Diffuse LEED theory from surfaces partially covered with molecules. I. Calculation of the transition matrix of a molecule

Diffuse LEED theory from surfaces partially covered with molecules: I. Calculation of the transition matrix of a molecule

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Abstract. Diffuse backscattering of electrons at a single crystal surface is often due to the adsorption of atoms or molecules whose presence breaks the translational symmetry of the substrate surface. Two different approaches to the diffuse LEED problem have been given. The first, due to Saldin and Pendry, considers only a single molecule adsorbed at the surface. The second, due to the present authors, considers a partially ordered overlayer of molecules and takes up the statistical aspect of the diffuse LEED problem. The first aim of this paper is to compare both approaches. In the case of adsorbates randomly and sparsely distributed at the surface, we show that they are equivalent. However, each of them uses a different concept for the *renormalized* t-matrix of the adsorbate.

The renormalized t-matrix used in the present approach depends on the t-matrix of the molecule alone and on the scattering amplitude of the bare substrate. The problem of the determination of the latter quantity has already been treated: LEED theories have been published and many LEED computer programs are now available. Paradoxically, the similar problem for a molecule, that is to say for a cluster with a small number of atoms, has not been so well studied as the previous one concerning an infinity of atoms. The second aim of this paper is to provide a theory of multiple scattering of electrons from a molecule, from which we can derive a suitable expression for the t-matrix that one can easily use in the diffuse LEED theory. Application to the simple case of the CO molecule is examined here.

1. Introduction

The diffuse LEED theory aims to provide an expression of the intensity per unit of solid angle of electrons which are elastically backscattered from a partially ordered crystal surface, in the non-Bragg directions. On the basis of this expression, a comparison of measured and calculated diffuse intensities can be carried out to yield a set of optimal parameters characterizing the nature and the location of atoms at the surface.

Partial order at the surface is due to the fact that atoms or groups of atoms located in the first atomic surface layers are not perfectly arranged to form a 2D regular lattice. The breaking of the 2D translational symmetry of the substrate can be due to the presence of atoms or molecules sparsely adsorbed at the surface (Pendry and Saldin 1984) or to

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the presence of geometrical defects such as vacancies (Rous and Pendry 1985), steps ·(Rous and Pendry 1986), displacements of substrate atoms induced by chemisorption (Rous *et al* 1986) and so on. In previous papers (Le Bossé *et al* 1988, 1990) we examined the first case where disorder has a chemical origin. We have shown that the diffuse LEED intensity can be expressed in terms of the Fourier transform of the site occupancy pair correlation functions and of the *renormalized* **t**-matrices of molecules adsorbed at the surface. Here, *renormalized* means that certain multiple scattering processes between admolecules and substrate are taken into account, namely those involving one scattering event at a molecule. The renormalized **t**-matrix of a molecule adsorbed at a site of type p is given by (Le Bossé *et al* 1988 equation (4.14), 1990 equation (3a)):

$$\mathbf{K}_1(p, k_f^- \leftarrow k_i^+) = \mathbf{t}_1(p, k_f^- \leftarrow k_i^+) + \sum_{\{g\}} \mathbf{t}_1(p, k_f^- \leftarrow k_{ig}^-) \mathbf{M}_s(k_{ig}^- \leftarrow k_i^+)$$

$$+ \sum_{\{g\}} \frac{K_{f\perp}}{K_{fg\perp}} \mathbf{M}_s(k_f^- \leftarrow k_{fg}^+) \mathbf{t}_1(p, k_{fg}^+ \leftarrow k_i^+)$$

$$+ \sum_{\{g_1\}} \sum_{\{g_2\}} \frac{K_{f\perp}}{K_{fg_2\perp}} \mathbf{M}_s(k_f^- \leftarrow k_{fg_2}^+) \mathbf{t}_1(p, k_{fg_2}^+ \leftarrow k_{ig_1}^-) \mathbf{M}_s(k_{ig_1}^- \leftarrow k_i^+). \tag{1}$$

In this expression, the wave vectors are defined by

$$K_\perp = \sqrt{E - V_{opt} - \|k_\|\|^2} \tag{2a}$$

$$K_{g\perp} = \sqrt{E - V_{opt} - \|k_\| + g\|^2} \tag{2b}$$

$$k_g^\mp = k_\| + g \mp K_{g\perp} \hat{z}. \tag{2c}$$

In equation $(2c)$, $\hat{z}$ is the unit vector in the direction of the z axis. So, as the substrate lies in the region $z > 0$, k_g^+ is a wave vector oriented from the vacuum to the substrate. Equations $(2a)$, $(2b)$ and $(2c)$ implicitly assume that the molecular scattering potential due to ion cores is added to a constant potential V_{opt} due to the conduction or valence electrons of the adsorbate–substrate system. Labels f and i in equation (1) denote the final and initial states respectively, and label 1 in $\mathbf{t}_1$ and K_1 refers to the reference site of the surface taken as the origin. The label p denotes the kind of site considered; for instance, $p = 1$ and $p = p_{max} = 2$ could denote on-top and hollow sites respectively if both kinds of chemisorption site are occupied. The determination of K_1 requires knowledge of:

(i) the transition matrix $\mathbf{t}_1(p)$ of each isolated adsorbate p;

(ii) the scattering matrices $\mathbf{M}_s$ of the substrate for wave vectors parallel to the surface in the direction of the electron gun $(k_{i\|})$ and in the direction of the electron detector $(k_{f\|})$.

Equation (1) is derived from a *statistical* approach to the diffuse LEED problem (Le Bossé *et al* 1988). With this approach, a large number of molecules, which can occupy one or several kinds of chemisorption sites, are considered. It turns out to be convenient to separate the total scattered wave associated with a given configuration of the overlayer into its average over a statistical ensemble of configurations and its fluctuation from this average. We have shown that two approximations are needed to get a tractable expression for the diffuse intensities in terms of K_1:

(i) the total wave function scattered at the adsorbate–substrate system is approximated by a first-order expansion in the fluctuations of the wave function;

(ii) a part of the wave illuminating a scatterer i, is emitted from the scatterers other than i; so this wave is approximated by its statistical average (this is nothing other than a molecular field approximation).

In the particular case where there is only one kind of chemisorption site and where the occupied sites are randomly and sparsely distributed at the surface, the expression for the diffuse LEED intensity reduces to the product of the square modulus of K_1 by a factor proportional to the surface coverage in molecules (Le Bossé *et al* 1988).

Another approach (Pendry and Saldin 1984, Saldin and Pendry 1986, 1987) consists of considering only one molecule adsorbed at a perfect infinite single crystal surface. In this way, the statistical aspect of the diffuse LEED probem has been totally ignored. In the course of this approach, these authors are led to define a renormalized **t**-matrix of the molecule:

$$\tau = \mathbf{T}_M(\mathbf{1} - \mathbf{ST}_M)^{-1}. \tag{3}$$

In this expression, $\mathbf{T}_M$ is the molecular **t**-matrix denoted here by $\mathbf{t}_1$ and $\mathbf{S}$ is the reflection matrix of a cluster of substrate atoms which is related to the scattering matrix $\mathbf{M}_s$ of the substrate in equation (1).

In section 2, we discuss the present work in relation to the work of Saldin and Pendry. However, we can *a priori* assert that $\mathbf{K}_1$ and τ cannot be identical for the following reason. The calculation of Saldin and Pendry (henceforth SP) is split into three steps (Pendry and Saldin 1984): steps 1 and 3 take account of all multiple-scattering events which either begin or end with a multiple-scattering event at the bare substrate and step 2 takes into account all the other scattering events, that is to say those which begin and end with a single multiple-scattering event at the molecule. The SP renormalized **t**-matrix only refers to processes included in step 2. On the other hand, we carry out a global calculation and consequently our definition of the renormalized **t**-matrix includes all processes of steps 1 to 3. Hence our renormalized **t**-matrix cannot have the same meaning as the one introduced by Saldin and Pendry.

Equation (1) of the renormalized **t**-matrix of the molecule can be calculated from the **t**-matrix $\mathbf{t}_1$ of the single molecule and the scattering matrix $\mathbf{M}_s$ of the bare substrate. Expressions for the scattering matrix $\mathbf{M}_s$ of a semi-infinite single crystal can be found in a lot of reference books (Pendry 1974, Van Hove and Tong 1979, Marcus and Jonas 1984). In the case where the adsorbates are atoms, the **t**-matrix is related to their phase-shifts by a standard expression which can be found in most classical quantum mechanics books (see equation (20) of section 3). On the other hand, it is difficult to find in the literature a sharply stated expression of the molecular **t**-matrix that we could use straightforwardly in the diffuse LEED theory previously presented (Le Bossé *et al* 1988, 1990). So, applications for the case of molecular chemisorption require that we develop a theory of multiple scattering inside a molecule, leading to an accurate expression for the molecular transition matrix.

In section 3, such an expression is given. Use of this expression requires that we know the location in space and all the non-negligible phase-shifts at a given energy of each atom of the molecule. In section 4, a short numerical application is carried out for the simple case of the CO molecule with the geometrical parameters determined in the case of adsorption on a Pt(111) single crystal surface. This paper is followed by a second one containing a diffuse LEED study of the Pt(111) surface partially covered with CO molecules.

2. Statistical and single-adsorbed-molecule approaches of the diffuse LEED problem

The statistical approach to the diffuse LEED problem (Le Bossé *et al* 1988) is too complicated to be described clearly here in a few words. However, it is possible to provide a new and very simple approach to this problem presenting a great similarity to the single-adsorbed-molecule approach due to SP. So, thanks to this similarity, both approaches can be compared. Moreover, it will be seen that this new approach and the statistical approach rigorously lead to the same concept of the renormalized **t**-matrix. However, these approaches cannot be equivalent in that the new approach does not include the statistical aspect of the diffuse LEED problem. They are equivalent only when the molecules are randomly and sparsely distributed at one kind of chemisorption site. A description of this new approach only needs to use two standard results given in any reference book about scattering theory:

(i) the Lipmann–Schwinger equation:

$$|\psi\rangle = |\phi\rangle + G_0^+(V_S + V_1)|\psi\rangle \tag{4}$$

(ii) the **t**-matrix definition:

$$(V_S + V_1)|\psi\rangle = \mathbf{T}_{S+1}|\phi\rangle. \tag{5}$$

$|\phi\rangle$ denotes the quantum state of the free incident electron and $|\psi\rangle$ is that of the scattered electron. V_S and V_1 are the substrate and adsorbate potentials and thus $V_S + V_1$ and $\mathbf{T}_{S+1}$ are the potential and the **t**-matrix of the adsorbate–substrate system respectively. G_0^+ is the retarded Green function of a free electron of kinetic energy E moving in a constant potential V_{opt}. Our aim is to find $|\psi\rangle$ by solving equation (4). We proceed as follows. We define $|\varphi_1\rangle$ and $|\varphi_S\rangle$ as the effective incident waves which illuminate the adsorbate and the substrate respectively:

$$|\varphi_1\rangle = |\phi\rangle + G_0^+ V_S|\psi\rangle \tag{6a}$$

$$|\varphi_S\rangle = |\phi\rangle + G_0^+ V_1|\psi\rangle. \tag{6b}$$

Now, there are two ways of writing the total scattered wave $|\psi\rangle$:

$$|\psi\rangle = |\varphi_1\rangle + G_0^+ V_1|\psi\rangle \tag{7a}$$

$$|\psi\rangle = |\varphi_S\rangle + G_0^+ V_S|\psi\rangle. \tag{7b}$$

Adsorbate and substrate **t**-matrices are straightforwardly obtained from the definition (5):

$$V_1|\psi\rangle = \mathbf{t}_1 |\varphi_1\rangle \tag{8a}$$

$$V_S|\psi\rangle = \mathbf{t}_S |\varphi_S\rangle. \tag{8b}$$

Then, equations (6) and (7) can be rewritten in the form

$$|\varphi_1\rangle = |\phi\rangle + G_0^+ \mathbf{t}_S|\varphi_S\rangle \tag{9a}$$

$$|\varphi_S\rangle = |\phi\rangle + G_0^+ \mathbf{t}_1|\varphi_1\rangle \tag{9b}$$

$$|\psi\rangle = (\mathbf{1} + G_0^+ \mathbf{t}_1)|\varphi_1\rangle \tag{9c}$$

$$|\psi\rangle = (\mathbf{1} + G_0^+ \mathbf{t}_S)|\varphi_S\rangle. \tag{9d}$$

It is very convenient to give a kinematic form to the total transition matrix $\mathbf{T}_{S+1}$, that is

$$\mathbf{T}_{S+1} = \mathbf{t}_S^* + \mathbf{t}_1^* \tag{10}$$

in which $\mathbf{t}_S^*$ and $\mathbf{t}_1^*$ are the substrate and adsorbate *effective* (and not renormalized) **t**-matrices respectively. So, using equations (5), (9) and (10), it can be straightforwardly shown that

$$\mathbf{t}_S^* = \mathbf{t}_S + \mathbf{t}_S G_0^+ \mathbf{t}_1^* \tag{11a}$$

$$\mathbf{t}_1^* = \mathbf{t}_1 + \mathbf{t}_1 G_0^+ \mathbf{t}_S^*. \tag{11b}$$

From equations (4), (5), (10) and (11), the total wave function is expressed in terms of the **t**-matrix of the molecule alone $\mathbf{t}_1$; the **t**-matrix of the substrate alone $\mathbf{t}_S$; and the effective **t**-matrix of the substrate $\mathbf{t}_S^*$. So we obtain

$$|\psi\rangle = |\phi\rangle + G_0^+ \mathbf{t}_S|\phi\rangle + G_0^+ \mathbf{t}_1|\phi\rangle + G_0^+ \mathbf{t}_S G_0^+ \mathbf{t}_1|\phi\rangle + G_0^+ \mathbf{t}_1 G_0^+ \mathbf{t}_S^*|\phi\rangle$$

$$+ G_0^+ \mathbf{t}_S G_0^+ \mathbf{t}_1 G_0^+ \mathbf{t}_S^*|\phi\rangle. \tag{12}$$

Let us point out that the physical meaning of $G_0^+ \mathbf{t}|\phi\rangle$ is more obvious than that of the **t**-matrix **t** because if $|\phi\rangle$ is the primary incident beam, then $G_0^+ \mathbf{t}|\phi\rangle$ is the scattered wave and $G_0^+ \mathbf{t}$ is the scattering amplitude matrix. So, equation (12) can be easily interpreted.

The two first terms represent the total LEED wave $|\psi_{\text{LEED}}\rangle$ because $G_0^+ \mathbf{t}_S$ is the scattering amplitude matrix of the substrate alone, for which 2D translational symmetry exists. As a consequence, the remaining terms denoted by $|\psi_{\text{DLEED}}\rangle$ represent the diffuse LEED wave which can be written in the form

$$|\psi_{\text{DLEED}}\rangle = G_0^+ K_1|\phi\rangle. \tag{13}$$

By comparing equations (12) and (13), we obtain the renormalized transition matrix of the molecule:

$$K_1 = \mathbf{t}_1 + \mathbf{t}_S G_0^+ \mathbf{t}_1 + \mathbf{t}_1 G_0^+ \mathbf{t}_S^* + \mathbf{t}_S G_0^+ \mathbf{t}_1 G_0^+ \mathbf{t}_S^*. \tag{14}$$

Let us remark that this expression, which is very similar to equation (1), is *exact*. If we replace $\mathbf{t}_S^*$ with $\mathbf{t}_S$ in equation (14) it is easy to show that the representation of the operator K_1 in the basis set of the plane waves exactly coincides with equation (1). From that point of view, statistical and single-adsorbed-molecule approaches are in perfect agreement. However, there are two reasons that they cannot lead to the same expression for the diffuse LEED intensity per unit of solid angle. Firstly, the average distance between admolecules is not generally large enough to consider them in isolation. Secondly, they are not randomly distributed at the surface and consequently the waves scattered from the admolecules do not have a random phase. So, interferences between these waves have to be taken into account via a structure factor (Le Bossé *et al* 1988). Finally, the two approaches are equivalent only in the particular case where the admolecules are randomly and sparsely distributed at the surface. Let us recall that we can get equation (1) from the statistical approach only if we assume that the fluctuations of the scattered waves from their average are negligible (Le Bossé *et al* 1988). On the other hand, it is shown here that the single-adsorbed-molecule approach leads to equation (1) when we neglect the relaxation of the substrate **t**-matrix induced by the presence of the molecule ($\mathbf{t}_S^* \simeq \mathbf{t}_S$).

To make the subsequent developments clearer, the physical meanings of the four terms in equation (14) have to be examined. It is important to note that there are three kinds of diffuse multiple-scattering event:

(i) those which are terminated with a single-scattering event at the molecule (first and third terms of equation (14)). For these terms, a left-hand factorization of the t-matrix $\mathbf{t}_1$ can be achieved;

(ii) those which begin with a single-scattering event at the molecule (first and second terms of equation (14)). for these terms, a right-hand factorization of $\mathbf{t}_1$ can be achieved;

(iii) the fourth term of equation (14) for which one can do neither left-hand nor right-hand factorization of $\mathbf{t}_1$.

Let us now come back to equation (3) of SP. All the multiple-scattering events involved in this expression are terminated with a single-scattering event at the molecule because of the left-hand factorization of $\mathbf{T}_M$. So equation (3) does not take into account all the multiple-scattering events which are terminated with a scattering event at the bare substrate. Moreover, if we expand equation (3) in a power series in $\mathbf{ST}_M$, it appears that we can do a right-hand factorization of $\mathbf{T}_M$. Consequently, equation (3) does not take into account any multiple-scattering event which begins with a scattering at the bare substrate. Note that such a limitation could be envisaged in the EXAFS, XANES and ELNES problems in which the emission of a photoelectron from a molecule is necessarily the first event which participates in any multiple-scattering process.

Let us now examine how to derive equation (3) of SP from our result. Firstly, we have to remove all terms associated with multiple-scattering events terminated by a reflection at the bare substrate, because they are already taken into account in step 3 of the SP calculation. Then equation (14) reduces to

$$\mathbf{K}_1 = \mathbf{t}_1 + \mathbf{t}_1 G_0^+ \mathbf{t}_S^* = \mathbf{t}_1^*. \tag{15a}$$

This amounts to assuming that the effective and renormalized t-matrices of the molecule are identical. Secondly, we have to remove all the terms associated with multiple-scattering events which begin with a reflection at the bare substrate, because they have already been taken into account in step 1 of the SP calculation. This condition necessitates the replacement of (11a) by

$$\mathbf{t}_S^* = \mathbf{t}_S G_0^+ \mathbf{t}_1^*. \tag{15b}$$

Then, from equations (15a), (15b) and (11b), we can straightforwardly show that $\mathbf{K}_1$ becomes

$$\mathbf{K}_1 = \mathbf{t}_1 [1 - (G_0^+ \mathbf{t}_S)(G_0^+ \mathbf{t}_1)]^{-1} \tag{15c}$$

which is rigorously equivalent to equation (3). So, it is clear that the renormalized t-matrix introduced in the statistical approach to the diffuse LEED problem (Le Bossé *et al* 1988, 1990), and rediscovered here by another approach, is totally different to the renormalized t-matrix of SP.

3. Multiple scattering from a molecule

3.1. Basic definitions

Let us consider a molecule with N_a atoms. The atom α of this molecule is characterized by

(i) the vector r_α which defines its location,

(ii) all its non-negligible phase shifts δ_l^α $(l = 0, 1, \ldots, l_\alpha)$.

We assume that this molecule is immersed in a homogeneous medium with a potential V_{opt}. The characterization of the scattering properties of each atom by phase shifts implicitly requires the use of their ion core potential described by a muffin-tin model. For convenience, the origin of space will be chosen at the centre of the smallest sphere of radius R_m including all the atomic muffin-tin spheres. Let us call $V(r)$ the molecular scattering potential:

$$V(r) = \sum_{\alpha=1}^{N_a} \mathcal{V}_\alpha(r - r_\alpha). \tag{16}$$

In this expression, $\mathcal{V}_\alpha(r)$ is the scattering potential of atom α located at the origin of space. If $r = |r| > R_m$, then the molecular potential $V(r)$ cancels as in the usual muffin-tin model.

Let us now consider the quantum state $|\phi\rangle$ of the incident electron and the quantum state $|\psi\rangle$ of the electron scattered at atom α. The scattering potential $\mathcal{V}_\alpha(r_\alpha)$ of this atom is related to its t-matrix $\mathbf{t}_\alpha(r_\alpha)$ by the relation

$$\mathcal{V}_\alpha(r_\alpha)|\Psi\rangle = \mathbf{t}_\alpha(r_\alpha)|\phi\rangle. \tag{17}$$

The t-matrix of the molecule is given by

$$\mathbf{T}_m = \sum_{\alpha=1}^{N_a} \mathbf{t}_\alpha^*(r_1, \ldots, r_\alpha, \ldots r_N) \tag{18}$$

in which the effective transition matrix $\mathbf{t}_\alpha^*(r_1, \ldots, r_\alpha, \ldots r_{N_a})$ provides the amplitude of the wave scattered at atom α in the presence of the other atoms of the molecule. These effective transition matrices are self-consistent solutions of the N_a multiple-scattering equations:

$$\mathbf{t}_\alpha^*(r_\alpha) = \mathbf{t}_\alpha(r_\alpha) + \mathbf{t}_\alpha(r_\alpha) \sum_{\substack{\beta=1 \\ \beta \neq \alpha}}^{N_a} G_0^+(E - V_{opt})\mathbf{t}_\beta^*(r_\beta). \tag{19}$$

In the above equation, $G_0^+(E - V_{opt})$ is the retarded Green function for a free electron of kinetic energy E moving in a constant potential V_{opt}. Let us note that the dependence of $\mathbf{t}_\alpha^*$ on vectors $r_\mu \neq r_\alpha$ has been intentionally omitted; in this way, we get a closely packed form of the multiple-scattering equations (19).

In the angular-momentum representation, the operator $\mathbf{t}_\alpha(0)$ associated with atom α centred at the origin is represented by the diagonal matrix $\mathcal{T}_\alpha(0)$ whose elements are given by

$$\mathcal{T}_\alpha(0, lm, l'm') = [(1 - e^{2i\delta_l^\alpha})/2iK] \, \delta_{ll'} \, \delta_{mm'} \tag{20}$$

in which $K = \sqrt{E - V_{opt}}$. In practice, $\mathcal{T}_\alpha(0)$ is a square matrix of order $(l_\alpha + 1)^2$ (l_α is the maximum value of l for which the phase shifts δ_l^α are not small enough to be neglected). Unfortunately, atoms α are not centred at the origin: equation (19) clearly shows that operators $\mathbf{t}_\alpha^*(r_\alpha)$ and $\mathbf{t}_\alpha(r_\alpha)$ associated with atoms α are centred at the molecular sites. Thus, in the basis set of spherical waves centred at the origin, these

operators cannot be represented by a diagonal matrix. At this stage, it is convenient to introduce the translation operators $F(r_\alpha)$ from origin to sites α defined by

$$F(r_\alpha)|r\rangle = |r - r_\alpha\rangle. \tag{21}$$

By using equation (21) in the obvious identity:

$$\mathbf{t}_\alpha(r_\alpha, r, r') = \mathbf{t}_\alpha(0, r - r_\alpha, r' - r_\alpha)$$

we obtain:

$$\mathbf{t}_\alpha(r_\alpha) = F(-r_\alpha)\mathbf{t}_\alpha(0)F(r_\alpha). \tag{22}$$

In a similar way, we can show that

$$\mathbf{t}_\alpha^*(r_1, \ldots, r_\alpha, \ldots r_{N_a}) = F(-r_\alpha)\mathbf{t}_\alpha^*(r_1 - r_\alpha, \ldots, 0, \ldots r_{N_a} - r_\alpha)F(r_\alpha). \tag{23}$$

Henceforth, $\mathbf{t}_\alpha^*(r_1 - r_\alpha, \ldots, 0, \ldots r_{N_a} - r_\alpha)$ will be denoted by $\mathbf{t}_\alpha^*(0)$. In this section, we have to find a matrix representation of operators $F(r_\alpha)$, $\mathbf{t}_\alpha(r_\alpha)$, $G_0^+(E - V_{opt})$ and $\mathbf{t}_\alpha^*(r_\alpha)$ in the basis set of the free spherical waves. Before achieving this work, let us first write down the essential mathematical results which have to be known for the understanding of the subsequent developments.

3.2. Mathematical background

First, let us recall that the free spherical waves are defined by

$$\Psi_{Klm}(r) = (\mathrm{i})^l j_l(kr) Y_{lm}(r/r). \tag{24}$$

The expression for $G_0^+(E - V_{opt})$ in the angular momentum representation also requires the use of the free spherical outgoing wave functions:

$$\chi_{Klm}(r) = (\mathrm{i})^{l+1} h_l^{(1)}(Kr) Y_{lm}(r/r). \tag{25}$$

Definitions of all the special functions occurring in equations (24) and (25) can be found in standard texts (Pendry 1974, Marcus and Jonas 1984). All subsequent developments are mainly based upon the use of the well known translation theorems (Marcus and Jonas 1984):

$$\psi_{Kl_1m_1}(r_1 + r_2) = 4\pi(-1)^{m_1} \sum_{l_2m_2}\sum_{l_3m_3} C(l_1m_1, l_2 - m_2, l_3 - m_3)$$

$$\times \psi_{Kl_2m_2}(r_1)\psi_{Kl_3m_3}(r_2) \tag{26a}$$

$$\chi_{Kl_1m_1}(r_1 + r_2) = 4\pi(-1)^{m_1} \sum_{l_2m_2}\sum_{l_3m_3} C(l_1m_1, l_2 - m_2, l_3 - m_3)$$

$$\times \psi_{Kl_2m_2}(r_1)\chi_{Kl_3m_3}(r_2). \tag{26b}$$

The last expression is only valid if $r_1 < r_2$ and in both expressions $C(l_1m_1, l_2m_2, l_3m_3)$ are Gaunt's coefficients, given by

$$C(l_1m_1, l_2m_2, l_3m_3) = \iint_{4\pi} Y_{l_1m_1}(r/r) \, Y_{l_2m_2}(r/r) \, Y_{l_3m_3}(r/r) \sin\theta \, d\theta \, d\varphi \tag{26c}$$

3.3. Matrix representation of operators $\mathbf{t}(r_\alpha)$

From the first translation theorem (26a) and the definition (21), we can easily establish that, on the basis of free spherical waves, the translation operators $F(r_\alpha)$ have the following matrix representation:

$$\mathscr{T}(r_\alpha, lm, l'm') = 4\pi(-1)^{m'} \sum_{l_1 m_1} C(l - m, l_1 - m_1, l'm') \psi_{Kl_1 m_1}(r_\alpha). \tag{27}$$

Then, using this relation and equations (20), (22) and (26), we can obtain a matrix representation of the operator $\mathbf{t}_\alpha(r_\alpha)$:

$$\mathscr{T}_\alpha(r_\alpha) = \mathscr{F}(-r_\alpha)\mathscr{T}_\alpha(0)\mathscr{F}(r_\alpha). \tag{28}$$

Let us emphasize that, in contrast to $\mathscr{T}_\alpha(0)$, $\mathscr{T}_\alpha(r_\alpha)$ does not generally reduce in practice to a square matrix of order $(l_\alpha + 1)^2$. From a quantum mechanical point of view, this can be easily understood. The radial part of the free spherical waves $\Psi_{Klm}(r)$ for which $l > 0$ is actually very small inside a sphere centred at the origin. We can estimate that the radius r_l of this sphere is roughly the classical impact radius $\sqrt{l(l+1)}/K$ (in Rydberg atomic units). This radius r_l appears as an increasing function of the angular momentum l. Let us now consider an electron described by a free spherical wave $\Psi_{Klm}(r)$. According to the previous remarks, this wave function is practically unaffected by a scattering potential centred at the origin whose range (in fact, the muffin-tin radius) is less than the impact radius r_l. In other words, for this angular-momentum state, the atomic potential acts in a region where the probability of finding an electron is very small. Consequently, scattered wave, $\mathbf{t}$-matrix elements $\mathscr{T}_\alpha(0, lm, l'm')$ and phase shift δ_l^α are negligible. Obviously, this is no longer true if the atomic scatterer α is not located at the origin: in this case, the atomic potential can act in a region where the probability of finding an electron with an angular momentum $l > l_\alpha$ is no longer negligible. In this way, larger angular momenta than l_α have to be considered. Finally, the order of matrices $\mathscr{T}_\alpha(r_\alpha)$ and of the molecular transition matrix have to be determined by considering the range of the atomic potentials together with the size of the molecule. In practice, we start with an initial value l_{max} which is the largest value of $l_1, l_2, \ldots, l_{N_a}$. Then we try larger and larger values of l_{max} until the molecular $\mathbf{t}$-matrix elements converge. We finally deal with square matrices of dimension $(l_{max} + 1)^2$.

3.4. Matrix representation of $G_0^+ (E - V_{opt})$

Examination of the multiple scatttering equations (19) shows that the Green operator $G_0^+ (E - V_{opt})$ is multiplied from the right by $\mathbf{t}_\beta^* (r_\beta)$ and from the left by $\mathbf{t}_\alpha(r_\alpha)$, and that all pairs (α, β) of distinct indices are considered. Thus, for each pair (α, β), a matrix representation of $G_0^+ (E - V_{opt})$ using both complete basis sets of free spherical waves centred at r_α and r_β has to be introduced. For this purpose, we can write the relation

$$G_0^+ (E - V_{opt}) = F(-r_\alpha)H(r_\alpha - r_\beta)F(r_\beta) \tag{29a}$$

in which

$$H(r_\alpha - r_\beta) = F(r_\alpha)G_0^+ (E - V_{opt})F(-r_\beta). \tag{29b}$$

So, using the expression for the Green function in spherical co-ordinates:

$$G_0^+ (E - V_{opt}, r - r') = K \sum_{lm} [\psi_{Klm}(r)\chi_{Klm}^*(r')\theta(r' - r)$$

$$+ \chi_{Klm}^*(r)\psi_{Klm}(r')\theta(r - r')] \tag{30}$$

and the second translation theorem (26*b*), we can easily obtain a matrix representation of $H(r_\alpha - r_\beta)$:

$$\mathcal{H}(r_\alpha - r_\beta, lm, l'm') = 4\pi K(-1)^{m'} \sum_{l_1 m_1} C(l - m, l_1 - m_1, l'm') \chi_{Kl_1 m_1}(r_\alpha - r_\beta).$$

(31)

A matrix version of equation (29*a*) is directly obtained by using the definitions (27) and (31) of matrices $\mathcal{F}$ and $\mathcal{S}$. We obtain

$$\mathcal{G}(r_\alpha - r_\beta) = \mathcal{F}(-r_\alpha)\mathcal{S}(r_\alpha - r_\beta)\mathcal{F}(r_\beta)$$

(32)

in which $\mathcal{G}(r_\alpha - r_\beta)$ is a matrix representation of $G_0^+ (E - V_{opt})$ in both basis sets of spherical waves centred at r_α and r_β.

3.5. Multiple scattering and transition matrices of a molecule

Let us denote $\mathcal{T}_\alpha^*(r_\alpha)$ the matrix representation of $\mathbf{t}_\alpha^*(r_\alpha)$ in the basis set of free spherical waves. Then, the multiple-scattering equations (19) can be rewritten in the matrix form

$$\mathcal{T}_\alpha^*(r_\alpha) = \mathcal{T}_\alpha(r_\alpha) + \mathcal{T}_\alpha(r_\alpha) \sum_{\substack{\beta=1 \\ \beta \neq \alpha}}^{N_a} \mathcal{G}(r_\alpha - r_\beta)\mathcal{T}_\beta^*(r_\beta).$$

(33)

It is possible to reduce these N_a equations to one equation. For this purpose, let us construct a new representation by combining the matrices occurring in equation (33) into larger matrices with $N_a(l_{max} + 1)^2$ rows and columns. From matrices $\mathcal{T}_\alpha(r_\alpha)$, we define

$$\mathbf{T} = \begin{bmatrix} \mathcal{T}_1(r_1) & 0 \cdots \cdots \cdots 0 \\ 0 & \mathcal{T}_2(r_2) & \vdots \\ \vdots & \ddots & 0 \\ 0 & \cdots \cdots 0 & \mathcal{T}_{N_a}(r_{N_a}) \end{bmatrix}.$$

(34)

In a similar way, we can define a matrix $\mathbf{T}^*$ from the effective $\mathbf{t}$-matrices $\mathcal{T}_\alpha(r_\alpha)$. Let us also define the matrix $\mathbf{G}$ from the $N_a(N_a - 1)$ matrices $\mathcal{G}(r_\alpha - r_\beta)$:

$$\mathbf{G} = \begin{bmatrix} 0 & \mathcal{G}(r_1 - r_2) \cdots \cdots \cdots \cdots \mathcal{G}(r_1 - r_{N_a}) \\ \mathcal{G}(r_2 - r_1) & 0 \cdots & \mathcal{G}(r_2 - r_{N_a}) \\ \vdots & \ddots & \vdots \\ \mathcal{G}(r_{N_a} - r_1) \cdots \cdots \cdots \mathcal{G}(r_{N_a} - r_{N_a-1}) \cdots & 0 \end{bmatrix}.$$

(35)

Then, the N_α multiple scattering equations (33) reduce to one equation:

$$\mathbf{T}^* = \mathbf{T} + \mathbf{TGT}^*$$

(36)

that we can easily solve to find

$$\mathbf{T}^* = (\mathbf{1} - \mathbf{X})^{-1}\mathbf{T}.$$

(37)

In the above expression

$$\mathbf{X} = \mathbf{TG}$$

(38)

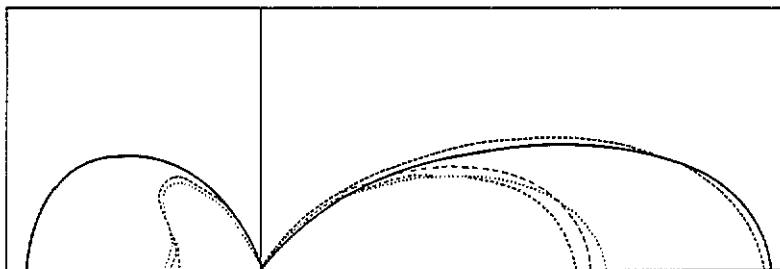is the multiple-scattering matrix of the molecule. A matrix representation $\mathcal{T}_m$ of the

Figure 1. Differential cross section of CO in polar coordinates for different values of l_{max}: ——, $l_{max} = 3$; ----, $l_{max} = 4$; . . . ., $l_{max} = 5$; —·—·, $l_{max} = 6$; ————, $l_{max} = 7$.

transition operator $\mathbf{T}_m$ of the molecule defined in equation (18) is simply obtained by summing the diagonal blocks of $\mathbf{T}^*$.

4. Application to the case of carbon monoxide on Pt(111)

The previous formalism is now applied to the simple case of a CO molecule whose bond length is that observed when it is chemisorbed on the (111) single-crystal surface of platinum (Ogletree *et al* 1986). Calculations are carried out for an energy of 60 eV and with our definition of the quantum number m, the z axis is parallel to the C—O bond. We assume here that the muffin-tin zero energy of carbon and oxygen atoms matches that of the substrate atoms. In this way, the carbon monoxide molecule is immersed in a homogeneous medium whose potential is the optical potential V_{opt}. At 60 eV, V_{opt} is taken equal to that of platinum, that is to say $-12.499 - 4.013i$ in electron volts (J Rundgren, private communication) and consequently the energy of incident electrons with respect to the muffin-tin zero energy of carbon and oxygen is 72.499 eV. At this energy, the atomic potential range of these atoms is such that only the first six atomic phase shifts are not negligible ($l_O = l_C = 5$). They are calculated without taking account of temperature effects.

According to Ogletree *et al* (1986) the C—O bond length has been fixed at 1.15 Å. As the C—O bond is normal to the surface, its orientation is that of the incident beam direction, which is also the z axis direction. The CO t-matrix elements depend on the choice of the origin of space: it is chosen at the centre of the C—O bond. As the oxygen atom is at the vacuum side and the carbon atom at the metal side, the t-matrix of CO is computed for $r_O = -0.575 \, \hat{z}$ and $r_C = +0.575 \, \hat{z}$ (in Å).

Increasing values of l are tried until the CO transition matrix elements converge. This convergence is examined through the differential cross-section σ of CO, given by

$$\sigma(\theta_f, \varphi_f, \theta_i, \varphi_i) = |f(\theta_f, \varphi_f, \theta_i, \varphi_i)|^2 \tag{39}$$

in which

$$f(\theta_f, \varphi_f, \theta_i, \varphi_i) = -4\pi \sum_{lm} \sum_{l'm'} Y_{lm}(\theta_f, \varphi_f) \mathcal{T}_m(lm, l'm') Y^*_{l'm'}(\theta_i, \varphi_i). \tag{40}$$

Values of l_{max} from 3 to 8 have been considered here. The incident plane wave has a wave vector in the positive direction of the z axis, (i.e. the O—C bond direction, $\theta_i = 0$). In this way, σ only depends on θ_f. Figure 1 shows $\sigma(\theta_f)$ in polar coordinates. We observe
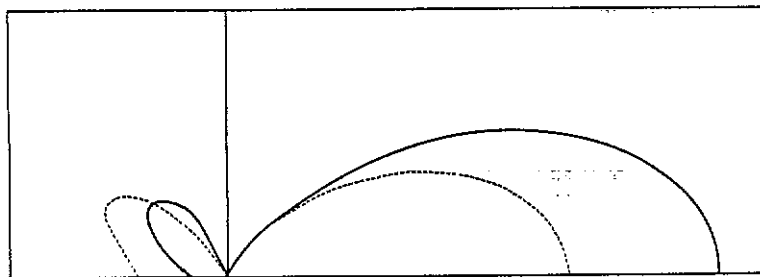
Figure 2. Differential cross section of CO in polar coordinates calculated with (---) and without (——) taking into account multiple scattering between oxygen and carbon.

here that the backward scattering is lower than the forward scattering. $\sigma(\theta_f)$ presents strong variations for $\theta_f > \pi/2$ when l_{max} goes from 3 to 4 and for $\theta_f < \pi/2$ when l_{max} goes from 4 to 5. For $l_{max} = 6$ and 7 we obtain very similar values of $\sigma(\theta_f)$ (difference about 10^{-3}). Between 7 and 8, the variations of $\sigma(\theta_f)$ are less than 10^{-6}. So we can choose $l_{max} = 6$, for which a satisfactory accuracy is obtained with a reasonable computational time.

Let us note here that multiple-scattering events between oxygen and carbon play an important role and consequently cannot be neglected. This is clearly apparent by comparing a complete calculation of the transition matrix $\mathcal{T}_m$ of the molecule to a calculation of this matrix in which the multiple-scattering matrix $\mathbf{X}$ is cancelled (see relation (37)). The results of both calculations, which are quite different, are shown in figure 2. In the present case, disregarding the multiple-scattering events increases the forward scattering and decreases the backward scattering.

5. Conclusion

We have revisited here the concept of the renormalized t-matrix, which was introduced on the one hand by Saldin and Pendry (1986, 1987) and on the other hand by the present authors in a work devoted to the statistical aspects of the diffuse LEED problem (Le Bossé *et al* 1988, 1990). We arrive at the conclusion that the renormalized t-matrices introduced in the two bodies of work do not have the same meaning. It appears that the renormalized t-matrix we define here takes into account all multiple-scattering processes involving adsorbate and substrate and can be used in a global calculation of the form factor. On the other hand, the SP renormalized t-matrix only takes into account multiple-scattering processes in which the first and last processes are scatterings at the molecule. However, this t-matrix is suitable for use in step 2 of the SP calculation.

The ways of computing both kinds of renormalized t-matrices are also totally different: in the SP approach the renormalized t-matrix τ is computed via the reflection matrix of a cluster of atoms surrounding the adsorbate; in the method presented here, the renormalized t-matrix $\mathbf{K}_1$ is computed via the first column $\mathbf{M}_S(k_g^- \leftarrow k^+)$ and the first line $\mathbf{M}_S(k^- \leftarrow k_g^+)$ of the substrate scattering matrix, in the directions of the initial $(k = k_i^+)$ and final $(k = k_f^-)$ wave vectors. The calculation of these matrices is a classical LEED calculation (Kambe's method for planar scattering and the Bloch wave method for interplanar scattering). After having stored these matrices, it only remains to determine the t-matrix of the single molecule.

For this purpose, we have presented in section 3 a method for calculating the t-matrix of a close-packed cluster of atoms. It is based upon the determination of a multiple scattering matrix **X** whose definition is quite similar to the one introduced in the classical LEED theory. This method provides an expression of the molecular **t**-matrix which can be easily used in our diffuse LEED theory. It can be shown that cluster **t**-matrix calculation becomes very time-consuming for large energies and for clusters of large size. For instance, in the case of an electron of 60 eV colliding with a small molecule such as CO, the numerical application of section 4 shows that all values of $l \leqslant l_{max} = 6$ have to be kept. Then, we have to deal with a multiple-scattering matrix whose dimension is $2(l_{max} + 1)^2 = 98$. It can be easily imagined that for larger molecules and larger energies, this dimension might become very important. For instance, if we assume that multiplication by 2 of the number N_a of atoms doubles the volume of the cluster, then the impact radius of the cluster and consequently l_{max} are roughly multiplied by $\sqrt[3]{2}$. On the other hand, if the electron energy is multiplied by 2, l_{max}, which roughly increases as $\sqrt{E}$, is multiplied by $\sqrt{2}$. So doubling the size of cluster and the energy amounts approximately to multiplying l_{max} by 1.8 and consequently to taking $l_{max} = 11$. Then the dimension of the multiple scattering matrix **X** would become $4(l_{max} + 1)^2 = 576$.

The single-crystal substrate is a cluster incomparably larger than a molecule. Nevertheless, the dimension of multiple-scattering matrices used in the conventional LEED theory is never very large. This comes from the fact that a monoatomic metal can be entirely described in terms of one of its atoms and by using operators of its translational group. In the same way, if a cluster has a particular symmetry, we can resort to its point group for reducing the dimension of the multiple-scattering matrix. So the theory described here can only be applied in its present form to the case of small molecules and for low energies. We cannot more accurately define the limitations of the practical applications of this theory because they are essentially determined by the performance of the computer which is used. In a second paper, the method will be applied to a diffuse LEED study of CO on Pt(111).

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