, T_{\nu\mu}(\vec{k}_i, E) = \sum_{\nu\mu\geq 2} e^{-i\vec{q}\cdot\vec{d}_\mu}\, T_{\nu\mu}(\vec{k}_f, E) \quad . \qquad \text{(B8)}$$

We note here that all scattering vertices and electronic propagators become symmetric matrices in the partial-wave representation if one uses an expansion in terms of real spherical harmonics. The time-reversal invariance of the quantity $A(\vec{k}_f, \vec{k}_i, E)$ is then easily shown by using this fact as well as relations (B7) and (B8).

To prove the invariance of the quantity $B(\vec{k}_f, \vec{k}_i, E)$, we note first that $\overline{Q}(\vec{k}_f, \vec{k}_i, E)$ defined in Eqs. (60b)–(60d) is invariant. This is a consequence of Eqs. (B7), (60e) and (60f). We use then the same argument as above together with Eqs. (B1) and (B7).

APPENDIX C: ZERO-TEMPERATURE LIMIT OF CROSS SECTION IN RENORMALIZED QUASICRYSTALLINE APPROXIMATION

We demonstrate in this Appendix that the renormalized quasicrystalline approximation (RQCA) described in Secs. III B and IV C 1 leads in the $T \equiv 0$ limit to the exact expressions for the scattering cross section of the substrate-overlayer system. An important consequence of this feature of the RQCA is the description of dynamical scattering from ordered superlattices adsorbed on periodic substrates in terms of layer-scattering amplitudes[30] without reference to a sublattice formalism.[14]

For $\gamma = \frac{1}{2}$ and repulsive nearest-neighbor interactions, the adatoms tend to occupy alternating lattice sites as the temperature decreases. The pair- and autocorrelation functions reflect this thermal behavior by reducing to the following $T \equiv 0$ limits:

$$\langle e_{\vec{P}_1} e_{\vec{P}_1+\vec{P}_0} \rangle_{T=0} = \gamma \quad (\text{if } \vec{P}_0 = \vec{P}_s)$$

$$= 0 \quad (\text{otherwise}) \quad , \tag{C1}$$

$$\Phi(\vec{q})_{T=0} = \Big|\sum_{\vec{P}_s} e^{-i\vec{q}\cdot\vec{P}_s}\Big|^2 \quad . \tag{C2}$$

The vector $\vec{P}$ designates a lattice site in the overlayer, i.e., $\vec{P} = a(n, m)$, where a denotes the spacing of the square lattice and n, m are integers. The sites of the superlattice are given by $\vec{P}_s$, i.e., $\vec{P}_s \equiv a(n, m)$, with $n+m$ even. We will use this notation throughout this Appendix.

The renormalized intra-adsorbate propagator $\overline{G}(\vec{k}, E)$ [Eqs. (54) and (61)] assumes at $T = 0$ the form

$$\overline{G}(\vec{k}, E)_{T=0} = \sum_{\vec{P}_s \neq 0} e^{i\vec{k}\cdot\vec{P}_s} G(\vec{P}_s, E) + \sum_{\vec{P}_s} e^{i\vec{k}\cdot\vec{P}_s} g(\vec{P}_s, E) \tag{C3a}$$

$$\equiv G_{11}(\vec{k}, E)_{T=0} + g^s(\vec{k}, E) \quad . \tag{C3b}$$

The superscript s indicates that we sum over superlattice sites. The first term in this equation represents (in momentum space) the subplane propagator of the superlattice. The sum in the second term can be performed by using the integral representation, Eq. (58), for $g(\vec{P}, E)$:

$$g^s(\vec{k}, E) = \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} d^2k' \, g(\vec{k}', E) \sum_{\vec{P}_s} e^{i(\vec{k}-\vec{k}')\cdot\vec{P}_s}$$

$$= \tfrac{1}{2}[g(\vec{k}, E) + \vec{g}(\vec{k} + g_1, E)] \quad , \tag{C4}$$

where $\vec{g}_1 \equiv (\pi/a)\,(1, 1)$ denotes the new reciprocal-lattice vector of the superlattice. The above result clearly indicates that the indirect intra-adsorbate scattering via the substrate also contributes to the overlayer beams. The renormalized subplane scattering amplitude of the adsorbate, Eq. (62), may then be written as

$$\overline{\tau}_1(\vec{k}, E)_{T=0} = [b_1^{-1}(k(E)) - G_{11}(\vec{k}, E)_{T=0}$$

$$- \tfrac{1}{2}(g(\vec{k}, E) + g(\vec{k} + \vec{g}_1, E))]^{-1} \quad . \tag{C5}$$

Moreover, from Eq. (C3) we obtain

$$\overline{G}(\vec{k} + \vec{g}_1, E)_{T=0} = \overline{G}(\vec{k}, E)_{T=0} \quad . \tag{C6}$$

Since at $T = 0$ only substrate and superlattice beams exist (see below), we have $\vec{k}_{f,\parallel} = \vec{k}_{i,\parallel} + \vec{g}_1$. Equation (C6) then implies that the renormalized scattering amplitude, Eq. (C5), obeys the relation

$$\overline{\tau}_1(\vec{k}_f, E)_{T=0} = \overline{\tau}_1(\vec{k}_i, E)_{T=0} \quad . \tag{C7}$$

Using Eqs. (68), we obtain for the dynamical scattering cross section of the adsorbate-substrate system at $T = 0$ the expression

$$\left\langle \frac{d\sigma}{d\Omega}(\vec{k}_f, \vec{k}_i, E) \right\rangle_{T=0}^{\text{RQCA}}$$

$$= \left(\frac{m}{2\pi\hbar^2}\right)^2 \left(\Big|\sum_{\vec{P}} e^{-i\vec{q}\cdot\vec{P}}\Big|^2 |A(\vec{k}_f, \vec{k}_i, E)|^2 \right.$$

$$+ \gamma \Big|\sum_{\vec{P}} e^{-i\vec{q}\cdot\vec{P}}\Big|^2 2\,\mathrm{Re}[A^*(\vec{k}_f, \vec{k}_i, E) B(\vec{k}_f, \vec{k}_i, E)_{T=0}]$$

$$\left. + \Big|\sum_{\vec{P}_s} e^{-i\vec{q}\cdot\vec{P}_s}\Big|^2 |B(\vec{k}_f, \vec{k}_i, E)_{T=0}|^2 \right) \quad , \tag{C8}$$

with

$$B(\vec{k}_f, \vec{k}_i, E)_{T=0} = \sum_{LL'} \Bigg[Y^*(\hat{k}_f) e^{-i\vec{q}\cdot\vec{d}_1}$$

$$\times \left(1 + \sum_{\nu\mu\geq 2} T_{\nu\mu}(\vec{k}_f, E)\right) \overline{\tau}_1(\vec{k}_i, E)_{T=0}$$

$$\times \left(1 + \sum_{\nu\mu\geq 2} G_{1\nu}(\vec{k}_i, E) T_{\nu\mu}(\vec{k}_i, E)\right)$$

$$\times Y(\hat{k}_i) \Bigg]_{LL'} \quad , \tag{C9}$$

where $A(\vec{k}_f, \vec{k}_i, E)$ is defined in Eq. (66). In Eq. (C8) we have used Eq. (C2). By employing now the identity[51]

$$\sum_{\vec{P}} e^{i\vec{q}\cdot\vec{P}} \sum_{\vec{P}_s} e^{-i\vec{q}\cdot\vec{P}_s} \equiv \frac{1}{2} \Big|\sum_{\vec{P}} e^{-i\vec{q}\cdot\vec{P}}\Big|^2 \tag{C10}$$

and using the definition of the substrate scattering amplitude, $R^B(\vec{k}_f, \vec{k}_i, E)$ [Eq. (37)] the zero-temperature limit of the cross section [Eq. (C8)] may finally be written as

$$\left\langle \frac{d\sigma}{d\Omega}(\vec{k}_f, \vec{k}_i, E) \right\rangle_{T=0}^{\text{RQCA}} = \left(\frac{m}{2\pi\hbar^2}\right)^2 \Big| R^B(\vec{k}_f, \vec{k}_i, E)$$

$$+ \sum_{\vec{P}_s} e^{-i\vec{q}\cdot\vec{P}_s} B(\vec{k}_f, \vec{k}_i, E)_{T=0} \Big|^2 . \tag{C11}$$

The interesting feature of this limit is that the quantity $B(\vec{k}_f, \vec{k}_i, E)_{T=0}$ depends only, via Eqs. (C4), (C5), (C9), and (57), on the intra- and interlayer scattering matrices of the bulk. Furthermore, the above expression reflects, via Eqs. (C5) and (C9), in a very explicit manner the mutual influence of the substrate and overlayer beams upon each other.

It remains to be verified that the expression given by Eq. (C11) represents the exact dynamical cross section for scattering from the ordered superlattice absorbed on the periodic substrate. In order to prove this identity, we utilize the so-called sublattice formulation,[14] in which each substrate layer is formally decomposed into two sublattices both having the geometry of the superlattice. Writing an arbitrary lattice vector as $\vec{R}=\vec{P}_s+\vec{D}_\nu$, where $\vec{D}_\nu$ denotes the position of the vector $\vec{P}_s\equiv 0$ in sublattice ν and $\vec{P}_s$ specifies the sites within this sublattice, we are able to evaluate the quantity $g^s(\vec{k},E)$ in Eq. (C3) [see Eq. (54b)]:

$$\begin{aligned} g^s(\vec{k},E) = & \sum_{\nu\neq 1} G^s_{1\nu}(\vec{k},E)\, b_\nu(k(E))\, G^s_{\nu 1}(\vec{k},E) \\ & + \sum_{\nu,\mu\neq 1} G^s_{1\nu}(\vec{k},E)\, b_\nu(k(E))\, G^s_{\nu\mu}(\vec{k},E) \\ & \times b_\mu(k(E))\, G^s_{\mu 1}(\vec{k},E) + \dots\ , \end{aligned} \tag{C12}$$

in which the $G^s_{\nu\mu}(\vec{k},E)$, $\nu,\mu\geqslant 1$, represent the intra- and intersublattice electron propagators (the adsorbed superlattice has the indes $\nu=1$):

$$G^s_{\nu\mu}(\vec{k},E) \equiv \sum_{\vec{P}_s\neq 0} e^{i\vec{k}\cdot\vec{P}_s} G(\vec{P}_s,E) \quad (\nu=\mu\geqslant 1) \tag{C13a}$$

$$\begin{aligned} & \equiv \sum_{\vec{P}_s} \exp[i\vec{k}\cdot(\vec{P}_s+\vec{D}_\mu-\vec{D}_\nu)] \\ & \times G(\vec{P}_s+\vec{D}_\mu-\vec{D}_\nu,E) \quad (\nu\neq\mu;\ \ \nu,\mu\geqslant 1). \end{aligned} \tag{C13b}$$

In analogy to Eq. (57), expression (C12) for $g^s(\vec{k},E)$ may be written as

$$g^s(\vec{k},E) = \sum_{\nu\mu\geqslant 2} G^s_{1\nu}(\vec{k},E)\, T^s_{\nu\mu}(\vec{k},E)\, G^s_{\mu 1}(\vec{k},E)\ . \tag{C14}$$

The $T^s_{\nu\mu}(\vec{k},E)$ are the intersublattice scattering matrices of the bulk. Using Eq. (C14) and the fact that $G_{11}(\vec{k},E)_{T=0}\equiv G^s_{11}(\vec{k},E)$, [see Eqs. (C3) and (C13), we notice that the quantity $\overline{G}(\vec{k},E)_{T=0}$ of Eq. (C3) represents the propagation within the superlattice either directly or via multiple scattering from the substrate sublattices. Consequently, $\overline{\tau}_1(\vec{k},E)_{T=0}$ in Eq. (C5) represents scattering processes that start and end in the superlattice but may involve dynamical scattering from the sublattices of the bulk. Finally, by using the definitions (36) and (56), we easily find the relations

$$\sum_{\nu\mu\geq 2} T_{\nu\mu}(\vec{k}_f,E)\, G_{\mu 1}(\vec{k}_f,E) \equiv \sum_{\nu\mu\geq 2} T^s_{\nu\mu}(\vec{k}_f,E)\, G^s_{\mu 1}(\vec{k}_f,E)\ , \tag{C15a}$$

$$\sum_{\nu\mu\geq 2} G_{1\nu}(\vec{k}_i,E)\, T_{\nu\mu}(\vec{k}_i,E) \equiv \sum_{\nu\mu\geq 2} G^s_{1\nu}(\vec{k}_i,E)\, T^s_{\nu\mu}(\vec{k}_i,E) \tag{C15b}$$

Thus, we have been able to express all contributions to the quantity $B(\vec{k}_f,\vec{k}_i,E)_{T=0}$ [Eq. (C9)] in the exact two-sublattice formulation. This derivation proves that the cross section given by Eq. (C1) is indeed identical to the exact cross section for the ordered substrate-superlattice system.

We conclude this Appendix by pointing out that the above result can be easily generalized. The dynamical scattering cross section for a superlattice of arbitrary geometry adsorbed on a periodic substrate is obtained from the expression given by Eq. (C11) through the following modification: The sums over lattice sites in the second term of Eq. (C11) and in both terms of Eq. (C3a) have to be taken over the new site vectors of the superlattice. The sum in the second term of Eq. (C11) then causes the occurrence of the new superlattice beams. The first term of Eq. (C3a) represents the new intrasuperlattice propagator. The sum in the second term of Eq. (C3a) can be performed as in Eq. (C4), leading to the expression

$$g^s(\vec{k},E) = \frac{1}{s+1}\left(g(\vec{k},E) + \sum_{i=1}^{s} g(\vec{k}+\vec{g}_i,E)\right)\ , \tag{C16}$$

where s is the number of the new nonequivalent superlattice beams in the first shell and the $\vec{g}_i$, $i=1,\dots,s$, are the corresponding reciprocal-lattice vectors.

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[50] The third paper of this series is devoted to the application of our analysis to two-dimensional models of adsorbed overlayers on periodic substrates exhibiting both long- and short-range order.

[51] This can be shown by a similar method to that of Kittel [*Quantum Theory of Solids* (Wiley, New York, 1967), p. 374].