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## Theory of band structure of molecular adsorbates on a surface

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**Abstract.** A theory of surface band structure of molecular adsorbates is presented. The surface Green function is expanded into scattering paths that start and end at the same atom. These can be classified into atomic, molecular, overlayer and substrate paths respectively and each calculated with the usual dynamical low-energy electron diffraction techniques. The numerical result for CO on a Ni surface will also be presented.

### 1. Introduction

Analysis of the band structure of molecules absorbed on transition-metal surfaces is important in understanding the catalytic effect of transition metals on molecular dissociation. It is also indispensable in understanding the effect of promoter and poison on the catalytic reaction. There have been calculations related to these problems based on the multiple scattering X- $\alpha$  (MSX $\alpha$ ) cluster [1] and full-potential linear augmented-plane-wave (FLAPW) [2] methods. Our approach here goes beyond the cluster method by taking into account the extended nature of the surface. It also treats the substrate properly as a semi-infinite stack of atoms instead of modelling the system as a thin film like in FLAPW. Another basic difference is that it is formulated as an electron-scattering problem similar to that of low-energy electron diffraction (LEED) [3]. This has been done for a clean metal surface [4] and is commonly known as the layer Korringa, Kohn and Rostoker (KKR) method. There have also been density-of-states calculation along this line for the case of atomic adsorbates [5], where only  $k_{\parallel} = 0$  was taken, which is appropriate for comparison with angle-resolved photo-electron experiments at normal emission angle. In the following, this method will be extended to a molecular adsorbate system with  $k_{\parallel}$  integrated over the surface Brillouin zone. It will be applied to calculate the band structure of CO on a nickel surface. Its connection with the angle-integrated photo-emission experiments such as x-ray absorption near-edge structure will also be discussed.

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## 2. Theory

The model adopted consists of spherically symmetric muffin tins with a constant interstitial region. Each molecule is enclosed by an outer sphere as in  $MSX\alpha$  calculations. A step surface barrier is taken for simplicity. The molecular potential  $V_m$  can be divided into an atomic part  $V_a$  and its molecular environment part  $V_{am}$ , i.e.

$$V_m = V_a + V_{am}. \quad (1)$$

The molecular Green function is given by

$$G_m = G_0(1 + T_m G_0) \quad (2)$$

where

$$T_m = V_m + V_m G_0 V_m + \dots \quad (3)$$

and  $G_0$  is the free-space Green function. Equation (2) can be factorised into two parts representing successive scattering processes

$$G_m = G_0(1 + T_a G_0)(1 + T'_m G_0) \quad (4)$$

where

$$T_a = V_a + V_a G_0 V_a + \dots \quad (5)$$

and  $T'_m$  contains all multiple scattering paths within the molecule with the restriction that the first scattering is by  $V_{am}$ .

By definition, the atomic Green function is

$$G_a = G_0(1 + T_a G_0) \quad (6)$$

Substituting into equation (4), we get

$$G_m = G_a + G_{am} \quad (7)$$

where

$$G_{am} = G_a T'_m G_0. \quad (8)$$

Next consider the potential of a layer of molecules  $V_l$ , which can be decomposed into a molecular part  $V_m$  and its environment part  $V_{ml}$ , i.e.

$$V_l = V_m + V_{ml}. \quad (9)$$

By exactly the same reasoning as above, the layer Green function is

$$G_l = G_m + G_{ml} \quad (10)$$

and

$$G_{ml} = G_m T'_l G_0 \quad (11)$$

where  $T'_l$  contains all scattering paths within the layer starting with a scattering by  $V_{ml}$ .

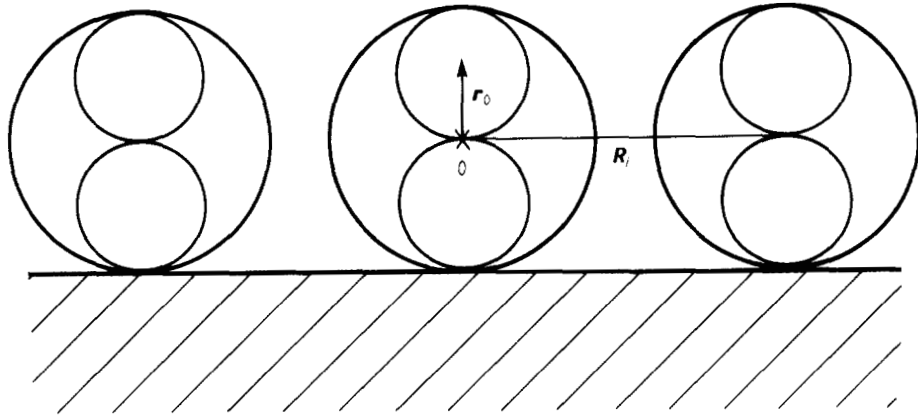
Finally, the total surface potential  $V_s$  can be divided into a molecular overlayer part  $V_l$  and potential of the substrate layers  $V_{ls}$ , i.e.

$$V_s = V_l + V_{ls}. \quad (12)$$

Again, the surface Green function can be written as

$$G_s = G_l + G_{ls} \quad (13)$$

where



**Figure 1.** Schematic diagram of molecular adsorbates on a surface. Origin 0 is taken at the centre of the reference molecule and centre of the reference atom is at  $r_0$ .

$$G_{ls} = G_j T'_s G_0 \quad (14)$$

where  $T'_s$  contains all scattering paths starting with a scattering by  $V_{ls}$ .

From equations (7), (10) and (13)

$$G_s = G_a + G_{am} + G_{ml} + G_{ls}. \quad (15)$$

The first term represents the Green function of an isolated atomic muffin tin while the other three terms represent corrections due to other atoms in the molecule, other molecules and the substrate respectively.

In the following, the centre of the molecule under consideration is taken to be the origin and the atom under consideration to be at  $r_0$  (see figure 1).  $j_l, h_l$  represent spherical Bessel and Hankel functions of order  $l$  and  $Y_L$  represents spherical harmonics with  $L = (l, m)$ ,  $\hat{r} = \mathbf{r}/|\mathbf{r}|$ .

We now consider each term of equation (15) individually.

### 2.1. Atomic Green function $G_a$

Assume that  $\mathbf{r}, \mathbf{r}'$  are inside the atom at  $\mathbf{r}_0$ , i.e.

$$|\mathbf{r} - \mathbf{r}_0| < |\mathbf{r}' - \mathbf{r}_0| < R_{MT}$$

where  $R_{MT}$  is the atomic muffin-tin radius. We have, by equation (6) and the Appendix

$$G_a(\mathbf{r}, \mathbf{r}') = -2ik \sum_L R_l(|\mathbf{r} - \mathbf{r}_0|) Y_L^*(\widehat{\mathbf{r} - \mathbf{r}_0}) I_l(|\mathbf{r}' - \mathbf{r}_0|) Y_L(\widehat{\mathbf{r}' - \mathbf{r}_0}) \quad (16)$$

where  $\exp(i\delta_{jl})R_l$  and  $\exp(-i\delta_{jl})I_l$  are the regular and irregular solutions inside the atom, which match outside the atom to  $j_l + t_l h_l$  and  $h_l$  respectively,  $\delta_{jl}$  is the phase shift of the  $j$ th atom,

$$t_{jl} = [\exp(2i\delta_{jl}) - 1]/2$$

and

$$k = (2E)^{1/2}.$$

### 2.2. Correction to Green function due to atoms in the same molecule $G_{am}$

Assume that  $|\mathbf{r} - \mathbf{r}_0| < |\mathbf{r}' - \mathbf{r}_0| < R_{MT} < |\mathbf{r}_1 - \mathbf{r}_0|$ . By equation (8),

$$G_{am}(\mathbf{r}, \mathbf{r}') = \iint G_a(\mathbf{r}, \mathbf{r}_1) T'_m(\mathbf{r}_1, \mathbf{r}_2) G_0(\mathbf{r}_2, \mathbf{r}') d^3 r_1 d^3 r_2. \quad (17)$$

From the Appendix

$$G_a(\mathbf{r}, \mathbf{r}_1) = -2ik \sum_L \exp(i\delta_{0l}) R_l(|\mathbf{r} - \mathbf{r}_0|) Y_L^*(\widehat{\mathbf{r} - \mathbf{r}_0}) h_l(k|\mathbf{r}_1 - \mathbf{r}_0|) Y_L(\widehat{\mathbf{r}_1 - \mathbf{r}_0}). \quad (18)$$

According to equation (17) this outgoing wave from the atom at  $\mathbf{r}_0$  is multiply scattered by atoms inside the molecule and finally back into the same atom. Therefore

$$G_{am}(\mathbf{r}, \mathbf{r}') = -2ik \sum_L \sum_{L'} \exp(i\delta_{0l}) R_l(|\mathbf{r} - \mathbf{r}_0|) Y_L^*(\widehat{\mathbf{r} - \mathbf{r}_0}) t_{0l}^{-1} [(1 - tG')^{-1}]_{0L,0L'} \\ \times \exp(i\delta_{0l'}) R_{l'}(|\mathbf{r}' - \mathbf{r}_0|) Y_{L'}(\widehat{\mathbf{r}' - \mathbf{r}_0}) \quad (19)$$

where [3, 6]

$$G'_{iL,jL'} = (1 - \delta_{ij}) G_{LL'}^+(\mathbf{r}_i - \mathbf{r}_j) \quad (20)$$

$$G_{LL'}^\pm(\mathbf{r}_j) = 4\pi \sum_{L''} i^{l-l'+l''} a(LL'L'') \begin{pmatrix} h_{l''}(kr_j) Y_{L''}(\hat{r}_j) \\ j_{l''}(kr_j) Y_{L''}(\hat{r}_j) \end{pmatrix} \quad (21)$$

and

$$a(LL'L'') = \int Y_L^* Y_{L'} Y_{L''}^* d\Omega \quad (22)$$

and  $\mathbf{r}_i$  is position of the  $i$ th atom in the molecule.

### 2.3. Correction to Green function due to other molecules in the overlayer $G_{ml}$

From equation (11),

$$G_{ml}(\mathbf{r}, \mathbf{r}') = \iint G_m(\mathbf{r}, \mathbf{r}_1) T'_1(\mathbf{r}_1, \mathbf{r}_2) G_0(\mathbf{r}_2, \mathbf{r}') d^3 r_1 d^3 r_2 \quad (23)$$

where  $|\mathbf{r} - \mathbf{r}_0| < |\mathbf{r}' - \mathbf{r}_0| < R_{MT}$  and  $r_1 > R_{out}$  and  $R_{out}$  is the outer-sphere radius. From the Appendix

$$G_m(\mathbf{r}, \mathbf{r}_1) = -2ik \sum_L (-1)^m \Phi_{\bar{L}}(\mathbf{r}) h_l(kr_1) Y_L(\hat{r}_1) \quad (24)$$

where the regular solution for the molecule  $\Phi_L(\mathbf{r})$  is defined as the scattered wave inside the molecule resulting from the incident wave  $j_l Y_L$  outside the molecule;  $\bar{L} = (l, -m)$ .

It can be shown that

$$\Phi_L(\mathbf{r}) = \sum_{L'} \Phi_{LL'} \exp(i\delta_{0l'}) R_{l'}(|\mathbf{r} - \mathbf{r}_0|) Y_{L'}(\widehat{\mathbf{r} - \mathbf{r}_0}) \quad (25)$$

where

$$\Phi_{LL'} = \sum_j \sum_{L''} G_{LL''}^-(\mathbf{r}_j) [1 - tG']_{jL'',0L'}^{-1}. \quad (26)$$

$G^-$  means re-expanding the incoming wave  $j_l Y_L$  (which is with respect to the centre of the molecule) about the  $j$ th atom in the molecule.  $1 + tG' + tG'tG' + \dots$  represent all multiple scattering corrections within the molecule. It goes back to  $r$  inside the atom under consideration.

According to equation (23) the outgoing wave from the molecule in equation (24) will be multiply scattered within the layer and finally come back to  $r'$  inside the atom at  $r_0$ . Analogous to equation (19), we can write equation (23) as

$$G_{ml}(r, r') = -2ik \sum_L \sum_{L'} \sum_{L''} (-1)^m \Phi_{\bar{L}}(r) T_{L\bar{L}'}^{-1} [(1 - TG')^{-1} - 1]_{0L', 0L''} \Phi_{L''}(r') \quad (27)$$

where  $T$  is the scattering matrix of the molecule [6]. In equation (27)  $G'$  is defined as in equation (20) except now the indices  $i, j$  go over positions of molecules in the overlayer.

Define

$$\tau = (1 - TG')^{-1} T. \quad (28)$$

It can be shown [7] that

$$\tau_{0L, 0L'} = (1/\Omega_{BZ}) \int_{BZ} d^2 k_{\parallel} [T^{-1} - G(k_{\parallel})]_{L\bar{L}'}^{-1} \quad (29)$$

where

$$G_{LL'}(k_{\parallel}) = \sum_i \exp(-ik_{\parallel} \cdot R_i) G'_{iL, 0L'} \quad (30)$$

( $R_i$  is the position of the  $i$ th lattice point of the overlayer and  $k_{\parallel}$  is the parallel momentum vector inside the first surface Brillouin zone) and  $\Omega_{BZ}$  is the two-dimensional Brillouin zone area.

Therefore equation (27) can be written as

$$G_{ml}(r, r') = (-2ik) (1/\Omega_{BZ}) \int_{BZ} d^2 k_{\parallel} \sum_{LL'} (-1)^m \Phi_{\bar{L}}(r) \times [(1 - G(k_{\parallel})T)^{-1} G(k_{\parallel})]_{LL'} \Phi_{L'}(r'). \quad (31)$$

#### 2.4. Correction to Green function due to substrate $G_{ls}$

From equation (14)

$$G_{ls}(r, r') = \iint G_1(r, r_1) T'_s(r_1, r_2) G_0(r_2, r') d^3 r_1 d^3 r_2 \quad (32)$$

where  $|r - r_0| < |r' - r_0| < R_{MT}$ . Here  $G_1$  is the same as  $G_{ml}$  in equation (27) except now the final wave, instead of being an incoming wave about the origin, is an outgoing wave from the  $j$ th molecule incident upon the substrate.

By definition (28), it can be written as

$$G_1(r, r_1) = -2ik \sum_j \sum_L \sum_{L'} (-1)^m \Phi_{\bar{L}}(r) (T^{-1} \tau)_{0L, jL'} h_L(k|r_1 - R_j|) Y_{L'}(\widehat{r_1 - R_j}). \quad (33)$$

Next expand  $h_L Y_{L'}$  into plane waves towards the substrate [3], i.e.

$$h_L(k|r_1 - R_j|) Y_{L'}(\widehat{r_1 - R_j}) = \int_{BZ} d^2 k_{\parallel} \sum_g i^{-l} Y_{L'}(\widehat{k_g^+}) \times \exp[ik_g^+ \cdot (r_1 - R_j)] / (2\pi k k_{\perp g}^+) \quad (34)$$

where

$$\mathbf{k}_g^+ = (\mathbf{k}_{\parallel} + \mathbf{g}, k_{\perp g}^+) \quad k_{\perp g}^+ = [2E - (\mathbf{k}_{\parallel} + \mathbf{g})^2]^{1/2}$$

and  $\mathbf{g}$  is the two-dimensional reciprocal-lattice vector. Using

$$\tau_{LL'}(\mathbf{k}_{\parallel}) = \sum_j \tau_{0L,jL'} \exp(-i\mathbf{k}_{\parallel} \cdot \mathbf{R}_j) = [T^{-1} - G(\mathbf{k}_{\parallel})]_{LL'}^{-1} \quad (35)$$

equation (33) becomes

$$G_1(\mathbf{r}, \mathbf{r}_1) = -2ik(1/\Omega_{\text{BZ}}) \int_{\text{BZ}} d^2k_{\parallel} \sum_g \sum_L \sum_{L'} (-1)^m \Phi_{\bar{L}}(\mathbf{r}) [1 - G(\mathbf{k}_{\parallel})T]_{\bar{L}L'}^{-1} \\ \times i^{-l} Y_{L'}(\hat{\mathbf{k}}_g^+) \exp(i\mathbf{k}_g^+ \cdot \mathbf{r}_1) / (2\pi k k_{\perp g}^+ \Omega) \quad (36)$$

where  $\Omega$  is the unit-cell area.

Let  $R_{g'g}$  be the reflection matrix of the substrate, renormalised by all multiple scattering between overlayer and substrate. It can be calculated by the layer doubling method in LEED [3].

The reflected plane wave from the substrate is expanded into incoming spherical waves about the molecule at the origin, renormalised by multiple scattering by molecules in the same layer. Therefore

$$G_{\text{is}}(\mathbf{r}, \mathbf{r}') = -2ik(1/\Omega_{\text{BZ}}) \int_{\text{BZ}} d^2k_{\parallel} \sum_g \sum_{g'} \sum_L \sum_{L'} (-1)^m \Phi_{\bar{L}}(\mathbf{r}) [1 - G(\mathbf{k}_{\parallel})T]_{\bar{L}L'}^{-1} \\ \times i^{-l} Y_{L'}(\hat{\mathbf{k}}_g^+) / (2\pi k k_{\perp g}^+ \Omega) R_{g'g} \sum_j \sum_L \sum_{L'} 4\pi i^l \exp(i\mathbf{k}_{\parallel} \cdot \mathbf{R}_j) \\ \times Y_L^*(\hat{\mathbf{k}}_{g'}^-) [1 - TG']_{jL,0L'}^{-1} \Phi_{L'}(\mathbf{r}'). \quad (37)$$

It can be shown that

$$\sum_j \exp(i\mathbf{k}_{\parallel} \cdot \mathbf{R}_j) [1 - TG']_{jL,0L'}^{-1} = [1 - TG(\mathbf{k}_{\parallel})]_{\bar{L}L'}^{-1}. \quad (38)$$

Putting equation (38) into equation (37)

$$G_{\text{is}}(\mathbf{r}, \mathbf{r}') = -2ik(1/\Omega_{\text{BZ}}) \int_{\text{BZ}} d^2k_{\parallel} \sum_g \sum_{g'} \sum_L \sum_{L'} (-1)^m \Phi_{\bar{L}}(\mathbf{r}) [1 - G(\mathbf{k}_{\parallel})T]_{\bar{L}L'}^{-1} \\ \times i^{-l} Y_{L'}(\hat{\mathbf{k}}_g^+) / (2\pi k k_{\perp g}^+ \Omega) R_{g'g} \sum_L \sum_{L'} 4\pi i^l Y_L^*(\hat{\mathbf{k}}_{g'}^-) \\ \times [1 - TG(\mathbf{k}_{\parallel})]_{\bar{L}L'}^{-1} \Phi_{L'}(\mathbf{r}'). \quad (39)$$

The spherically symmetrised local density of states inside atom at  $\mathbf{r}_0$  is (including spin)

$$\rho(\mathbf{r}, E) = -(2/\pi) \text{Im}(1/4\pi) \int d\Omega_r G_s(\mathbf{r}, \mathbf{r}). \quad (40)$$

Substituting equations (16), (19), (31) and (39) into equation (40), we get

$$\rho(\mathbf{r}, E) = \text{Im}(ik/\pi^2 \Omega_{\text{BZ}}) \int_{\text{BZ}} d^2k_{\parallel} \left( \sum_L R_l(|\mathbf{r} - \mathbf{r}_0|) I_l(|\mathbf{r} - \mathbf{r}_0|) \right. \\ \left. + \sum_L \exp(i\delta_{0l}) R_l(|\mathbf{r} - \mathbf{r}_0|) S_{0L,0L} \exp(i\delta_{0l}) R_l(|\mathbf{r} - \mathbf{r}_0|) \right) \quad (41)$$

where

$$S_{0L,0L} = t_{0l}^{-1} [(1 - tG')^{-1} - 1]_{0L,0L} + \sum_{L'} \sum_{L''} (-1)^{m'} \Phi_{L'L} H_{L'L''} \Phi_{L''L} \quad (42)$$

$$H = [1 - G(\mathbf{k}_{\parallel})T]^{-1} [G(\mathbf{k}_{\parallel}) + E(\mathbf{k}_{\parallel})] \quad (43)$$

and

$$E_{LL'}(\mathbf{k}_{\parallel}) = \sum_g \sum_{g'} \sum_{L''} i^{-l} Y_L(\hat{k}_g^+) (1/2\pi k k_{\perp g}^+ \Omega) R_{g'g} 4\pi i^{l''} Y_{L''}^*(\hat{k}_g^-) [1 - TG(\mathbf{k}_{\parallel})]_{L'L'}^{-1}. \quad (44)$$

This generalises the expression given in [4, 5] to the case of molecular adsorbates.

### 3. Surface band structure of $c(2 \times 2)$ CO on Ni(100)

We adopt the geometry as determined from LEED [8]. The CO molecules are assumed to stand upright in a  $c(2 \times 2)$  pattern on top of the Ni atoms with  $d(\text{Ni-C}) = 1.7 \text{ \AA}$  and  $d(\text{C-O}) = 1.15 \text{ \AA}$ . The potential for a Ni-C-O cluster [9] is used for the carbon and oxygen atoms. As for the Ni atoms, a band-structure potential is used [10]. As a first test of our method, no potential discontinuity exists except those at the atomic muffin-tin boundaries and at the surface barrier, which is taken to be a step of  $0.57 H$ . In order to improve convergence, we have added an arbitrary constant damping, which effectively smoothes out all the secondary features. This corresponds to the fact that in photoemission experiments, what is being observed is actually the band structure with finite lifetimes [11].

The atomic phase shifts, regular and irregular solutions are found by Runge-Kutta integration techniques [3]. All the other quantities appearing in equations (41)–(44) can be implemented by the usual LEED and XANES subroutines [3, 6]. The  $\mathbf{k}_{\parallel}$  integration is performed by the special  $k$ -point methods commonly used in band-structure calculations [12]. We define the local density of states within a muffin tin to be

$$\rho(E) = \int \rho(\mathbf{r}, E) d^3r. \quad (45)$$

The result for  $\rho(E)$  as a function of energy  $E$  is shown in figure 2 for the oxygen, carbon and two nickel atoms (one of them is directly below the carbon atom).

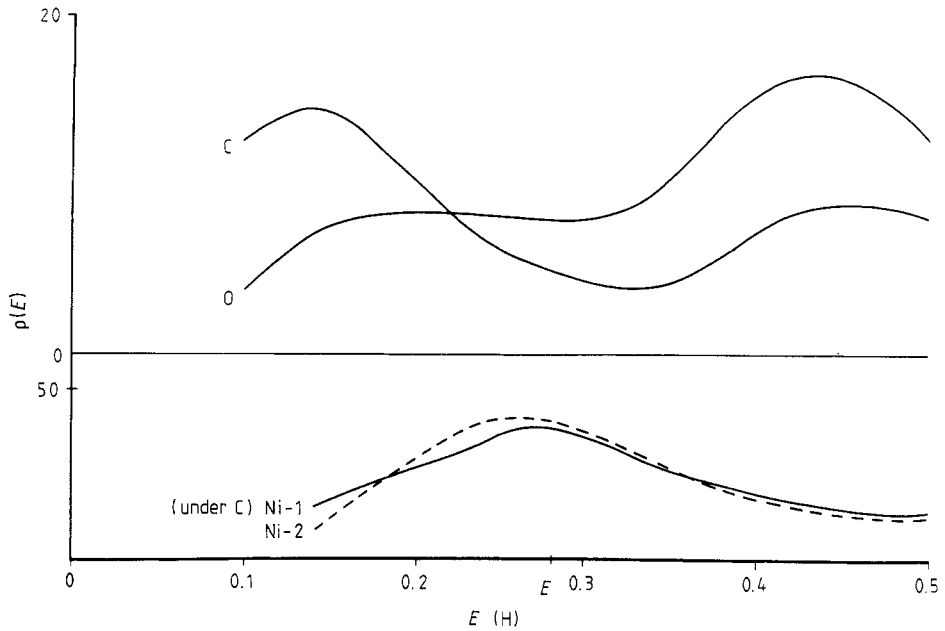
According to equation (41), the density of states can be decomposed into different angular-momentum components in the form

$$\rho(E) = \sum_L \rho_L(E). \quad (46)$$

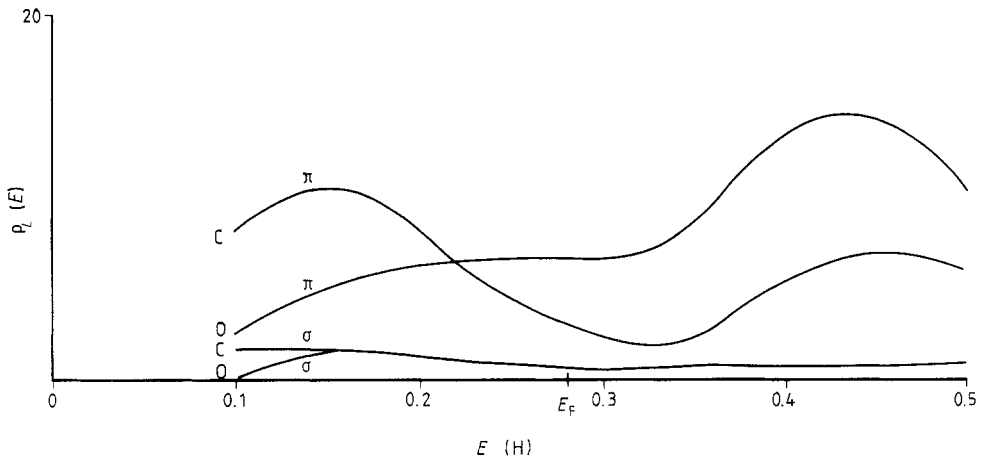
The contributions from the different  $l = 1$  components for the carbon and oxygen atoms are shown in figure 3. The  $l = 1, m = 0$  component corresponds to a  $\sigma$  state and  $l = 1, m = \pm 1$  correspond to  $\pi$  states.

The two major features for CO can be identified as the  $2\pi^*$  (above Fermi level) and  $1\pi-5\sigma$  (below Fermi level) molecular resonances. However the  $5\sigma$  orbital of the CO molecule is depleted upon chemisorption on Ni. A bond is formed between the carbon and its neighbouring Ni atom, which is mainly of  $\pi$  character. It means that the charge below the Fermi level has been transferred from the C-O  $\sigma$  to the  $\pi$  bond region. This is consistent with the usual picture of  $\sigma$  donation to the Ni substrate and  $\pi$  back-donation, which leads to the catalytic effect of Ni on CO dissociation.





**Figure 2.** Theoretical local density of states within different muffin tins for  $c(2 \times 2)$  CO on Ni(100). Ni-1 represents the nickel atom directly under the carbon atom.



**Figure 3.** Theoretical local density of states projected into different angular momentum within the carbon and oxygen muffin tins for  $c(2 \times 2)$  CO on Ni(100).  $\sigma$  means  $l = 1, m = 0$  and  $\pi$  means  $l = 1, m = \pm 1$ .

#### 4. Conclusions

We have generalised the Green function method for surface band structure to the case of molecular adsorbate systems and show how the local density of states is related to scattering paths on the surface. The theory was formulated in such a way that traditional LEED techniques can be used. In our model, the molecule is treated as a single unit, which can be translated and rotated in different ways on a surface [8]. It also allows for the possibility of an outer-sphere potential discontinuity, which can readily be incorporated in our scheme [13]. In fact, in the case where the atoms in the same molecule are lying almost in the same plane, the inter-planar scattering would not converge at all if the atoms are put into separate atomic planes and a plane-wave basis is used for the scattering processes. Approaches using a spherical-wave basis such as the one presented here is the only way to proceed. The numerical results, although non-self-consistent, provide a semi-quantitative picture of the charge distribution of CO on a Ni surface, which agrees with the general Blyholder's model and also the previous results [1, 2] by other methods. It is expected since we start with a self-consistent cluster potential. For a more refined picture of the charge distribution, self-consistency has to be included, which can be done in a way similar to [4]. Further work in this direction is under way. On the experimental side, our '*k*-integrated' density of states below the Fermi level is usually probed by ultraviolet photo-electron spectroscopy (UPS). On the other hand, the states above the Fermi level can be probed by an angle-integrated photo-emission experiment such as XANES. This has indeed been done for various molecules on metal surfaces [14, 15]. In particular, for CO on Ni(100), the  $2\pi^*$  resonance above the Fermi level has been identified by its polarisation dependence. Our theory provides an easy and economical way of calculating the surface band structure and can be extended to other more complex molecules with only a moderate increase in cost. It can readily be modified into XANES theory with photo-emission matrix elements included, which would provide a more quantitative way of interpreting the XANES spectra of molecular adsorbate systems.

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#### Appendix

The general expression for the Green function in coordinate representation can be written as

$$G(\mathbf{r}, \mathbf{r}') = G(\mathbf{r}', \mathbf{r}) = \int d^3r_1 G_0(\mathbf{r}', \mathbf{r}_1) \left( \delta(\mathbf{r}_1 - \mathbf{r}) + \int d^3r_2 T(\mathbf{r}_1, \mathbf{r}_2) G_0(\mathbf{r}_2, \mathbf{r}) \right) \quad (\text{A1})$$

where  $T$  is the scattering  $T$  matrix and  $G_0$  is the free-space Green function.

Assume that the range of the potential is  $R$ , i.e.

$$T(\mathbf{r}_1, \mathbf{r}_2) \neq 0 \quad \text{only for } r_1 < R \quad \text{and} \quad r_2 < R$$

In spherical-wave representation [3],

$$G_0(\mathbf{r}_1, \mathbf{r}_2) = -2ik \sum_L j_l(kr_<) Y_L^*(\hat{r}_<) h_l(kr_>) Y_L(\hat{r}_>) \quad (\text{A2})$$

where

$$r_< = \min(r_1, r_2)$$

$$r_> = \max(r_1, r_2)$$

$$k = (2E)^{1/2}$$

$$\hat{r} = \mathbf{r}/|\mathbf{r}|$$

$$L = (l, m).$$

If  $R < r < r'$ , equation (A1) becomes

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}') &= -2ik \sum_l j_l(kr) Y_L(\hat{r}) h_l(kr') Y_L^*(\hat{r}') \\ &\quad - 2ik \sum_L \sum_{L'} h_l(kr') Y_L^*(\hat{r}') T_{LL'} h_{l'}(kr) Y_{L'}(\hat{r}) \end{aligned} \quad (\text{A3})$$

where

$$T_{LL'} = \iint d^3r_1 d^3r_2 j_l(kr_1) Y_L(\hat{r}_1) T(\mathbf{r}_1, \mathbf{r}_2) j_{l'}(kr_2) Y_{L'}^*(\hat{r}_2) \quad (\text{A4})$$

is the definition of the  $T$  matrix in  $(l, m)$  space.

Equation (A3) can be rewritten as

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}') &= -2ik \sum_l (-1)^m \left( j_l(kr) Y_L(\hat{r}) + \sum_{L'} T_{\bar{L}L'} h_{l'}(kr) Y_{L'}(\hat{r}) \right) h_l(kr') Y_L(\hat{r}') \\ &= -2ik \sum_L (-1)^m \Phi_{\bar{L}}(\mathbf{r}) \Psi_L(\mathbf{r}') \end{aligned} \quad (\text{A5})$$

where  $\Phi_{\bar{L}}(\mathbf{r})$  is called the regular solution and  $\Psi_L(\mathbf{r})$  is called the irregular solution.

By definition  $G(\mathbf{r}, \mathbf{r}')$  is a continuous function of  $\mathbf{r}$  and  $\mathbf{r}'$ , implying that (A5) is valid for all  $\mathbf{r}, \mathbf{r}'$  both inside and outside  $R$  provided  $r < r'$ . In particular, if  $R < r < r'$ , we have

$$\Phi_L(\mathbf{r}) = j_l(kr) Y_L(\hat{r}) + \sum_{L'} T_{\bar{L}L'} h_{l'}(kr) Y_{L'}(\hat{r}) \quad (\text{A6})$$

$$\Psi_L(\mathbf{r}') = h_l(kr') Y_L(\hat{r}'). \quad (\text{A7})$$

## References

- [1] Maclaren J M, Pendry J B, Joyner R W and Meeham P 1986 *Surf. Sci.* **175** 263
- [2] Wimmer E, Fu C L and Freeman A J 1985 *Phys. Rev. Lett.* **55** 2618
- [3] Pendry J B 1974 *Low Energy Electron Diffraction* (London: Academic)
- [4] Maclaren J M, Vedensky D D, Blake R J, Larsson C G and Pendry J B to be published
- [5] Maca F and Scheffler M 1985 *Comput. Phys. Commun.* **38** 403

- [6] Durham P J, Pendry J B and Hodges C H 1982 *Comput. Phys. Commun.* **25** 193
- [7] Gyoryffy B L and Stott M J 1972 *Band Structure Spectroscopy of Metals and Alloys* ed. D J Fabian and L M Watson (New York: Academic)
- [8] Andersson S and Pendry J B 1980 *J. Phys. C: Solid State Phys.* **13** 3547
- [9] Tong S Y, Maldonado A, Li C H and Van Hove M A 1980 *Surf. Sci.* **94** 73
- [10] Wakoh S 1965 *J. Phys. Soc. Japan* **20** 1894
- [11] Pendry J B 1976 *Surf. Sci.* **57** 679
- [12] Cunningham S L 1974 *Phys. Rev. B* **10** 4988
- [13] Poon H C and Saldin D K 1989 *J. Phys.: Condens. Matter* **1** 1551
- [14] Stohr J and Jaeger R 1982 *Phys. Rev. B* **26** 4111
- [15] Stohr J and Outka D A 1987 *J. Vac. Sci. Technol. A* **5** 919