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A Multiple-Scattered Method for Chemisorption Systems

The objective of this work is to discuss in detail the theoretical background of the Korringa-Kohn-Rostocker multiple-scattered method with an application to the study of electronic structure of clean surfaces and adsorption systems.

The method presented here can be applied to periodic systems with slab configurations. By means of the above mentioned method the theoretical study of the electronic structure of the ordered overlayers adsorbed on the crystal surface, the chemical bonds of adsorbate species and adsorbate-induced electron states can be performed.

Nomenclature

SUC — surface unit cell,	Y_{lm} — spherical harmonics,
AS — atomic segment,	$R_l^{(i)}$ — radial functions,
Ψ, G — wave and Green's functions respectively,	$A_{lm}^{(ii)}, i'm', A_{lm}^{(ij)}, i'm'$ — diagonal and off-diagonal structure constants,
\vec{k}, \vec{q} — wave vectors,	$C_{LM, lm, i'm'}$ — Gaunt integrals,
\vec{u} — two-dimensional lattice vector,	ρ — radius of atomic sphere,
\vec{K}_n — vector of the two-dimensional reciprocal lattice,	A — cross-section of SUC.

1. Introduction

The multiple-scattered, or Korringa-Kohn-Rostocker (KKR) method has proved very useful for calculation of energy levels in solids and molecules, whenever the muffin-tin (MT) model is appropriate. The calculational scheme presented here is a generalization of the (KKR) formalism to films and surfaces which are represented by thin films.

The film or the slab is a simple model designed for the calculation of surface properties of solids. Such a model has great flexibility enabling clean surfaces, reconstructed surfaces and chemisorbed atoms or molecules to be studied within it. One of the advantages of the thin-film approach is that the chemisorption can be treated rather easily.

The multiple-scattered technique can be used for calculation of electronic structure of adsorbed overlayers, adsorbate-induced electron states and chemical bonds of adsorbed atoms and molecules. The method takes into account not only the local aspects of the bonds

of adsorbed species but also long-range effects due to the extended nature of a substrate as well as adsorbate-adsorbate interactions.

The model of the physical system, shown in Fig. 1, is periodic in two dimensions.

It consists of M atomic layers of substrate bounded on both sides by an adsorbed atomic layer which is denoted by shaded circles.

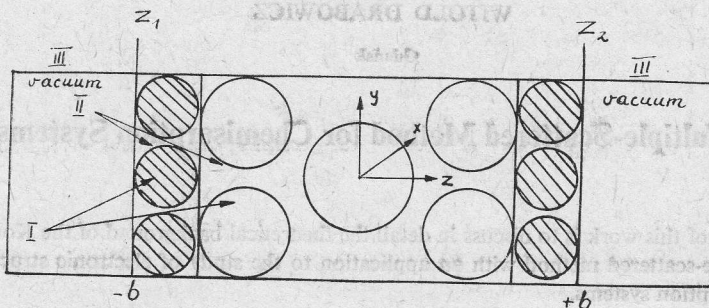


Fig. 1. The crystal slab with adsorbed overlayers

In the scattered-wave formulation the film is divided into surface unit cells (SUC) each of which extends to $\pm\infty$ in the z direction. The film boundaries can be described by the relations $z=z_1$ and $z=z_2$ and the space of each SUC is divided into three regions. The region of nonoverlapping atomic spheres surrounding each nuclear site in an atomic segment (AS) we denote as region *I*. The part of the SUC which contains all the atoms we call atomic segment. The boundaries of the AS lie in $z=z_1$ and $z=z_2$ planes. The interstitial space between the atomic spheres in AS we denote as region *II*. Two surface strips of not overlapping atomic spheres and for which $z > z_2$ or $z < z_1$ constitute region *III*. Excluding the region *III*, this division of space is analogous to the muffin-tin approximation used in the band theory.

2. Green's function and the system of integral equations

The integral equation is a convenient theoretical tool for investigating, among others, problems concerning the electron band structure of bulk, clean and chemisorbed surfaces, as well as low energy electron diffraction on the crystal surface and other scattering problems. The basis of the integral formulation is the Green function.

We derive now an integral equation for wave function which is a solution of the Schrödinger equation

$$[-\nabla^2 + V(\vec{r})]\Psi(\vec{r}) = E\Psi(\vec{r}), \quad (2.1)$$

which written in the form

$$(\nabla^2 + k^2)\Psi(\vec{r}) = V(\vec{r})\Psi(\vec{r}), \quad (2.2)$$

with $k^2 = E$, can be interpreted as an inhomogeneous differential equation with the term $V(\vec{r})\Psi(\vec{r})$ that can be considered as inhomogeneity. Introducing the differential operator

$$D = \nabla^2 + k^2, \quad (2.3)$$

and the inhomogeneity term

$$F(\vec{r}) = V(\vec{r})\Psi(\vec{r}), \quad (2.4)$$

we can write now (2.2) in an abbreviated form

$$D\Psi(\vec{r}) = F(\vec{r}). \quad (2.5)$$

Similarly, for the Green function satisfying the inhomogeneous differential equation [1]

$$\nabla^2 G(\vec{r}, \vec{r}') + k^2 G(\vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}'), \quad (2.6)$$

where δ is the three-dimensional Dirac delta function, we can write

$$DG(\vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}'). \quad (2.7)$$

Multiplying both sides of Eq. (2.7) by $F(\vec{r}')$ and integrating over the volume V with respect to \vec{r}' we get

$$\int_V DG(\vec{r}, \vec{r}')F(\vec{r}')d^3\vec{r}' = \int_V F(\vec{r}')\delta(\vec{r} - \vec{r}')d^3\vec{r}'. \quad (2.8)$$

The integration on the right can be carried out by making use of the integral property of the delta function [2]

$$\int_V f(\vec{r}')\delta(\vec{r} - \vec{r}')dv = f(\vec{r}). \quad (2.9)$$

Thus, we get

$$\int_V DG(\vec{r}, \vec{r}')F(\vec{r}')d^3\vec{r}' = F(\vec{r}). \quad (2.10)$$

Due to the fact that Laplace operator ∇^2 in (2.3) acts on functions of the \vec{r} coordinates, the differential operator D can be taken out from under the sign of integration. Therefore, we obtain

$$D \int_V G(\vec{r}, \vec{r}')F(\vec{r}')d^3\vec{r}' = F(\vec{r}). \quad (2.11)$$

By comparison of (2.11) with (2.5) we see that the integral in (2.11) must be identified with the wave function $\Psi(\vec{r})$. Our final result is then

$$\Psi(\vec{r}) = \int_V G(\vec{r}, \vec{r}')F(\vec{r}')d^3\vec{r}', \quad (2.12)$$

or

$$\Psi(\vec{r}) = \int_V G(\vec{r}, \vec{r}')V(\vec{r}')\Psi(\vec{r}')d^3\vec{r}'. \quad (2.13)$$

We have found thus the solution of (2.1) for various inhomogeneity terms and for the same boundary conditions imposed on Ψ and G functions. This solution is in the form of an integral equation, where the Green function has appeared as a kernel.

Since the potential in region *II* is assumed to be zero the integration in Eq. (2.13) is confined to the atomic sphere and two surface strips. Equation (2.13) can now be written as

$$\Psi(\vec{r}) = \sum_{j+s} \int_{V_{I+III}} G(\vec{r}, \vec{r}')V(\vec{r}')\Psi(\vec{r}')d^3\vec{r}', \quad (2.14)$$

where j, s denote the number of spheres in an atomic segment and number of surface strips, respectively, whereas V_{I+III} is the volume of regions I and III . Putting $V(\vec{r}')\Psi(\vec{r}')$ from (2.1) into (2.13) and with the help of Green's theorem [3]

$$\int_V (\Psi \nabla^2 G - G \nabla^2 \Psi) dv = \int_S \left(\Psi \frac{\partial G}{\partial n} - G \frac{\partial \Psi}{\partial n} \right) dS, \quad (2.15)$$

we get

$$\begin{aligned} \Psi(\vec{r}) = \sum_{j+s} \int_{V_{I+III}} \{ \Psi(\vec{r}') [\nabla^2 G(\vec{r}, \vec{r}') + EG(\vec{r}, \vec{r}')] \} d^3\vec{r}' + \\ + \int_{S_{I+III}} \left[G(\vec{r}, \vec{r}') \frac{\partial \Psi(\vec{r}')}{\partial n} - \Psi(\vec{r}') \frac{\partial G(\vec{r}, \vec{r}')}{\partial n} \right] dS', \quad (2.16) \end{aligned}$$

where n is the outer normal to the atomic spheres and to the surfaces z_1 and z_2 . We denote by S_{I+III} the surface bounding regions I and III . The total surface S_{I+III} consists of all the surfaces of atomic spheres and of two planes $z = z_1$ and $z = z_2$.

On account of (2.6) and (2.9) the first term on the right side of (2.16) cancels with the left side and one obtains

$$\sum_{j+s} \int_{S_{I+III}} \left[G(\vec{r}, \vec{r}') \frac{\partial \Psi(\vec{r}')}{\partial n} - \Psi(\vec{r}') \frac{\partial G(\vec{r}, \vec{r}')}{\partial n} \right] dS' = 0. \quad (2.17)$$

We have obtained the system of integral equations the number of which is equal $j+s$.

3. Green's function for a thin film

The thin film, which represents the surface region, is divided into SUC as is shown in Fig. 1. The three-dimensional SUC, defined by the right parallelepiped whose cross-section is denoted by A and whose z extent is in principle $\pm\infty$, is assumed to be truncated at $z = \pm L$. The length L is sufficiently large for the electronic charge density to be considered negligible at $z = \pm L$. The plane boundaries of the film are of infinite extension and retain translational symmetry parallel to the surface. There is no translational invariance along the direction perpendicular to the surface.

Turning now to the evaluation of the Green function we multiply both sides of equation (2.6) by

$$(2\pi)^{-\frac{1}{2}} \exp[-i(\vec{k}' + \vec{K}_n) \cdot \vec{r}], \quad (3.1)$$

where the vector \vec{k}' is $\vec{k}' = (k'_x, k'_y, k'_z)$ and $\vec{K}_n = (K_{nx}, K_{ny}, 0)$ is the vector of the two-dimensional reciprocal lattice. Integrating over the volume of the SUC and taking into account the integral property of the Dirac delta function (2.9) we get

$$\begin{aligned} (2\pi)^{-\frac{1}{2}} \int_V \{ \exp[-i(\vec{k}' + \vec{K}_n) \cdot \vec{r}] [\nabla^2 G(\vec{r}, \vec{r}') + k^2 G(\vec{r}, \vec{r}')] \} d^3\vec{r} = \\ = (2\pi)^{-\frac{1}{2}} \exp[-i(\vec{k}' + \vec{K}_n) \cdot \vec{r}']. \quad (3.2) \end{aligned}$$

Denoting $\Psi(\vec{r}) = \exp[-i(\vec{k}' + \vec{K}_n) \cdot \vec{r}]$ and using Green's formula (2.15) we get

$$\int_V \Psi \nabla^2 G dV = \int_V G \nabla^2 \Psi dV + \int_S \left(\Psi \frac{\partial G}{\partial n} - G \frac{\partial \Psi}{\partial n} \right) dS. \quad (3.3)$$

The surface integral vanishes, since the flux through the surfaces perpendicular to the x and y axes cancels out and the planes perpendicular to the z axis are removed to infinity.

Hence, we have

$$(2\pi)^{-\frac{3}{2}} \int_V [G(\vec{r}, \vec{r}') \nabla^2 \Psi(\vec{r}) + k^2 \Psi(\vec{r}) G(\vec{r}, \vec{r}')] d^3 \vec{r} = (2\pi)^{-\frac{3}{2}} \exp[-i(\vec{k}' + \vec{K}_n) \cdot \vec{r}']. \quad (3.4)$$

Carrying out the surface integration in the (x, y) plane we obtain

$$(2\pi)^{-\frac{3}{2}} A [-(k'_x + K_{xn})^2 - (k'_y + K_{yn})^2 - k_z'^2 + E] \exp\{-i[(k'_x + K_{xn})x - (k'_y + K_{yn})y]\} \times \\ \times \int_{-\infty}^{\infty} G(\vec{r}, \vec{r}') \exp(-ik'_z z) dz = (2\pi)^{-\frac{3}{2}} \exp[-i(\vec{k}' + \vec{K}_n) \cdot \vec{r}'], \quad (3.5)$$

where $E = k^2$. Since the integration region extends to infinity along the z axis we can use the one-dimensional Fourier transform pair [4]

$$f(k) = (2\pi)^{-\frac{1}{2}} \int_{-\infty}^{\infty} f(z) \exp(-ikz) dz, \quad (3.6)$$

and

$$f(z) = (2\pi)^{-\frac{1}{2}} \int_{-\infty}^{\infty} f(k) \exp(ikz) dk. \quad (3.7)$$

Hence equation (3.5) can be written as

$$G(\vec{k}', \vec{r}) = -\frac{1}{(2\pi)^{\frac{3}{2}} A} \sum_n \frac{\exp[i(\vec{q}' + \vec{K}_n) \cdot (\vec{u} - \vec{u}')] \exp(-ik'_z z')}{k_z'^2 - [E - (\vec{q}' + \vec{K}_n)^2]}, \quad (3.8)$$

where $\vec{q}' = (k'_x, k'_y, 0)$ and $\vec{u} = (x, y, 0)$. The summation in Eq. (3.8) is over all the reciprocal lattice vectors \vec{K}_n .

Now we insert (3.8) using (3.7) and obtain

$$G(\vec{r}, \vec{r}') = -\frac{1}{2\pi A} \sum_n \exp[i(\vec{q}' + \vec{K}_n) \cdot (\vec{u} - \vec{u}')] I, \quad (3.9)$$

where

$$I = \int_{-\infty}^{\infty} \frac{\exp[ik'_z(z - z')]}{k_z'^2 - [E - (\vec{q}' + \vec{K}_n)^2]} dk'_z. \quad (3.10)$$

This integral we analyze by means of contour integration in the complex k'_z -plane [5]. The singularities in the integral are at $k'_z = \pm [E - (\vec{q}' + \vec{K}_n)^2]^{\frac{1}{2}}$ for $E - (\vec{q}' + \vec{K}_n)^2 > 0$ and at $k'_z = \pm i[(\vec{q}' + \vec{K}_n)^2 - E]^{\frac{1}{2}}$ for $E - (\vec{q}' + \vec{K}_n)^2 < 0$.

On account of

$$k'_z = \text{Re } k'_z + i \text{Im } k'_z, \quad (3.11)$$

and

$$\exp[ik'_z(z-z')] = \exp[i(z-z') \operatorname{Re} k'_z] \exp[-(z-z') \operatorname{Im} k'_z], \quad (3.12)$$

we can write

$$I = \oint_C \frac{\exp[ik'_z(z-z')]}{k_z'^2 - [E - (\vec{q}' + \vec{K}_n)^2]} dk'_z, \quad (3.13)$$

where C is the contour which for $z-z' > 0$ is closed by a large semicircle C_2 in the upper half plane and for $z-z' < 0$ the contour is closed by semicircle C_3 in the lower half plane as is shown in Fig. 2.

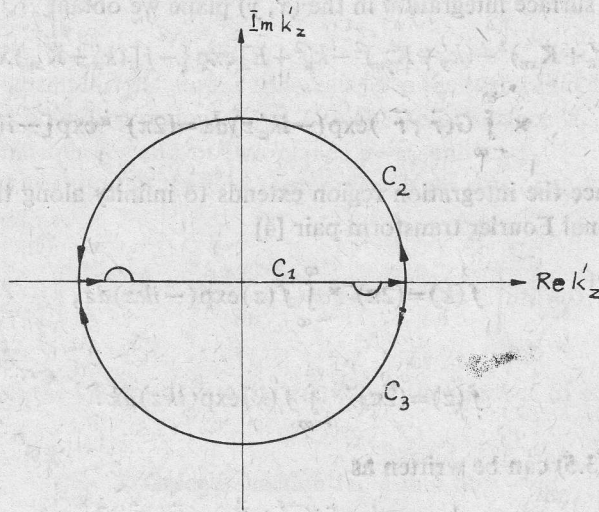


Fig. 2. The complex k'_z -plane

In the limit as the radius of the semicircles becomes infinite, the contribution therefrom to the integrals becomes zero. The integrals are then equal to their values along the real axis C_1 .

For $z-z' > 0$ the contour integral along $C_1 + C_2$ is equal to the residue at the pole $[E - (\vec{q}' + \vec{K}_n)^2]^{\frac{1}{2}}$.

Thus

$$I = (2\pi i) \{ \operatorname{Res} [E - (\vec{q}' + \vec{K}_n)^2]^{\frac{1}{2}} \}, \quad (3.14)$$

and

$$I = \pi i \frac{\exp\{i[E - (\vec{q}' + \vec{K}_n)^2]^{\frac{1}{2}}(z-z')\}}{[E - (\vec{q}' + \vec{K}_n)^2]^{\frac{1}{2}}}. \quad (3.15)$$

Similarly for $z-z' < 0$ the contour integral along $C_1 + C_3$ is equal to the residue at the pole $-[E - (\vec{q}' + \vec{K}_n)^2]^{\frac{1}{2}}$.

Hence

$$I = (-2\pi i) \{ \operatorname{Res} [-[E - (\vec{q}' + \vec{K}_n)^2]^{\frac{1}{2}}] \}, \quad (3.16)$$

and

$$I = \pi i \frac{\exp\{i[E - (\vec{q}' + \vec{K}_n)^2]^{\frac{1}{2}}(z - z')\}}{[E - (\vec{q}' + \vec{K}_n)^2]^{\frac{1}{2}}} \quad (3.17)$$

Inserting (3.17) into (3.9) we get finally

$$G(\vec{r}, \vec{r}') = \frac{1}{2A} \sum_n \frac{\exp[i(\vec{q}' + \vec{K}_n) \cdot (\vec{u} - \vec{u}')] }{i[E - (\vec{q}' + \vec{K}_n)^2]^{\frac{1}{2}}} \exp\{i[E - (\vec{q}' + \vec{K}_n)^2]^{\frac{1}{2}}(z_y - z_z)\} \quad (3.18)$$

where z_z and z_y denote the smaller and the greater of the quantities z and z' , respectively.

In the case of $E - (\vec{q}' + \vec{K}_n)^2 < 0$ and $z - z' > 0$ or $z - z' < 0$ we obtain the following result

$$G(\vec{r}, \vec{r}') = -\frac{1}{2A} \sum_n \frac{\exp[i(\vec{q}' + \vec{K}_n) \cdot (\vec{u} - \vec{u}')] }{[(\vec{q}' + \vec{K}_n)^2 - E]^{\frac{1}{2}}} \exp\{-[(\vec{q}' + \vec{K}_n)^2 - E]^{\frac{1}{2}}(z_y - z_z)\} \quad (3.19)$$

4. Representation of the wave function and Green's function

Our further considerations are based on the system of integral equations (2.17) by means of which we can derive the final secular equation of atomic system being investigated. For that purpose, however, we need the representations of the wave function and Green's function in regions *I* and *III*, respectively, because of the spherical symmetry of the potential.

Inside each atomic sphere of the first region, say the one centered at the atom located at \vec{C}_i as shown in Fig. 3, we can expand the wave function in terms of products of radial functions and spherical harmonics

$$\psi^{(i)}(\vartheta_i, \varphi_i) = \sum_{l=0}^{\infty} \sum_{m=-l}^l C_{lm}^{(i)} R_l^{(i)}(r_i) Y_{lm}(\vartheta_i, \varphi_i), \quad (4.1)$$

where ϑ_i, φ_i are the polar angles of $\vec{r}_i = \vec{r} - \vec{C}_i$ and Y_{lm} are normalized spherical harmonics.

$R_l^{(i)}$ are radial functions which satisfy the radial differential equation

$$\left[-\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + \frac{l(l+1)}{r^2} + V^{(i)}(r) - E \right] R_l^{(i)}(r) = 0, \quad (4.2)$$

with the boundary conditions requiring the functions $R_l^{(i)}$ of the coordinate system to be finite at the origin and $R_l^{(i)}(\rho_i) = 1$, where ρ_i is the radius of the atomic sphere about the *i*th atom in AS. These functions should be calculated for each kind of atoms in SUC.

To make use of the spherical symmetry, we also need an expansion of $G(\vec{r}, \vec{r}')$ in spherical harmonics. Introducing $\vec{r} = \vec{r}_i + \vec{C}_i$ and $\vec{r}' = \vec{r}'_j + \vec{C}_j$, where \vec{r}_i and \vec{r}'_j are the position vectors of the *i*th and *j*th nucleus in the AS, as illustrated in Fig. 3, we can expand Green's function in spherical harmonics with angular coordinates \vec{r}, \vec{r}' , $\vec{r}_i = \vec{r} - \vec{C}_i$ and $\vec{r}'_j = \vec{r}' - \vec{C}_j$ as their arguments [6, 7].

Thus, we have

$$G^{(ii)}(\vec{r}_i, \vec{r}'_j) = \sum_{l_m} \sum_{l'_m} A_{l_m, l'_m}^{(ii)} j_l(\kappa r_i) j_{l'}(\kappa r'_i) + \kappa \delta_{ll'} \delta_{mm'} n_l(\kappa r'_i) j_l(\kappa r_i) Y_{lm}(\vartheta_i, \varphi_i) Y_{l'm'}^*(\vartheta'_j, \varphi'_j), \quad (4.3)$$

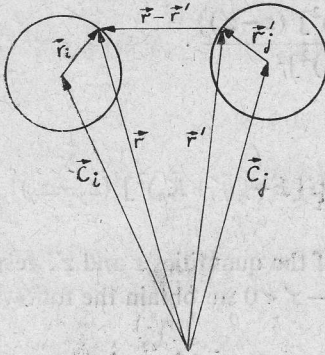


Fig. 3. The position vectors \vec{r} and \vec{r}' relative to some chosen origin

and

$$G^{(ij)}(\vec{r}_i, \vec{r}_j) = \sum_{lm} \sum_{l'm'} A_{lm, l'm'}^{(ij)} j_l(\kappa r_i) j_{l'}(\kappa r_j) Y_{lm}(\vartheta_i, \varphi_i) Y_{l'm'}^*(\vartheta_j, \varphi_j), \tag{4.4}$$

where $\kappa = E^{\frac{1}{2}}$ for $E > 0$ and $\kappa = +i(-E)^{\frac{1}{2}}$ for $E < 0$.

The quantities $j_l, n_l, A_{lm, l'm'}^{(ii)}$ and $A_{lm, l'm'}^{(ij)}$ denote the spherical Bessel, the spherical Neumann functions, the diagonal and the off-diagonal structure constants. These constants are given by

$$A_{lm, l'm'}^{(ii)} = 4\pi i^{(l-l')} \sum_{LM} i^{-L} D_{LM}^{(ii)} C_{LM, lm, l'm'}, \tag{4.5}$$

and

$$A_{lm, l'm'}^{(ij)} = 4\pi i^{(l-l')} \sum_{LM} i^{-L} D_{LM}^{(ij)} C_{LM, lm, l'm'}, \tag{4.6}$$

where the coefficients $D_{LM}^{(ij)}$ for $i = j$ and $i \neq j$ are defined as follows:

$$D_{LM}^{(ij)} = D_{LM}^{(ij)}(1) + D_{LM}^{(ij)}(2) + \delta_{L0} \delta_{ij} D_{00}. \tag{4.7}$$

A practical scheme for evaluating these coefficients is based on Ewald's method [8].

The explicit expressions for the terms in (4.7) can be written in the form [9]

$$D_{LM}^{(ij)}(1) = -\frac{4\pi i^L}{\Omega \kappa^L} \sum_n \frac{\exp[i(\vec{q} + \vec{K}_n) \cdot (\vec{C}_i - \vec{C}_j)]}{(\vec{q} + \vec{K}_n)^2 - E} \exp\{[-(\vec{q} + \vec{K}_n)^2 + E]/\eta\} \times |\vec{q} + \vec{K}_n|^L Y_{LM}^*(\vartheta_n, \varphi_n), \tag{4.8}$$

$$D_{LM}^{(ij)}(2) = -\frac{2^{L+1}}{(\pi)^{\frac{1}{2}} \kappa^L} \sum_m' \exp(i\vec{q} \cdot \vec{R}_m) |\vec{R}_m - \vec{C}_i + \vec{C}_j|^L Y_{LM}(\vartheta_m, \varphi_m) \times \int_{\eta^{1/2}/2}^{\infty} \exp\left[-(\vec{R}_m - \vec{C}_i + \vec{C}_j)^2 \xi^2 + \frac{E}{4\xi^2}\right] \xi^{2L} d\xi, \tag{4.9}$$

$$D_{00}(3) = -\frac{\eta^{\frac{1}{2}}}{2\pi} \sum_{\nu=0}^{\infty} \frac{(E/\eta)^{\nu}}{\nu!(2\nu-1)}, \tag{4.10}$$

where Ω is the volume of the AS, whereas ϑ_n, φ_n and ϑ_m, φ_m are the polar angles of vectors $\vec{q} + \vec{K}_n$ and $\vec{R}_m - \vec{C}_i + \vec{C}_j$, respectively.

The summation in (4.9) is carried out over all two-dimensional lattice vectors and the prime indicates that the term with $\vec{R}_m=0$ is to be omitted for $i \neq j$. The parameter η in (4.8), (4.9) and (4.10) is chosen arbitrarily in order to optimize the convergence of the summations.

The quantities $C_{LM, lm, l'm'}$ are the Gaunt integrals of the form

$$C_{LM, lm, l'm'} = \int_0^{2\pi} d\varphi \int_0^\pi \sin \vartheta d\vartheta Y_{LM}(\vartheta, \varphi) Y_{lm}^*(\vartheta, \varphi) Y_{l'm'}(\vartheta, \varphi). \tag{4.11}$$

The coefficient $C_{LM, lm, l'm'}=0$ if $M \neq m-m'$, whereas the sum over L runs only the values $|l-l'| \leq L \leq (l+l')$ and $(l+l'+L)$ is an even integer. The C 's vanish for other L 's.

We turn now to the region III in which the wave function has the representation [10]

$$\psi(\vec{r}) = \sum_n C_n^{(k)} \exp [i(\vec{q} + \vec{K}_n) \cdot \vec{u}] u_n^{(k)}(z), \tag{4.12}$$

where $k=1, 2$ correspond to $z_1 = -b$ and $z_2 = b$, respectively, and $C_n^{(k)}$ are the coefficients. The function $u_n^{(2)}(z)$ satisfies the Schrödinger equation

$$\left\{ -\frac{d^2}{dz^2} + V(z) - [E - (\vec{q} + \vec{K}_n)^2] \right\} u_n^{(2)}(z) = 0, \tag{4.13}$$

with the boundary conditions $u_n^{(2)}(+\infty) = 0$ and $u_n^{(2)}(b) = 1$. An analogous equation is satisfied by the function $u_n^{(1)}(z)$.

The representation of the Green function for this region is given by expression (3.18).

5. Secular equation

Having determined the representations of the wave function and Green's function we can derive the secular equation for our system. For that purpose we will need the standard expansions of plane waves into spherical harmonics and spherical Bessel functions [11]

$$\exp(i\vec{k} \cdot \vec{r}) = 4\pi \sum_{lm} i^l j_l(kr) Y_{lm}(\vartheta_r^-, \varphi_r^-) Y_{lm}^*(\vartheta_k^-, \varphi_k^-), \tag{5.1}$$

and

$$\exp(-i\vec{k} \cdot \vec{r}) = 4\pi \sum_{lm} (-i)^l j_l(kr) Y_{lm}^*(\vartheta_r^+, \varphi_r^+) Y_{lm}(\vartheta_k^+, \varphi_k^+), \tag{5.2}$$

where $\vartheta_r^-, \varphi_r^-$ and $\vartheta_k^-, \varphi_k^-$ are the polar angles of \vec{r} and \vec{k} in a fixed coordinate system.

Substituting (3.18), (4.3), (4.4) and (4.12) into (2.17), using (5.1), multiplying (2.17) by $Y_{lm}^*(\vartheta_{r_i}^-, \varphi_{r_i}^-)$, using orthonormal properties of spherical harmonics carrying out integration over atomic surfaces S_I with respect to \vec{r} and over the entire surface S_{I+III} with respect to \vec{r}' we obtain the set of equations [12]

$$\begin{aligned} & \rho_i j_l \left\{ \sum_{l'm', i=j} \rho_i^2 [\kappa \delta_{ll'} \delta_{mm'} (n_{l'} L_{l'}^{(i)} - n_{l'}) + A_{lm, l'm'}^{(ii)} (j_{l'} L_{l'}^{(i)} - j_{l'})] C_{l'm'}^{(i)} + \right. \\ & + \sum_{l'm', i \neq j} \rho_j^2 [A_{lm, l'm'}^{(ij)} (j_{l'} L_{l'}^{(j)} - j_{l'})] C_{l'm'}^{(j)} + \sum_{n'} A [A_{lm, n'}^{(i, 2)} (-L_{n'}^{(2)} + i\Gamma_{n'}) C_{n'}^{(2)} + \\ & \left. + A_{lm, n'}^{(i, 1)} (L_{n'}^{(1)} + i\Gamma_{n'}) C_{n'}^{(1)} \right\} = 0, \tag{5.3} \end{aligned}$$

where

$$n'_i = \left[\frac{d}{dr_i} n'_i(\kappa r_i) \right]_{r_i=\rho_i}, \quad j'_i = \left[\frac{d}{dr_i} j'_i(\kappa r_i) \right]_{r_i=\rho_i},$$

$$L'_i{}^{(i)} = \left[\frac{dR'_i{}^{(i)}(r_i)}{dr_i} \right]_{r_i=\rho_i} = \left[\frac{dR'_i{}^{(i)}(r_i)}{dr_i} \right]_{r_i=\rho_i}, \quad (5.4)$$

$$L_{n'}^{(1)} = \left[\frac{du_{n'}^{(1)}}{dz} \right]_{z=-b} = \left[\frac{du_{n'}^{(1)}}{dz} \right]_{z=-b}, \quad L_{n'}^{(2)} = \left[\frac{du_{n'}^{(2)}}{dz} \right]_{z=b} = \left[\frac{du_{n'}^{(2)}}{dz} \right]_{z=b}.$$

The corresponding structure constants $A_{lm,n'}^{(i,2)}$ and $A_{lm,n'}^{(i,1)}$ are

$$A_{lm,n'}^{(i,2)} = 4\pi i^l \frac{\exp(i\vec{P}_{n'}^{(1)} \cdot \vec{C}_i) \exp(i\Gamma_{n'} b)}{2iA\Gamma_{n'}} Y_{lm}^*(\vartheta_{n'}^{(1)}, \varphi_{n'}^{(1)}), \quad (5.5)$$

and

$$A_{lm,n'}^{(i,1)} = 4\pi i^l \frac{\exp(i\vec{P}_{n'}^{(2)} \cdot \vec{C}_i) \exp(i\Gamma_{n'} b)}{2iA\Gamma_{n'}} Y_{lm}^*(\vartheta_{n'}^{(2)}, \varphi_{n'}^{(2)}), \quad (5.6)$$

where

$$\vec{P}_{n'}^{(1)} = (q_x + K_{n'x}, q_y + K_{n'y}, -\Gamma_{n'}), \quad (5.7)$$

and

$$\vec{P}_{n'}^{(2)} = (q_x + K_{n'x}, q_y + K_{n'y}, \Gamma_{n'}). \quad (5.8)$$

The normal components of the vectors $\vec{P}_{n'}^{(1)}$ and $\vec{P}_{n'}^{(2)}$ are

$$\Gamma_n = [E - (\vec{q} + \vec{K}_n)^2]^{\frac{1}{2}} \quad \text{if} \quad E > (\vec{q} + \vec{K}_n)^2, \quad (5.9)$$

$$\Gamma_n = +i[(\vec{q} + \vec{K}_n)^2 - E]^{\frac{1}{2}} \quad \text{if} \quad E < (\vec{q} + \vec{K}_n)^2. \quad (5.10)$$

and the polar angles of these vectors are denoted by $\vartheta_{n'}^{(1)}, \varphi_{n'}^{(1)}$ and $\vartheta_{n'}^{(2)}, \varphi_{n'}^{(2)}$, respectively. For $E < (\vec{q} + \vec{K}_n)^2$ the vectors $\vec{P}_{n'}^{(1)}$ and $\vec{P}_{n'}^{(2)}$ have imaginary components. The spherical harmonics, in this case, have complex arguments and are defined by [7]

$$Y_{lm}(\vartheta_n^{(1,2)}, \varphi_n^{(1,2)}) = \left[\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!} \right]^{\frac{1}{2}} (\mp i)^{|m|} P_l^{|m|} \left[\pm \frac{i\Gamma_n}{E} \right] \exp(im\varphi_n^{(1,2)}), \quad (5.11)$$

where $P_l^{|m|}(x)$ is Hobson's associated Legendre function.

Now choosing \vec{r} to lie above the plane surface z_2 , putting (3.18), (4.1) and (5.2) into (2.17), multiplying it by $\exp[-i(\vec{q}' + \vec{K}_n) \cdot \vec{u}]$, integrating \vec{r} over the atomic segment boundary of area A on the plane $z_2 = b$ and \vec{r}' over the surface S_{I+III} we get

$$A[\rho_j^2 \sum_{j,l,m'} A_{n,l'm'}^{(2,j)} (j_l L'_l{}^{(j)} - j'_l) C_{l'm'}^{(j)} + AA_n^{(2,1)} (L_n^{(1)} + i\Gamma_n) C_n^{(1)} + AA_n^{(2,2)} (-L_n^{(2)} - i\Gamma_n) C_n^{(2)}] = 0, \quad (5.12)$$

where the structure constants are

$$A_{n,l'm'}^{(2,j)} = 4\pi(-i)^l \frac{\exp(i\vec{P}_n^{(2)} \cdot \vec{C}_j) \exp(ib\Gamma_n)}{2i\Gamma_n A} Y_{l'm'}(\vartheta_n^{(2)}, \varphi_n^{(2)}), \quad (5.13)$$

$$A_n^{(2,1)} = \frac{\exp(2i\Gamma_n b)}{2i\Gamma_n A}, \quad A_n^{(2,2)} = \frac{1}{2i\Gamma_n A}. \quad (5.14), (5.15)$$

Proceeding similarly as before and taking \vec{r} below the surface z_1 we obtain

$$A[\rho_j^2 \sum_{j,l'm'} A_{n,l'm'}^{(1,j)} (j_r L_r^{(j)} - j'_r) C_{l'm'}^{(j)} + AA_n^{(1,1)} (L_n^{(1)} - i\Gamma_n) C_n^{(1)} + AA_n^{(1,2)} (-L_n^{(2)} + i\Gamma_n) C_n^{(2)}] = 0. \quad (5.16)$$

The structure constants are

$$A_{n,l'm'}^{(1,j)} = 4\pi(-i)^l \frac{\exp(i\vec{P}_n^{(1)} \cdot \vec{C}_j) \exp(ib\Gamma_n)}{2i\Gamma_n A} Y_{l'm'}(\vartheta_n^{(1)}, \varphi_n^{(1)}), \quad (5.17)$$

$$A_n^{(1,2)} = \frac{\exp(2i\Gamma_n b)}{2i\Gamma_n A}, \quad A_n^{(1,1)} = \frac{1}{2i\Gamma_n A}. \quad (5.18), (5.19)$$

The basic equations (5.3), (5.11) and (5.15) represent a set of linear equations for the coefficients $C_{lm}^{(j)}$, $C_n^{(1)}$, $C_n^{(2)}$. The solution of these equations will be nontrivial if the determinant of the coefficients vanishes. The secular equation obtained in such a way contains the required stationary connection between the energy E and the two-dimensional wave vector \vec{q} . The order of this equation equals the number of atoms in the AS times the number of coefficients $C_{lm}^{(j)}$ in (4.1) plus the double number of reciprocal lattice, needed to describe the wave function (4.12) in each surface strip.

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Wielorozproseniowa metoda do analizy chemisorpcji

Streszczenie

Praca dotyczy szczegółów metody teoretycznej wielokrotnego rozproszenia stosowanej do analizy powierzchniowych własności kryształów czystych graniczących z próżnią oraz powierzchni pokrytych cienką warstwą ośrodka adsorbowanego. Metodę tę stosuje się do uporządkowanych układów periodycznych w ramach modelu cienkiej płytki. Pozwala ona na wyznaczenie wiązań chemicznych adsorbowanego ośrodka, jak również struktury elektronowej podłoża oraz zmian tej struktury w wyniku oddziaływania tego ośrodka.

Метод многократного рассеяния для систем с хемосорбцией

Резюме

В настоящей работе рассматриваются теоретические основы метода многократного рассеяния Корринги, Кона, Ростокера, служащего для исследования электронной структуры чистых поверхностей, а также адсорбционных поверхностных свойств.

Этот метод применяется, в рамках модели тонкой пластинки, для исследований электронной структуры периодических упорядоченных систем, адсорбированных на поверхности кристалла, электронных состояний, а также химических связей адсорбата.