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CHEMISORPTION AT FINITE COVERAGES: THE COHERENT POTENTIAL APPROXIMATION vs THE EQUATION OF MOTION FOR GREEN FUNCTION METHOD

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1. Introduction

The physical processes arising in chemisorption systems are of great interest both from theoretical and practical points of view. Especially, the properties of chemisorbed surfaces at submonolayer coverages are important, for example, in heterogeneous catalysis or phase transition (in the adsorbate component) theories. The chaotic distribution of adatoms in the chemisorbed overlayer can be treated within the coherent potential approximation (CPA) /1/ as it was done in papers /2,3,4/ (see also /5,6/), but it is well known that CPA requires great numerical efforts for solving the corresponding nonlinear equations. On the other hand, similar information about the chemisorbed system can be obtained by using the equation of motion method for the corresponding Green Function. In order to break up the infinite system of higher-and-higher order Green Functions one can use, for example, the assumption of uncorrelated distribution of chemisorbed atoms. Thus, the results of such calculations should be comparable, with those obtained within the single site CPA although the numerical efforts are much smaller. The aim of this paper is to compare the results obtained within these two approaches. The paper is organized as follows. In section 2, we describe the model Hamiltonian intended to represent the chemisorbed overlayer. In section 3, we present the derivation of the required Green Function within the appropriate approximation concerning the stochastic distribution of adatoms and the last section is devoted to presentation of the numerical results.

2. The model Hamiltonian

Recently, the Hamiltonian intended to describe the sys-

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tem of adatoms chemisorbed on the metal surface has been
derived from microscopic considerations /7,8/. Here, we pre-
sent the most important, for our cosideration, parts of this
Hamiltonian

$$H = \sum_{k\sigma} \varepsilon_k n_{k\sigma} + \sum_{\alpha\sigma} N_\alpha \left\{ E_\alpha n_{A\sigma} + \frac{U}{2} n'_{\alpha\sigma} n_{\alpha-\sigma} - \sum_k \left[\left(V_{\alpha\alpha\alpha k} n_{\alpha-\sigma} - V_{\alpha k} \right) a^+_{\alpha\sigma} a_{k\sigma} + h.c \right] \right\}$$

$$+ \sum_{\substack{\alpha\neq\beta \\ \sigma}} N_\alpha N_\beta a^+_{\alpha\sigma} a_{\beta\sigma} \left[E_{\alpha\beta} + V_{\alpha\beta\beta\alpha} \left(n_{\alpha-\sigma} + n_{\beta-\sigma} \right) \right] +$$

$$+ \frac{1}{2} \sum_{\substack{\alpha\neq\beta \\ \sigma\sigma'}} N_\alpha N_\beta V_{\alpha\beta\alpha\beta} a^+_{\alpha\sigma} a^+_{\beta\sigma'} a_{\beta\sigma'} a_{\alpha\sigma} + H_{rest} .$$

(1)

All symbols have their usual meaning as for the Newns-
Anderson model /18/ and here we only remind that the func-
tions $V_{\alpha\alpha\alpha k}$, $V_{\alpha\beta\beta\alpha}$ and $V_{\alpha\beta\alpha\beta}$ are the matrix elements of the
Coulomb interaction between electrons calculated with the
appropriate wave functions – see /7,9/ for details. The sum
over α is carried out over all the adsorption centers. The
operator $N_\alpha = c^+_\alpha c_\alpha$ has eigenvalues equal to 0 or 1 and the
operators c^+_α, c_α are the creation and annihilation opera-
tors of the adsorbed atom at the adsorption center with the
coordinate $\vec{R}_\alpha$. We consider only the case when there is no
more than one adatom in each adsorption center. At complete
monolayer coverage the adatoms form a two-dimensional lat-
tice commensurate with that of the substrate surface but for
the coverage less than unity the chemisorbed layer can be
considered as a substitutional alloy composed of two types
of species, adatoms and vacancies. The parameter $E_{\alpha\beta}$ can be
treated as an electron hopping integral between the adatoms
located at the α-th and β-th chemisorption centers. The
third term describes the metallization of the chemisorbed
layer caused by enveloping the valence orbitals of the ada-
toms. It leads to the dispersion of the virtual level and
arising of a virtual surface band.

The Hamiltonian (1) (but without the last three terms) was investigated by us in several approximations. Some approximations have been introduced into this Hamiltonian and (or) the many-body terms were treated within (beyond) the mean-field approximations /10-15/. This Hamiltonian has an interesting structure. With respect to ion variables N_α it has the form of the Ising model but with the operator coefficients consisting of Fermi operators. With respect to the electron operators it is a generalization of the Anderson model.

All the properties of the system can be calculated from the one-particle retarded double time Green Function (GF) $\langle\langle N_\alpha(t)a_{\alpha\sigma}(t)|N_\beta(t)a_{\beta\sigma}^+(t)\rangle\rangle$. For example, the adatom electron charge can be calculated as follows:

$$q=1-\langle N_\alpha n_{\alpha\uparrow}\rangle/\theta-\langle N_\alpha n_{\alpha\downarrow}\rangle/\theta, \quad \theta=\langle N_\alpha\rangle$$

and the magnetic moment as

$$m=\langle N_\alpha n_{\alpha\uparrow}\rangle/\theta-\langle N_\alpha n_{\alpha\downarrow}\rangle/\theta.$$

Here, we use the form $\langle N_\alpha n_{\alpha\sigma}\rangle/\theta$ rather than $\langle n_{\alpha\sigma}\rangle$ for the mean adatom occupation number. It is a consequence of the composite structure of the Hamiltonian. Namely, the correlation function $\langle N_\alpha n_{\alpha\sigma}\rangle/\theta$ should be interpreted as the conditional probability of finding an electron at the adsorption center α when this center is already occupied by the adatom. Working with the Green Function mentioned above within the equation of motion method one obtains the higher GF built up from many adatom and electron operators. Because of the unclosed system of coupled equations for higher-and-higher GFs, one has to accept some decoupling scheme for terminating these equations. Note, however, that in the case of the one adatom chemisorbed on the substrate surface this infinite set of equations is present only for the Hamiltonian with the many-body terms included. On the contrary, in the submonolayer chemisorption case, even the one-electron Hamiltonian is able to produce the infinite system of equa-

tions for higher-and-higher order (with respect to the ad-atom operators N_α) Green Functions. Fortunately, this infinite set of equations can be exactly solved for the one-particle GF $\langle\langle N_\alpha a_{\alpha\sigma} | N_\beta a_{\beta\sigma}^+ \rangle\rangle$ (but only for the one-electron Hamiltonian), although the result can be written down only in terms of the infinite sum of correlation functions $\langle N_\alpha N_{\alpha_1}...N_{\alpha_n} \rangle$ of increasing order /12/. If we start with the many-body Hamiltonian, obtaining a similar result is not possible. Now we have many new higher-order GF's for which new functions appear. In such a case, in our recent work /12/ we have used the approximation which can be compared with the Bogolubov-Tyablikov decoupling (see, for example /16/)

$$\langle\langle N_\alpha N_{\alpha_1}...N_{\alpha_i} a_{\alpha_i\sigma} n_{\alpha_i-\sigma} | N_\beta a_{\beta\sigma}^+ \rangle\rangle \approx \frac{\langle N_{\alpha_i} n_{\alpha_i-\sigma}\rangle}{\theta} \langle\langle N_\alpha N_{\alpha_1}...N_{\alpha_i} a_{\alpha_i\sigma} | N_\beta a_{\beta\sigma}^+ \rangle\rangle .$$

(2)

Also, a similar decoupling scheme was used in our investigations of the chemisorption phenomena within the matrix self-energy formalism exact to second order in the hybridization matrix elements $V_{\alpha k}$ /13,15/. In all the cases mentioned above the Ising type correlators were calculated by the Kirkwood superposition formula (see, for example /11,17/)

$$\langle N_\alpha N_{\alpha_1}.....N_{\alpha_n}\rangle \approx \langle N_\alpha N_{\alpha_1}\rangle\langle N_{\alpha_1} N_{\alpha_2}\rangle .....\langle N_{\alpha_{n-1}} N_{\alpha_n}\rangle/\theta^{n-1}$$

(3)

and, as a next step, the Bragg-Williams /17/ approximation for the correlator $\langle N_\alpha N_\beta\rangle$ was used

$$\langle N_\alpha N_\beta\rangle \approx \delta_{\alpha\beta}\langle N_\alpha\rangle + (1-\delta_{\alpha\beta})\langle N_\alpha\rangle\langle N_\beta\rangle .$$

(4)

This approximation implies that we have neglected the possible correlated distribution of the adatoms on the substrate surface. In this way, our calculations should be comparable with those done within the single-site CPA /2,3,4/. As it is well known, CPA gives us self-consistent equations for the self-energy (this function describes the effect of

disorder in the adatom distribution on the electron motion).
The solution of these equations guarantees that any electron
scattering in the assumed average medium does not take
place. Unfortunately, CPA theory, especially when one is
trying to include the electron correlation effects, is
complicated and requires relatively great numerical efforts
to find their solutions. On the other hand, our treatment of
the adatom disorder looks very simple and can serve as an
efficient method for that kind of investigations.

The purpose of this work is not to present the formal
proof of equivalency between the method described above
which takes into consideration the adatom chaotic distribu-
tion on the substrate surface and the coherent potential
approximation adopted to the chemisorption problems. Instead
of this we are going to compare the numerical results
obtained within these two approaches.

There are only a few papers to be quoted as closely
related to the problem we are going to discuss. Here, we
will compare our results with those presented in papers of
Tsukada /2/ and Kudrnovsky and Velicky /3/ (cf. /4/). We
adopt more simple version of the model Hamiltonian than pre-
sented in Eq.(1), namely

$$H = \sum_{k\sigma} \varepsilon_k n_{k\sigma} + \sum_{\alpha\sigma} N_\alpha \left\{ E_\alpha n_{A\sigma} + \frac{U}{2} n_{\alpha\sigma} n_{\alpha-\sigma} + \sum_k V_{\alpha k} a^+_{\alpha\sigma} a_{k\sigma} + h.c \right\} +$$

$$+ \sum_{\substack{\alpha\neq\beta \\ \sigma}} N_\alpha N_\beta a^+_{\alpha\sigma} a_{\beta\sigma} E_{\alpha\beta} .$$

(5)

We have decided to work with that Hamiltonian mainly to
make our results most compatible with the results of papers
/2,3/. On the other hand, all parameters present in the
Hamiltonian (5) can be seen as some effective one and may
represent in the mean-field approximation, to some extent,
the rejected terms of the model (1). For example, the elec-
tron correlations on the adatom can be included in the

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Hartree-Fock approximation through the spin dependent parameter E_σ /9,14/

$$E_\sigma = E_\alpha + U \langle N_\alpha n_{\alpha-\sigma} \rangle / \theta - \zeta \sum_k \left[V_{\alpha k} \langle N_\alpha a^+_{\alpha\sigma} a_{k\sigma} \rangle / \theta + h.c \right] \qquad (6)$$

and in this case E_σ should be self-consistently adjusted during the calculations. The parameter ζ, $0 \leq \zeta \leq 1$, appears in Eq.(6) because of the approximation of the matrix element $V_{\alpha\alpha\alpha k}$ in the form $V_{\alpha\alpha\alpha k} \approx \zeta V_{\alpha k}$ (for details, see Refs./7,8/). The so-called dynamical hopping in the second term of (1) can be taken into consideration by replacing $V_{\alpha k}$ in (5) by the expression /14/

$$V^\sigma_{\alpha k} = \left[1 - \zeta \langle N_\alpha n_{\alpha-\sigma} \rangle / \theta \right] V_{\alpha k} .$$

In this case $V^\sigma_{\alpha k}$ should be found in a self-consistent way, too.

We consider the model in which the term describing the metallization of the adatom layer is represented by the last term in Eq.(2). The general form of the matrix element $E_{\alpha\beta}$ is given in Ref./7/ and here we identify it simply with the hopping integral between the α-th and β-th chemisorption sites. Thus, our model allows for the so-called indirect interaction between the chemisorbed adatoms (through the substrate electron subsystem), as well as for a direct interaction. For hydrogen chemisorption on the transition metal substrates, in our opinion, the role of this direct interaction is rather small (see, e.g./19/), and here we consider this additional interaction in the Hamiltonian only for the sake of comparison with Ref./3/.

3. The one-particle adatom Green Function

Writing down the equation of motion for the Green Functions $\langle\langle N_\alpha a_{\alpha\sigma} | N_\beta a^+_{\beta\sigma} \rangle\rangle, \ldots, \langle\langle N_\alpha N_{\alpha_1} \cdots N_{\alpha_i} a_{\alpha_i\sigma} | \cdots \rangle\rangle, \langle\langle N_\alpha a_{k\sigma} | \cdots \rangle\rangle, \langle\langle N_\alpha N_{\alpha_1} \cdots N_{\alpha_i} a_{k\sigma} | \cdots \rangle\rangle$

$$E \langle\langle N_\alpha a_{\alpha\sigma} | N_\beta a^+_{\beta\sigma} \rangle\rangle = \delta_{\alpha\beta}\langle N_\alpha N_\beta \rangle + \sum_{\alpha_1} E_{\alpha\alpha_1} \langle\langle N_\alpha N_{\alpha_1} a_{\alpha_1\sigma} | \cdots \rangle\rangle +$$

$$+ \sum_k V_{\alpha k} \langle\langle N_\alpha a_{k\sigma} | \cdots \rangle\rangle .$$

$$\vdots$$

$$E \langle\langle N_\alpha N_{\alpha_1} \cdots N_{\alpha_i} a_{\alpha_i\sigma} | \cdots \rangle\rangle = \delta_{\alpha\beta}\langle N_\alpha N_{\alpha_1} \cdots N_{\alpha_i} N_\beta \rangle + \sum_{\alpha_{i+1}} E_{\alpha_i \alpha_{i+1}} \times$$

$$\times \langle\langle N_\alpha N_{\alpha_1} \cdots N_{\alpha_{i+1}} a_{\alpha_{i+1}\sigma} | \cdots \rangle\rangle + \sum_k V_{\alpha_i k} \langle\langle N_\alpha N_{\alpha_1} \cdots N_{\alpha_i} a_{k\sigma} | \cdots \rangle\rangle .$$

$$(7)$$

$$(E - \varepsilon_k) \langle\langle N_\alpha a_{k\sigma} | \cdots \rangle\rangle = \sum_{\alpha_1} V^*_{\alpha_1 \vec{k}} \langle\langle N_\alpha N_{\alpha_1} a_{\alpha_1\sigma} | \cdots \rangle\rangle$$

$$\vdots$$

$$(E - \varepsilon_k) \langle\langle N_\alpha N_{\alpha_1} \cdots N_{\alpha_i} a_{k\sigma} | \cdots \rangle\rangle = \sum_{\alpha_{i+1}} V^*_{\alpha_1 \vec{k}} \langle\langle N_\alpha N_{\alpha_1} \cdots N_{\alpha_{i+1}} a_{\alpha_{i+1}\sigma} | \cdots \rangle\rangle$$

one can find the solution for the required one-particle Green Function $\langle\langle N_\alpha a_{\alpha\sigma} | N_\beta a^+_{\beta\sigma} \rangle\rangle$ in the form

$$E \langle\langle N_\alpha a_{\alpha\sigma} | N_\beta a^+_{\beta\sigma} \rangle\rangle = \delta_{\alpha\beta}\langle N_\alpha N_\beta \rangle + \frac{Q_{\alpha\beta}\langle N_\alpha N_\beta)}{E} +$$

$$+ \sum_{n=1}^{\infty} \sum_{\alpha_1 \cdots \alpha_n} \frac{P_{\alpha\alpha_1}(E) \cdots P_{\alpha_n \beta}(E)}{E^{n+1}} \langle N_\alpha N_{\alpha_1} \cdots N_{\alpha_n} N_\beta \rangle , \qquad (8)$$

where

$$Q_{\alpha\beta} = E_{\alpha\beta} + \sum_k \frac{V_{\alpha k} V_{k\beta}}{E - \varepsilon_k} \equiv E_{\alpha\beta} + P_{\alpha\beta} . \qquad (9)$$

Formula (8) represents the exact expression for the required Green Function $\langle\langle N_\alpha a_{\alpha\sigma} | N_\beta a^+_{\beta\sigma} \rangle\rangle$ but contains the higher-order correlation functions which cannot be calculated exactly. The series can be summed up if the higher-order Ising-type correlators are approximated in the spirit of the Kirkwood

superposition formula (3). One then obtains

$$\langle\langle N_\alpha a_{\alpha\sigma} | a^+_{\alpha\sigma}\rangle\rangle = \frac{1}{N} \sum_q e^{iq(\alpha-\beta)} \frac{\theta}{E - \overline{Q}_q(E)} \tag{10}$$

where

$$\overline{Q}_q(E) = \frac{1}{N} \sum_{\alpha\beta} e^{-iq(\alpha-\beta)} \frac{Q_{\alpha\beta}(E)\langle N_\alpha N_\beta\rangle}{\theta} \tag{11}$$

and q denotes a two-dimensional wave vector lying in the first Brillouin zone of the reciprocal lattice corresponding to the adsorption centers. Finally, using the Bragg-Williams approximation (4) for the correlator $\langle N_\alpha N_\beta\rangle$ we get

$$\langle\langle N_\alpha a_{\alpha\sigma} | a^+_{\alpha\sigma}\rangle\rangle = \frac{1}{N} \sum_q e^{iq(\alpha-\beta)} \theta \left[E - E_\alpha - (1-\theta)\Lambda(E) - \theta(P_q(E) + E_q) \right]^{-1} \tag{12}$$

where

$$E_q = \frac{1}{N} \sum_{\alpha\beta}^{\alpha\neq\beta} e^{-iq(\alpha-\beta)} E_{\alpha\beta} .$$

The function $P_q(E)$ is a Fourier transform of $P_{\alpha\beta}(E)$ and $\Lambda(E) = P_{\alpha\alpha}(E)$. This form of GF should be compared with the Hartree-Fock result for the Hamiltonian (5) (without the direct interaction term but with inclusion of the Coulomb repulsion between two electrons of opposite spins located on the same adatom) which differs from (12) only by the function E_q (but with the convention that E_α in (12) denotes an effective level E_α —see Eq.(6)) /10,11/. Based on the above considerations, we can say that the results obtained using the Hamiltonian (5) with the terms corresponding to the direct interactions between adatoms included can be restored using a model without these interactions but with an energy-dependent renormalization of the matrix elements $V_{\alpha k}$.

4. Numerical results

To compare the results obtained in our approach with

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the results of Refs./2,3/ we have taken the same numerical
values for the parameters present in the model. Thus, as a
first step we have used a following ansatz for the substrate
electronic structure

$$-\frac{1}{\pi} \text{Im} \frac{1}{N_\parallel} \sum_q \frac{1}{E^+ - E_\parallel(q)} = \begin{cases} \Delta/2 & \text{for } |E| \leq \Delta \\ 0 & \text{for } |E| > \Delta \end{cases} \tag{13}$$

and

$$-\frac{1}{\pi} \text{Im} \frac{1}{N_\perp} \sum_{k_z} \frac{1}{E^+ - E_\perp(k_z)} = \frac{1}{\pi} \frac{\Gamma}{E^2 + \Gamma^2}, \quad \varepsilon_k = E_\parallel(q) + E_\perp(k_z) \tag{14}$$

as it was done in Ref./2/.

In the following, we have computed the adatom local
density of states, the adatom electron charge and the chemi-
sorption energy. All the results were calculated for a
vanishing value of the direct interaction (as in /2/). Our
results confirm those given in Ref./2/ for the adatom local
density of states curves, even with all details. Once we
have shown the equivalence between CPA and our treatments of
the chemisorbed layer problem (but with vanishing direct
interactions among adatoms), it should be interesting to
check whether all the properties of the solutions obtained
for artificial band structure, see Eqs.(12,13), can be again
confirmed for realistic situations. For that reason, we cal-
culated $P_q(E)$ as follows:

$$P_q(E) = \frac{1}{N} \sum_{\alpha\beta k} \frac{V_{\alpha k} V_{k\beta} e^{-iq(\alpha-\beta)}}{E - \varepsilon_k} = N \sum_{k_z} \frac{|V_{\alpha q k_z}|^2}{E - \varepsilon_{q k_z}} = \gamma_q(E) - i\eta_q(E) \tag{15}$$

where $\eta_q(E) = \pi N \sum_{k_z} |V_{\alpha q k_z}|^2 \delta(E - \varepsilon_{q k_z})$

and $\gamma_q(E)$ is its Hilbert transform. Assuming a chemisorption
on a simple cubic substrate lattice we have taken $\varepsilon_{q k_z}$ in
the form

$$\varepsilon_{q k_z} \approx \cos(q_x a) + \cos(q_y a) + \cos(k_z a)$$

and, similarly as in the Newns paper /18/

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$$V_{\alpha q k_z} \approx V \, e^{i q R_\parallel} \sin k_z a \, .$$

In this way, we have obtained the surface (substrate) density of states in a more realistic form (as in Ref./4/) than a rectangular shape assumed in /3/, Eq.(15).

Our results are presented in Figs. (1-5). Figures (1-3) should be compared with those in Ref./2/ and Figs. (4,5) with the results of Ref./3/. As in Ref. /2/, the calculations were done for zero values of the direct interaction so in order to compare our results with results given in Ref./2/ we also have taken $E_{\alpha\beta}=0$ for $\alpha\neq\beta$. In Fig. (1) we have shown the adatom density of states calculated for increasing values of V for three values of the coverage. The parameter values to be taken in units of the half-width of the substrate energy band. The main conclusions resulting from these Figure are as follows (compare with /3/). For a weak coupling between the adatom and the substrate metal there appears a single peak of the adatom density of states for small values of the coverage. As the coverage increases, this single peak splits into two peaks and this splitting is more and more pronounced with increasing coveraging. For a case of larger values of the coupling V there are two peaks of the adatom density of states at every coverage and the influence of increasing coverage is clearly visible. The peaks shift inwards and the minimum of the adatom density of states between these peaks deepens. The peak heights become larger (with increasing coverage) for high-energy peaks and smaller for low-energy peaks. Only in this point these results differ from the corresponding one calculated by using Eqs.(13,14); namely, in a latter case the peak heights become larger for both peaks. In general, we can say that the considered approximations of the substrate electronic structure influence the results only in minor details. The same can be said about other characteristics, i.e. about the adatom electron charge and chemisorption energy. In Fig. (2) we present the adatom electron charge vs. coverage for the
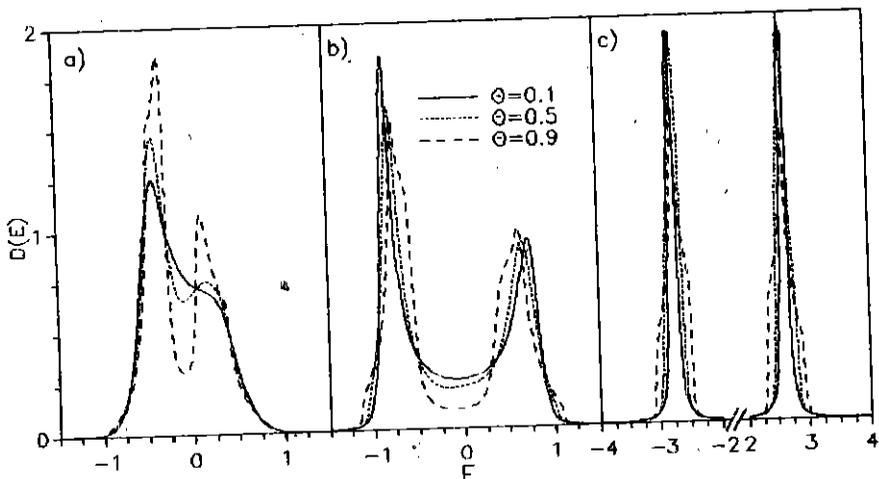
Fig.1.— The adatom density of states calculated by using
the cubium (100) surface density of states for
$V = \sqrt{0.9}$, 1 and 4 (in units of half band width)
respectively, for differents rates of the
coverage.
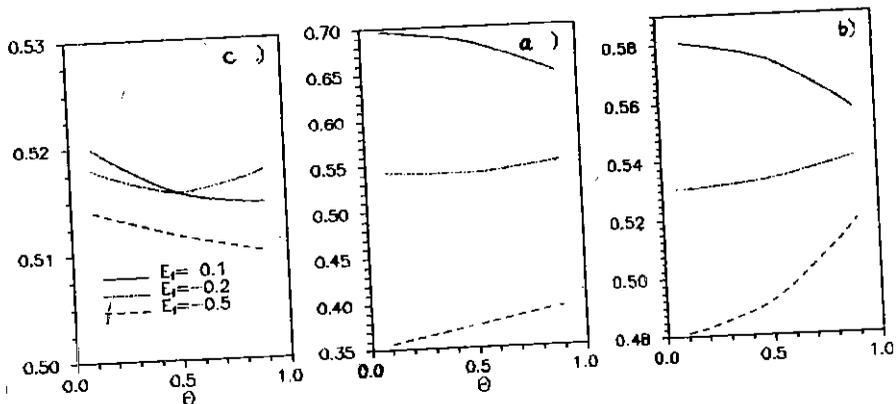
Fig.2.—The coverage dependence of the adatom occupation
number for diferent values of the Fermi level.
The parameter values correspond to those of Fig.
(1).

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parameters corresponding to Figs. (1), for three values of the Fermi level position. In Fig. (3) we shown the chemisorption energy vs. coverage for the parameters values corresponding to Figs. (1a and 1b), respectively.

In Fig. (4) we depict the adatom density of states calculated for the parameters taken from Ref./3/ for vanishing and nonvanishing values of the direct interaction. respectively. The adatom density of states has a double-peaked structure due to strong adatom-substrate coupling. These bonding and antibonding peaks are broadened and shifted inwards. We should like to note a very small value of the density of states between two peaks for the monolayer coverage, as well as, the double-peaked structure of each of the main high- and low-energy lying peaks. Even these details of the density of states are in agreement with the calculations of Ref./3/. Fig. (4b) shows the adatom density of states for the same parameters as in Fig. (4a) but with the direct interaction between adatoms included. One can observe, in comparison with Fig. (4a), a significant broadening of the main peaks. This effect is most pronounced for the case of monolayer coverage. Note that for a coverage equal to 0.5 there are rather small differences between curves displayed in Fig. (4a) $(E_{\alpha\beta}=0)$ and Fig. (4b) $(E_{\alpha\beta}\neq0)$. For that reason, it is justified to ignore the direct interactions for coverages smaller than approximately equal to 0.7, even for sufficiently large values of these interactions. Comparing our results, Figs. (4a,4b), with the results of Ref./3/-case A, one can observe only small differences in a shape of the adatom density of states for the monolayer coverage for the case of a nonvanishing direct interaction. These differences of minor importance can arise because in our calculations we have simulated a finite life-time for the metal electron states - see e.g. /20/.

In conclusion, the electronic structure of the chemisorbed submonolayer and the chemisorption energy calculated within the composite Hamiltonian method with the Bragg-
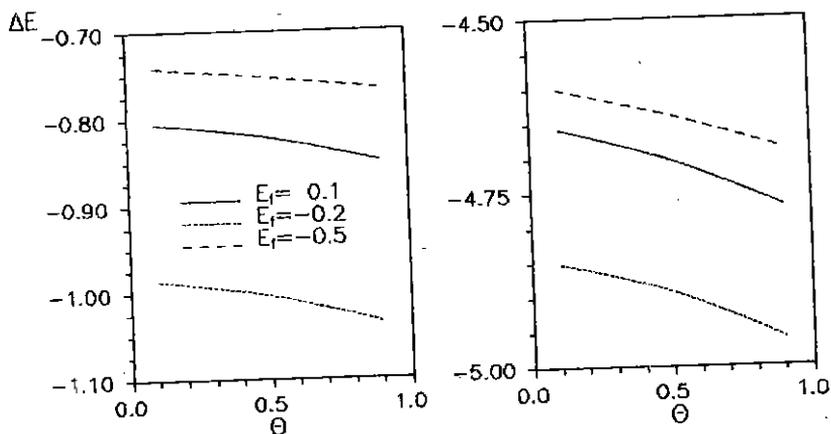
Fig.3.-The coverage dependence of the chemisorption energy (in half band width units) for parameters corresponding to Fig. (1b) and (1c), respectively.
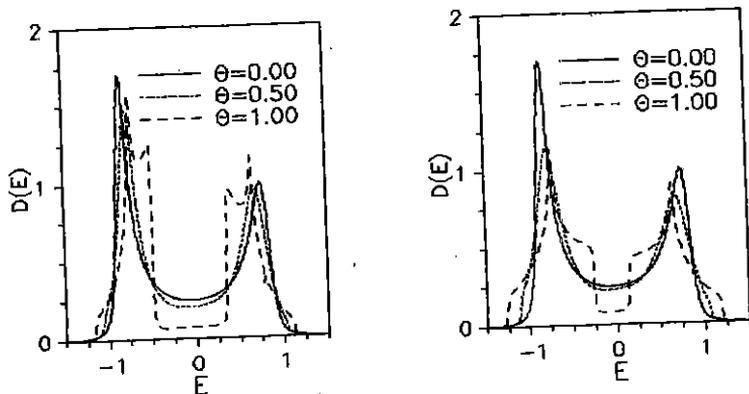
Fig.4.- The adatom density of states calculated using the cubium (100) surface density of states without (left panel) and with (right panel) direct interactions between adatoms. The parameters values are taken from Ref./3/.

Williams approximation for the Ising type correlation functions are in very good agreement with those obtained within the coherent potential approximation. Our method can be very useful especially when one is trying to include the electron correlation effects /15/ and seems to be sufficiently simple to include also spatial correlations in the adatom distribution on the substrate surface.

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