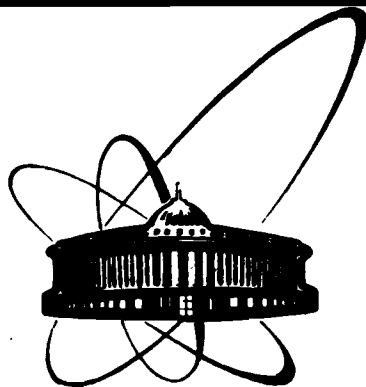


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CHEMISORPTION AT FINITE SUBMONOLAYER  
COVERAGES: INFLUENCE OF THE ELECTRON  
CORRELATION EFFECTS

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## 1. INTRODUCTION

The literature on chemisorption theory can be roughly divided into three classes depending on methods used in calculations of various chemisorption characteristics. These are the density functional theory and its local approximation [1], the cluster methods consisting of the quantum chemistry methods and the model Hamiltonian methods (see, for example [2]). Especially, the method of model Hamiltonians can be well suited for better understanding and not only for reproducing the experimentally observed features. In recent years there has been a considerable amount of works dealing with semiphenomenological calculations on the basis of the Anderson-News Hamiltonian within the Hartree-Fock approximation (see, for example [3]). In most of these papers the case of one adatom on a surface was considered. Nevertheless, the description of the coverage dependence of the properties of chemisorbed overlayers is very interesting, both from theoretical and practical point of view. For the first time, the chemisorbed overlayer problem was investigated within the local density functional method [4]. Despite many successes gained within this method some problems have not been solved (see, for example [2]). In addition, as a rule, the density functional theory involves a large amount of computer calculations. The chemisorbed overlayers can be treated also for model Hamiltonians within the coherent potential approximation generalized to these systems (see, for example [5]). However, there are great difficulties within this method when one is going to take into account the many-body effects due to the correlations in the electronic and ionic (adatoms) components of the chemisorbed overlayer.

In the present paper, the problem of many adatoms simultaneously existing on a surface (up to the coverage equal to unity) and correlation effects treated beyond the Hartree-Fock approximation are investigated within the model Hamiltonian method. A simple model Hamiltonian is derived from the general one which has recently been obtained by us from microscopic considerations [6-8]. The electron correlation effects are included (up to second order in  $V$  - the single particle hopping strength between the adatom and the substrate atom) within the second-order self-energy matrix formalism of Brenig and

Schönhammer [9]. In view of the growing wealth of the photoemission data, emphasis is laid on the electronic structure of a chemisorbed atom and a charge localized at an adatom rather than on the binding energy.

The paper is organized as follows. In the section 2 we give the approximate model Hamiltonian intended to describe the chemisorbed hydrogen overlayer on a model transition metal surface. In the section 3 we present the formulas for the adatom Green function obtained beyond the Hartree-Fock approximation and discuss the approximations introduced during its derivation. Section 4 contains the numerical results obtained for the adatom charge and adatom local density of states for a system modeling the hydrogen chemisorption on Ti and Ni surfaces.

## 2. Hamiltonian

Recently, we have derived from the microscopic considerations the Hamiltonian intended to describe the system of adatoms located on the metal surface [6-8]. The most important part of this Hamiltonian is as follows:

$$H = \sum_{k\sigma} \epsilon_k n_{k\sigma} + \sum_{\alpha\sigma} N_{\alpha} \left\{ \epsilon_{\alpha} n_{\alpha\sigma} + \frac{U}{2} n_{\alpha\sigma} n_{\alpha-\sigma} - \sum_k \left[ (v_{\alpha\alpha k} n_{\alpha-\sigma} - v_{\alpha k}) a_{\alpha\sigma}^{\dagger} a_{k\sigma} + \text{h.c.} \right] \right\} + \sum_{\substack{\alpha\beta \\ \alpha\beta k k' \sigma \sigma'}} v_{\alpha\beta k k'} N_{\alpha} N_{\beta} a_{\alpha\sigma}^{\dagger} a_{k\sigma}^{\dagger} a_{\beta\sigma} a_{k'\sigma} + R \quad (1)$$

The Hamiltonian in the form presented above contains the contributions which play the most important role in describing the electronic properties of adlayers. The other terms not written explicitly here are contained in R and involve processes which are not usually considered in simple chemisorption models. These terms describe the interaction of the valence adatom electrons with the redistributed charge cloud in the substrate metal induced by the adatom electrons themselves, effects connected with the correlations between adatom charge fluctuations and the redistributed substrate charge density and others effects of much high order (for detailed see Refs. [6,7]). The interaction constants  $v_{\alpha k}$ ,  $v_{\alpha\alpha k'}$ , and  $v_{\alpha\beta k k'}$  are the appropriate matrix elements calculated over the valence adatom orbitals and wave functions

of electrons in a pure substrate [6,7]. When we consider only a single adatom localized at the adsorption center  $\alpha$  and neglect the last two terms, we come to the well known Anderson model (firstly introduced in the chemisorption theory by Edwards and Newns [10] and Grimley [11]) but with the additional term describing the influence of the occupation of the adatom level on the hybridization of the adatom and substrate electron wave functions [8]. In this paper, we want to describe the properties of the chemisorbed layers - the charge distribution and the density of states on the adatom - with general coverages beyond the mean field description (cf. Refs. [12-13]). Having in mind such a complicated system we restrict ourselves in the first step to the simplest case, namely, we consider the Hamiltonian (it is a generalization of the Anderson-Newns Hamiltonian):

$$H = \sum_{k\sigma} \epsilon_k n_{k\sigma} + \sum_{\alpha\sigma} \epsilon_{\alpha} N_{\alpha} n_{\alpha\sigma} + \frac{U}{2} \sum_{\alpha\sigma} N_{\alpha} n_{\alpha\sigma} n_{\alpha-\sigma} + \sum_{\alpha k\sigma} v_{\alpha k} N_{\alpha} a_{\alpha\sigma}^{\dagger} a_{k\sigma} + \text{h.c.} \quad (2)$$

Here we consider a plane metal surface composed of N atomic sites with  $N_A$  adsorbed hydrogen-like atoms (adatoms) which are distributed in a completely random way over these N active centers of the crystal substrate surface. The summation over  $\alpha$  is carried out over all adsorption centers and the operator  $N_{\alpha} = c_{\alpha}^{\dagger} c_{\alpha}$  has an eigenvalue equal to 1 or 0 depending on whether the adatom is (or not) present in the adsorption center. The operators  $c_{\alpha}^{\dagger}$ ,  $c_{\alpha}$  are the creation and annihilation of the adsorbed adatom (ion) at the center  $\alpha$ . We consider only the case when there is no more than one adatom ion in each adsorption center and all effects connected with its migration and other degrees of freedom are neglected. The other parameters present in formulas (1) and (2) are the usual parameters of the Anderson-Newns Hamiltonian. At complete monolayer coverage the adatoms form a two-dimensional lattice with the periodicity commensurate with that of the substrate surface. For the coverages less than unity the two-dimensional chemisorbed layer is considered as a substitutional alloy composed of two types of species, i.e. adatoms and vacancies. All the adatom properties connected with its position on the substrate surface are involved in correlators of the Ising type  $\langle N_{\alpha} \rangle$ ,  $\langle N_{\alpha} N_{\beta} \rangle$ , ... Here, we shall use the Bragg-Williams approximation for these correlators, and for example,  $\langle N_{\alpha} N_{\beta} \rangle$  takes the form

$$\langle N_{\alpha} N_{\beta} \rangle \cong \delta_{\alpha\beta} \langle N_{\alpha} \rangle + (1 - \delta_{\alpha\beta}) \langle N_{\alpha} \rangle \langle N_{\beta} \rangle \quad (3)$$

where the equality  $N_{\alpha}^2 = N_{\alpha}$  was used.

Also, at the end of our calculations we use the correlators  $\langle N_{\alpha} n_{\alpha\sigma} \rangle / \langle N_{\alpha} \rangle$  rather than  $\langle n_{\alpha\sigma} \rangle$  in order to interpret them as a conditional probability of finding an electron with spin  $\sigma$  at the adsorption center when this center is already occupied by the adatom ion [12,13]. Though the Hamiltonian (2) is linear with respect to the operator  $N_{\alpha}$  (in the opposite case to the Hamiltonian (1)) it is not equivalent to the ideal lattice gas model because of the hopping interaction  $V_{\alpha k}$ . This interaction describes the adsorbate-substrate electron transfer and induces an indirect interaction between adatoms when the adatoms exchange electrons through the substrate. This interaction can be compared, to some extent, to an analogous interaction between magnetic impurities in metals - the so-called Rudermann-Kittel interaction. We suppose, the Hamiltonian (2) can describe the system adlayer-substrate for all rates of coverages. This is confirmed by the investigations performed in Ref. [14] (see also [15-17]) where it has been shown that, for example, for hydrogen's adsorption on platinum-like substrates the direct interaction between adatoms is not so important (even for coverages equal to unity). This phenomenon can be explained by a small hydrogen's atom radius in comparison with the lattice constant of the substrate metal, as well as, by a small adatom's charge (almost neutral adatoms) and the commensurate with the substrate adlayer surface structure [15]. The terms of the Hamiltonian, which correspond to the direct interactions between adatoms, play an essential role in the case of 5d adatoms [18]. As we are going to study the simplest chemisorption system, namely, the hydrogen-like atoms chemisorbed on the metal surface, neglecting of the third term in Hamiltonian (1) is fully justified.

### 3. Theory

In the current literature many attempts were made to take into account the Coulomb correlations in the Anderson-Newns model. Here, we are going along the line described in Ref. [9] with application to one adatom chemisorbed on the substrate surface (see also Ref. [16] for two adatoms on a surface and Ref. [19] for one adatom but for generalized Hamiltonian (1) without two last terms, and References quoted therein).

We shall work with the double time retarded Green functions intro-

duced by Zubarev [20] and for our purposes it is sufficient to consider the adsorbate Green function

$$\langle N_{\alpha} a_{\alpha\sigma}(t) | N_{\beta} a_{\beta\sigma}^{\dagger}(t') \rangle \equiv -i\theta(t-t') \langle [N_{\alpha} a_{\alpha\sigma}(t), N_{\beta} a_{\beta\sigma}^{\dagger}(t')] \rangle_{+} \quad (4)$$

where  $\theta(t)$  is the step function, unity for positive and zero for negative value of time,  $\langle \dots \rangle$  denotes a statistical average with the time independent Hamiltonian (2) within the grand canonical ensemble and operators are written in the Heisenberg picture. Most of the relevant information can be deduced from the knowledge of this function. In the following, we shall use the operators similar to that introduced by Hubbard [21], namely

$$\psi_{+, \sigma}^{\alpha} = N_{\alpha} a_{\alpha\sigma} n_{\alpha-\sigma}^{(+)} \equiv N_{\alpha} a_{\alpha\sigma} n_{\alpha-\sigma}, \quad \psi_{-, \sigma}^{\alpha} = N_{\alpha} a_{\alpha\sigma} (1 - n_{\alpha-\sigma}) \equiv N_{\alpha} a_{\alpha\sigma} n_{\alpha-\sigma}^{(-)}, \quad (5)$$

or in the matrix form

$$\psi_{\sigma}^{\alpha} = \begin{pmatrix} \psi_{+, \sigma}^{\alpha} \\ \psi_{-, \sigma}^{\alpha} \end{pmatrix}. \quad (6)$$

Why these operators are more suitable for our consideration has been explained, for example, in Ref. [9] by Brenig and Schönhammer. We can only shortly explain the main ideas of their approach. It is well-known that for a limiting case  $V=0, U \neq 0, \theta \langle n_{\alpha-\sigma} \rangle = 0$  one has for the Fourier transform of  $\langle a_{\alpha\sigma}(t) | a_{\alpha\sigma}^{\dagger}(t') \rangle$  a solution of the form

$$\langle a_{\alpha\sigma} | a_{\alpha\sigma}^{\dagger} \rangle_{E^{+}}^{(0)} = \frac{\langle n_{\alpha-\sigma} \rangle}{E^{+} - \epsilon_{\alpha} - U} + \frac{1 - \langle n_{\alpha-\sigma} \rangle}{E^{+} - \epsilon_{\alpha}}. \quad (7)$$

The spectral function of this solution possesses two delta functions corresponding to the propagation of an extra electron (or hole) in the system [9]. What one expects on the physical grounds is a broadening of this sharp structure after switching on the interaction  $V$  between the adatom and the substrate metal. It is very hard to obtain such a double peaked structure from simple pole free self-energy defined as  $\langle a_{\alpha\sigma} | a_{\alpha\sigma}^{\dagger} \rangle_{E^{+}} = (E^{+} - \epsilon_{\alpha} - \Sigma(E))^{-1}$  [9]. On the other hand, the zeroth-order Green function built up on operators (5) has only one pole term and even very simple self-energy expression (in a "space" of the Hubbard operators) can reproduce the double peaked structure.

Following this method we have after the differentiation over the

left-hand side time argument (and after doing the Fourier transform):

$$(E - \varepsilon_{\alpha'}) g_{\alpha'\beta'}^{\alpha\beta}(E) = A_{\sigma}^{\alpha\beta} + \langle \langle \varphi_{\alpha'\sigma}^{\alpha}(t) | \psi_{\beta'\sigma}^{\beta*}(t') \rangle \rangle \quad (8)$$

where we have introduced the matrix Green function  $g_{\alpha'\beta'}^{\alpha\beta}(t)$  (in a space of indices  $(\alpha'\beta')$ ,  $\alpha', \beta' = +, -$ ) as follows:

$$\langle \langle N_{\alpha} a_{\alpha\sigma}(t) | N_{\beta} a_{\beta\sigma}^*(t') \rangle \rangle \equiv \sum_{\alpha'\beta' = +, -} \langle \langle \varphi_{\alpha'\sigma}^{\alpha}(t) | \psi_{\beta'\sigma}^{\beta*}(t') \rangle \rangle \equiv \sum_{\alpha'\beta' = +, -} g_{\alpha'\beta'}^{\alpha\beta}(t-t'). \quad (9)$$

In the following we denote the adsorption centers as  $\alpha, \beta, \gamma, \dots$ , and  $\alpha', \beta', \gamma', \dots$  will denote the signs + or - (see definition (5)). The matrices  $A_{\sigma}^{\alpha\beta}$  and  $h$  (in the space of indices  $\alpha', \beta'$ ) are defined as:

$$A_{\sigma}^{\alpha\beta} = \delta_{\alpha\beta} \begin{pmatrix} \langle N_{\alpha} n_{\alpha-\sigma} \rangle & 0 \\ 0 & \langle N_{\alpha} (1-n_{\alpha-\sigma}) \rangle \end{pmatrix}, \quad (10)$$

$$h = \begin{pmatrix} \varepsilon_{\alpha} + U & 0 \\ 0 & \varepsilon_{\alpha} \end{pmatrix}, \quad A^{\sigma} = \begin{pmatrix} \langle n_{\alpha-\sigma} \rangle & 0 \\ 0 & 1 - \langle n_{\alpha-\sigma} \rangle \end{pmatrix}.$$

The operators  $\varphi_{\alpha'\sigma}^{\alpha}$  are defined in the following way:

$$\varphi_{+, \sigma}^{\alpha} = \sum_{k\sigma} N_{\alpha} \left[ v_{\alpha k} a_{k\sigma} n_{\alpha-\sigma} + v_{\alpha k} a_{\alpha\sigma} a_{\alpha-\sigma}^+ a_{k-\sigma} - v_{\alpha k}^* a_{k-\sigma}^+ a_{\alpha-\sigma} a_{\alpha\sigma} \right] \equiv \sum_{i=1}^3 \varphi_{+, \sigma}^{(i)\alpha} \quad (11)$$

$$\varphi_{-, \sigma}^{\alpha} = \sum_{k\sigma} N_{\alpha} \left[ v_{\alpha k} (1-n_{\alpha-\sigma}) a_{k\sigma} - v_{\alpha k} a_{\alpha\sigma} a_{\alpha-\sigma}^+ a_{k-\sigma} + v_{\alpha k}^* a_{k-\sigma}^+ a_{\alpha-\sigma} a_{\alpha\sigma} \right] \equiv \sum_{i=1}^3 \varphi_{-, \sigma}^{(i)\alpha} \quad (12)$$

or in the matrix form as

$$\varphi_{\sigma}^{\alpha} = \begin{pmatrix} \varphi_{+, \sigma}^{\alpha} \\ \varphi_{-, \sigma}^{\alpha} \end{pmatrix}. \quad (13)$$

In the next step, using Eq.(8) and the equation of motion obtained after the differentiation over the right-hand side time argument, we

obtain (in the matrix form)

$$[(E-h) \langle \langle \varphi_{\sigma}^{\alpha} | \psi_{\sigma}^{\beta*} \rangle \rangle - A_{\sigma}^{\alpha\beta}] (E-h) = \langle \langle \varphi_{\sigma}^{\alpha}, \psi_{\sigma}^{\beta*} \rangle \rangle + \langle \langle \varphi_{\sigma}^{\alpha} | \psi_{\sigma}^{\beta*} \rangle \rangle \quad (14)$$

Introducing the self-energy (or rather its  $q$ -Fourier transform) through the equation

$$g_{\sigma}(q, E) = g_{\sigma}^{\circ}(q, E) + g_{\sigma}^{\circ}(q, E) M_{\sigma}(q, E) g_{\sigma}(q, E), \quad (15)$$

where the zeroth-order Green function  $g_{\sigma}^{\circ}(q, E)$  reads as

$$g_{\sigma}^{\circ}(q, E) = \begin{pmatrix} \frac{\langle N_{\alpha} n_{\alpha-\sigma} \rangle}{E - \varepsilon_{\alpha}} & 0 \\ 0 & \frac{\langle N_{\alpha} (1-n_{\alpha-\sigma}) \rangle}{E - \varepsilon_{\alpha}} \end{pmatrix}, \quad (16)$$

one can express the Green function  $g_{\sigma}(q, E)$  in the form (cf. [9]):

$$g_{\sigma}(q, E) = A_{\sigma} \left[ (E-h) A_{\sigma} - A_{\sigma} M_{\sigma}(q, E) A_{\sigma} \right]^{-1} A_{\sigma}. \quad (17)$$

Here, the Fourier transforms were introduced by equation like this

$$g_{\sigma}(q, E) = \frac{1}{N} \sum_{\alpha\beta} e^{iq(\alpha-\beta)} g_{\sigma}^{\alpha\beta}(q, E) \quad (18)$$

where  $N$  denotes the number of adsorption centers and the indices  $\alpha, \beta$  in the exponent mean the position of these centers. Finally, the self-energy can be written as

$$M_{\sigma}(q, E) = \frac{1}{N} \sum_{\alpha\beta} e^{iq(\alpha-\beta)} A_{\sigma}^{-1} \left[ \langle \langle \varphi_{\sigma}^{\alpha}, \psi_{\sigma}^{\beta*} \rangle \rangle + \langle \langle \varphi_{\sigma}^{\alpha} | \psi_{\sigma}^{\beta*} \rangle \rangle \right] A_{\sigma}^{-1}. \quad (19)$$

It can be shown that the lowest order term in  $M_{\sigma}(q, E)$  is proportional to  $V^2$  [4] and in our further considerations we confine ourselves to evaluation of the self-energy up to second-order in  $V$ . First of all, let us calculate the expectation value of the anticommutator function standing on the right-hand side of Eq. (19). Since we are interested in calculation of the self-energy exact to second-order in  $V$ , we have to calculate the expectation values of all operators  $\psi_{\alpha'\sigma}^{\alpha+} a_{k\sigma}$  and  $\psi_{\alpha'\sigma}^{\alpha+} a_{k-\sigma}^*$  to first order in  $V$ . This statement follows from the equa-

tion

$$\langle [\varphi_{\alpha'\sigma}^\alpha, \psi_{\beta'\sigma}^{\beta+}] \rangle = \sum_{l=1}^3 \langle [\varphi_{\alpha'\sigma}^{(l)\alpha}, \psi_{\beta'\sigma}^{\beta+}] \rangle \quad (20)$$

which in the next step can be rewritten in terms of the expectation values of some operators multiplied by the matrix elements  $V_{\alpha k}$ . To this end, we have

$$\langle [\varphi_{\alpha'\sigma}^\alpha, \psi_{\beta'\sigma}^{\beta+}] \rangle = \alpha' \sum_k |V_{\alpha k}|^2 \left\{ \langle N_{\alpha} n_{\alpha-\sigma}^{(\beta')} \rangle \frac{f(\epsilon_k) - f(\epsilon_{\beta'})}{E - \epsilon_{\beta'}} - \langle N_{\alpha} n_{\alpha-\sigma}^{(-\beta')} \rangle \frac{f(\epsilon_k) - f(\epsilon_{-\beta'})}{E - \epsilon_{-\beta'}} \right\} \delta_{\alpha\beta} \quad (21)$$

and further (as in [9])

$$\langle [\varphi_{\alpha'\sigma}^\alpha, \psi_{\beta'\sigma}^{\beta+}] \rangle = \frac{\alpha'\beta'}{2} \langle N_{\alpha} \rangle \sum_k |V_{\alpha k}|^2 \left\{ \frac{f(\epsilon_k) - f(\epsilon_{\beta'})}{E - \epsilon_{\beta'}} - \frac{f(\epsilon_k) - f(\epsilon_{-\beta'})}{E - \epsilon_{-\beta'}} \right\} \delta_{\alpha\beta} \quad (22)$$

In Eq.(22) we have calculated the expectation values  $\langle N_{\alpha} n_{\alpha-\sigma}^{(-\alpha')} \rangle$  in zeroth-order in  $V$  and the normalization to  $\langle N_{\alpha} \rangle = \theta$  was chosen. In order to calculate the higher-order Green functions present in  $A_{\sigma} M_{\sigma}(q, E) A_{\sigma}$  - see Eq.(17), we have to obtain  $\langle \varphi_{\alpha'\sigma}^{(1)\alpha} | \varphi_{\beta'\sigma}^{(1)\beta+} \rangle$  exact up to second order in  $V$ . Following the procedure described above we obtain (in the weak-scattering limit [9]):

$$\langle \varphi_{\alpha'\sigma}^{(1)\alpha} | \varphi_{\beta'\sigma}^{(1)\beta+} \rangle = P_{\alpha\beta}(E) \langle N_{\alpha} N_{\beta} n_{\alpha-\sigma} n_{\beta-\sigma} \rangle \quad (23)$$

$$\langle \varphi_{\alpha'\sigma}^{(1)\alpha} | \varphi_{-\beta'\sigma}^{(1)\beta+} \rangle = \langle \varphi_{-\alpha'\sigma}^{(1)\alpha} | \varphi_{\beta'\sigma}^{(1)\beta+} \rangle = P_{\alpha\beta}(E) \left[ \langle N_{\alpha} N_{\beta} n_{\alpha-\sigma} \rangle - \langle N_{\alpha} N_{\beta} n_{\alpha-\sigma} n_{\beta-\sigma} \rangle \right] \quad (24)$$

$$\langle \varphi_{-\alpha'\sigma}^{(1)\alpha} | \varphi_{-\beta'\sigma}^{(1)\beta+} \rangle = P_{\alpha\beta}(E) \langle N_{\alpha} N_{\beta} (1 - n_{\alpha-\sigma} - n_{\beta-\sigma} + n_{\alpha-\sigma} n_{\beta-\sigma}) \rangle \quad (25)$$

$$\langle \varphi_{\alpha'\sigma}^{(2)\alpha} | \varphi_{\beta'\sigma}^{(2)\beta+} \rangle = \alpha'\beta' \left[ P_{\alpha\beta}(E) \langle N_{\alpha} N_{\beta} a_{\alpha\sigma}^{\dagger} a_{\alpha-\sigma} a_{\beta-\sigma}^{\dagger} a_{\beta\sigma} \rangle + \delta_{\alpha\beta} \sum_{kk'} \frac{V_{\alpha k} V_{\beta k'}}{E - \epsilon_k} \langle N_{\alpha} a_{k-\sigma}^{\dagger} a_{k'-\sigma} (n_{\alpha\sigma} - n_{\alpha-\sigma}) \rangle \right] \quad (26)$$

$$\langle \varphi_{\alpha'\sigma}^{(3)\alpha} | \varphi_{\beta'\sigma}^{(3)\beta+} \rangle = \sum_k \frac{V_{\alpha k} V_{\beta k}}{E + \epsilon_k - 2\epsilon_{\alpha} - U} \langle N_{\alpha} N_{\beta} a_{\beta\sigma}^{\dagger} a_{\beta-\sigma}^{\dagger} a_{\alpha-\sigma} a_{\alpha\sigma} \rangle + \delta_{\alpha\beta} \sum_{kk'} \frac{V_{\alpha k} V_{\beta k'}}{E + \epsilon_k - 2\epsilon_{\alpha} - U} \langle N_{\alpha} a_{k-\sigma}^{\dagger} a_{k'-\sigma} (1 - n_{\alpha\sigma} - n_{\alpha-\sigma}) \rangle \quad (27)$$

$$\langle \varphi_{-\alpha'\sigma}^{(3)\alpha} | \varphi_{-\beta'\sigma}^{(3)\beta+} \rangle = \langle \varphi_{\alpha'\sigma}^{(3)\alpha} | \varphi_{\beta'\sigma}^{(3)\beta+} \rangle \quad (28)$$

$$\langle \varphi_{\alpha'\sigma}^{(3)\alpha} | \varphi_{-\beta'\sigma}^{(3)\beta+} \rangle = \langle \varphi_{-\alpha'\sigma}^{(3)\alpha} | \varphi_{\beta'\sigma}^{(3)\beta+} \rangle = - \langle \varphi_{\alpha'\sigma}^{(3)\alpha} | \varphi_{\beta'\sigma}^{(3)\beta+} \rangle \quad (29)$$

$$\langle \varphi_{\alpha'\sigma}^{(1)\alpha} | \varphi_{\beta'\sigma}^{(2)\beta+} \rangle = 0 \quad , \quad \langle \varphi_{\alpha'\sigma}^{(2)\alpha} | \varphi_{\beta'\sigma}^{(3)\beta+} \rangle = 0 \quad (30)$$

The sums over  $k$  and  $k'$  vectors in Eqs.(26),(27) will be performed after decoupling of the corresponding correlation functions (we remember they are calculated in zeroth-order in  $V$ ) and calculating the resulting expectation value  $\langle a_{k'-\sigma}^{\dagger} a_{k-\sigma} \rangle$  from the Green function  $\langle a_{k-\sigma} | a_{k'-\sigma}^{\dagger} \rangle$  also in zeroth-order in  $V$ . In fact, we have decoupled the two-particle Green functions involving two electrons in the substrate metal in the Hartree approximation. Such decoupling is exact to second order in  $V$  and to all orders in  $U$  (see, for comparison [22]). The function  $P_{\alpha\beta}(E)$  present in Eqs.(23)-(26) defined as

$$P_{\alpha\beta}(E) = \sum_k \frac{V_{\alpha k} V_{\beta k}}{E - \epsilon_k} \quad (31)$$

was introduced by Grimley [11] for the description of the indirect interaction between two adatoms. Calculating the double sums over  $k, k'$  vectors according to the description given above, we obtain another function  $R(E)$  used on the latter stages of this paper [9]:

$$R(E) = \sum_k \frac{|V_{\alpha k}|^2}{E - \epsilon_k} f(\epsilon_k) \quad (32)$$

where  $f(E)$  is a Fermi function.

To this end, the main part of Eq.(17),  $A_{\sigma} M_{\sigma}(q, E) A_{\sigma}$  needed for the calculation of the Green function  $g_{\sigma}(q, E)$  can be written as

$$(AMA)_{\alpha'\beta'\sigma}^{\alpha\beta} = \sum_{l=1}^3 \langle \varphi_{\alpha'\sigma}^{(l)\alpha} | \varphi_{\beta'\sigma}^{(l)\beta+} \rangle \quad (33)$$

where  $\langle \varphi_{\alpha'\sigma}^{(l)\alpha} | \varphi_{\beta'\sigma}^{(l)\beta+} \rangle$  are given in Eqs.(23)-(27). At this stage of our calculations, in order to introduce simplifications in handling higher-order Green functions composed of ion and electron operators, we can use decoupling approximations. One of them concern the Ising type correlators and here we proceed along formula given by Eq.(3). The second approximation can be understood as neglecting of the correlations between electrons located on different adsorption sites. Only the first approximation is more serious because it means we have neglected the possible correlated distribution of the adatoms on the

metal surface. In this way our calculations should be comparable (to some extent) with those done, for example, within the single-site coherent potential approximation [23-25]. The second approximation is more justified, as it corresponds, for example, to neglecting the interatomic electron correlations in a Hubbard-type Hamiltonians. To demonstrate these decoupling procedures, let us calculate the correlation functions appearing in Eqs. (23), (24) and (26):

$$P_{\alpha\beta}(E) \langle N_{\alpha} N_{\beta} n_{\alpha-\sigma} n_{\beta-\sigma} \rangle \approx \delta_{\alpha\beta} \Lambda(E) \left[ \langle N_{\alpha} n_{\alpha-\sigma} \rangle (1 - \langle N_{\alpha} n_{\alpha-\sigma} \rangle) \right] + P_{\alpha\beta} \langle N_{\alpha} n_{\alpha-\sigma} \rangle \langle N_{\beta} n_{\beta-\sigma} \rangle, \quad (34)$$

$$P_{\alpha\beta}(E) \langle N_{\alpha} N_{\beta} n_{\alpha-\sigma} \rangle \approx \delta_{\alpha\beta} \Lambda(E) \left[ \langle N_{\alpha} n_{\alpha-\sigma} \rangle (1 - \langle N_{\alpha} \rangle) \right] + P_{\alpha\beta} \langle N_{\alpha} n_{\alpha-\sigma} \rangle \langle N_{\beta} \rangle, \quad (35)$$

$$P_{\alpha\beta}(E) \langle N_{\alpha} N_{\beta} a_{\alpha\sigma}^{\dagger} a_{\alpha-\sigma}^{\dagger} a_{\beta-\sigma} a_{\beta\sigma} \rangle \approx \delta_{\alpha\beta} \Lambda(E) \left[ \langle N_{\alpha} n_{\alpha-\sigma} \rangle - \langle N_{\alpha} n_{\alpha-\sigma} n_{\alpha\sigma} \rangle \right], \quad (36)$$

where

$$\Lambda(E) = \sum_k \frac{|V_{\alpha k}|^2}{(E - \epsilon_k)}$$

In order to obtain the last result we set up to zero the correlation function corresponding to the spin-flip processes on the adatom. The two-particle correlation function  $\langle N_{\alpha} n_{\alpha-\sigma} n_{\alpha\sigma} \rangle$  will be calculated to zeroth-order in  $V$  and for  $\epsilon_{\alpha} + U > \epsilon_f$ ,  $\epsilon_f$  - Fermi energy, (the case considered here) is equal to zero. Similarly as in [9], we have not replaced the expectation values  $\langle N_{\alpha} n_{\alpha\sigma} \rangle$  in Eq. (23) and (25) by its zeroth-order value. In this case, the resulting Green function  $\langle N_{\alpha} a_{\alpha\sigma} | a_{\alpha\sigma}^{\dagger} \rangle$  in the limit  $\theta \rightarrow 0$  (i.e. one adatom case) tends to correct Hartree-Fock limit (for small  $U$ ). Thus, for  $q$ -transform we obtain

$$(AMA)_{+, \sigma}^q = \Lambda(E) \left\{ n_{-\sigma} \left[ 1 - n_{-\sigma} \right] + n_{-\sigma}^{\circ} \right\} + R(-E + 2\epsilon_{\alpha} + U) \left[ \langle N_{\alpha} \rangle - n_{-\sigma}^{\circ} - n_{\sigma}^{\circ} \right] + R(E) \left[ n_{\sigma}^{\circ} - n_{-\sigma}^{\circ} \right] + P(q, E) n_{-\sigma}^2, \quad (37)$$

$$(AMA)_{-, \sigma}^q = (AMA)_{+, \sigma}^q = \Lambda(E) \left\{ -n_{-\sigma}^{\circ} \left[ \langle N_{\alpha} \rangle - n_{-\sigma}^{\circ} \right] - n_{-\sigma}^{\circ} \right\} - R(E) \left[ n_{\sigma}^{\circ} - n_{-\sigma}^{\circ} \right] - R(-E + 2\epsilon_{\alpha} + U) \left[ \langle N_{\alpha} \rangle - n_{-\sigma}^{\circ} - n_{\sigma}^{\circ} \right] + P(q, E) n_{-\sigma}^2 \left[ \langle N_{\alpha} \rangle - n_{-\sigma}^{\circ} \right], \quad (38)$$

$$(AMA)_{-, \sigma}^q = \Lambda(E) \left\{ \langle N_{\alpha} \rangle - n_{-\sigma}^{\circ} + n_{-\sigma}^{\circ} - \left[ \langle N_{\alpha} \rangle - n_{-\sigma}^{\circ} \right]^2 \right\} + R(E) \left[ n_{\sigma}^{\circ} - n_{-\sigma}^{\circ} \right] + R(-E + 2\epsilon_{\alpha} + U) \left[ \langle N_{\alpha} \rangle - n_{-\sigma}^{\circ} - n_{\sigma}^{\circ} \right] + P(q, E) \left[ \langle N_{\alpha} \rangle - n_{-\sigma}^{\circ} \right]^2, \quad (39)$$

where  $P(q, E)$  is a Fourier transform of  $P_{\alpha\beta}(E)$ ,  $q$  is a two dimensional vector parallel to the surface and  $n_{\sigma} \equiv \langle N_{\alpha} n_{\alpha\sigma} \rangle$ ,  $n_{\sigma}^{\circ} \equiv \langle N_{\alpha} n_{\alpha\sigma} \rangle^{\circ}$ .

Finally, for  $q$ -transform of the single-site adsorbate Green function ( $\alpha = \beta$ ) describing the charge distribution on the adatom level we obtain (we changed the normalization of  $\langle N_{\alpha} n_{\alpha\sigma} \rangle$  to unity)

$$\frac{\langle N_{\alpha} a_{\alpha\sigma} | a_{\alpha\sigma}^{\dagger} \rangle_{q, E^*}}{\langle N_{\alpha} \rangle} = \left\{ 2n_{-\sigma} (1 - n_{-\sigma}) D_{12} + n_{-\sigma}^2 \left[ (E - \epsilon_{\alpha}) (1 - n_{-\sigma}) - D_{22} \right] + (1 - n_{-\sigma})^2 \left[ (E - \epsilon_{\alpha} - U) n_{-\sigma} - D_{11} \right] \right\} \left\{ \left[ (E - \epsilon_{\alpha} - U) n_{-\sigma} - D_{11} \right] \times \left[ (E - \epsilon_{\alpha}) (1 - n_{-\sigma}) - D_{22} \right] - D_{12}^2 \right\}^{-1} \quad (40)$$

where  $D_{ik}$  ( $i, k=1, 2$ ) can be obtained from Eqs. (20) and (37)-(39). They are as follows:

$$D_{11} = \Lambda(E) \left[ n_{-\sigma} (1 - \theta n_{-\sigma}) + \frac{1}{2} \right] + \theta n_{-\sigma}^2 P(q, E) + \kappa$$

$$D_{12} = D_{21} = -\Lambda(E) \left[ \frac{1}{2} + \frac{\theta}{4} \right] + \frac{\theta}{4} P(q, E) - \kappa$$

$$D_{22} = \Lambda(E) \left[ 1 - \theta (1 - n_{-\sigma})^2 - n_{-\sigma} + \frac{1}{2} \right] + \theta (1 - n_{-\sigma})^2 P(q, E) + \kappa \quad (41)$$

$$\kappa = \frac{1}{2} \sum_k |V|^2 \left[ \frac{f(\epsilon_k) - f(\epsilon_{\alpha} + U)}{\epsilon_k - (\epsilon_{\alpha} + U)} - \frac{f(\epsilon_k) - f(\epsilon_{\alpha})}{\epsilon_k - \epsilon_{\alpha}} \right]$$

As  $\theta \rightarrow 0$ , formulas (40) and (41) tend to the well-known results of Brenig and Schönhammer [9].

### 3. Numerical results and discussion

The above developed scheme is adopted to describe the chemisorption of hydrogen-like adatoms on the transition metal surface for coverages extending from the single-adatom case to one adatom's monolayer on the substrate surface. More specifically, we have calculated the electron charge  $q$  and the local density states on the hydrogen adatoms chemisorbed on titanium and nickel substrates. As we only try to give a correct qualitative description of the chemisorption process then we approximate the substrate density of states by a semielliptical one as in Newns paper adding a small broadening of the substrate electronic structure as in ref. [9]. There is a general opinion that integral chemisorption characteristic like  $q$  and the magnetic momentum

slightly depend on the details of the substrate electronic structure so we expect that our results will be quite reasonable. The parameters we used are: the band width  $W$ , the Fermi energy, the hydrogen ionization potential and the Coulomb integral for the hydrogen adatom were taken from the Newns paper [3]. Some minor simplification were done in calculating the  $P(q,E)$  function. In principle, this function should be calculated as follows

$$P(q,E) = \frac{1}{N} \sum_{\alpha\beta k} \frac{V_{\alpha k} V_{\beta k}^*}{E^+ - \epsilon_k} e^{iq(\alpha-\beta)} = N \sum_{k_z} \frac{|V_{\alpha q k_z}|^2}{E^+ - \epsilon_{q k_z}} \equiv \gamma(q,E) - i\eta(q,E). \quad (42)$$

where  $\eta(q,E) = \pi N \sum_{k_z} |V_{\alpha q k_z}|^2 \delta(E - \epsilon_{q k_z})$  and  $\gamma(q,E)$  is its Hilbert transform.

Also, the function  $\Lambda(E)$ , or more precisely, its imaginary part should be calculated as  $\pi V^2 D_s(E)$  where  $D_s(E)$  is the substrate surface density of states and  $V$  is the parameter  $\beta$  defined in the Newns paper [3]. It should be remarked again that in our notation  $q$ -vectors are two-dimensional vectors connected with the adlayer, and  $k$ -vectors are three-dimensional. Unfortunately this method of calculating  $P(q,E)$  require the knowledge of the realistic  $\epsilon_k$  and a relatively great numerical effort. For that reason we calculate these function as follows

$$P(q,E) = \frac{1}{N} \sum_{\alpha\beta k} \frac{V_{\alpha k} V_{\beta k}^*}{E^+ - \epsilon_k} e^{i(\alpha-\beta)(q-k)} \approx \frac{V^2}{E^+ - \epsilon_q}. \quad (43)$$

and further  $\eta(q,E) = \pi V^2 \delta(E - \epsilon_q)$ . Here in fact we approximate  $k$  by a two dimensional vector or in other words, we approximate the semi-infinite three-dimensional substrate by a two-dimensional layer. The values of the parameter used in calculations are as follows [3]: for nickel:  $\epsilon_\alpha = -4.23$ ,  $U = 6.97$  and  $\epsilon_f = 0.925$ ; for titanium:  $\epsilon_\alpha = -2.9$ ,  $U = 3.0$  and  $\epsilon_f = -0.475$ . All values are given in half-bandwidth units  $W$  so the substrate energy band extends in limits  $(-1,+1)$ . Additionally we have performed also calculations for a model symmetric case for the parameters of the Brenig and Schönhammer paper [9].

In Fig.1 we present the results for the total electric charge of adatoms versus the hopping strength  $V$  and the coverage  $\theta$  for Ti (upper part of the figure) and Ni (lower part of the figure). The upper curves in both cases correspond to the single-adatom case and are

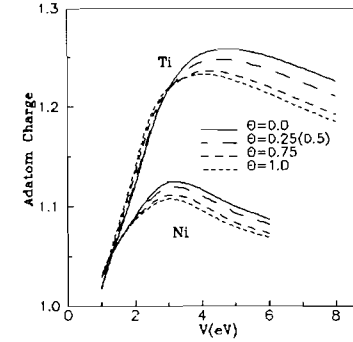


Fig.1- The adatom electron charge vs. the hopping  $V$  for different coverages

equivalent to Brenig and Schönhammer results. One sees that there is a progressive neutralization of adatoms as the coverage increases although decreasing of the adatom charge is not large. At this point our results agree with results obtained by other authors, -see for example, Ref. [26], where the calculations were performed within the Hartree-Fock approximation. In all cases the value of  $q$  is significantly lower than results of Hartree-Fock calculations for the same set of parameters. As for the magnetic momentum which is present on adatoms we observe it ( $n_\uparrow - n_\downarrow \approx 0.1e$ ) only in the region of small  $V$  (before the maximum in  $q$  is achieved). Thus for that values of the parameter  $V$  which are expected to be suitable for our systems, the negligible or vanishing magnetic momentum was observed.

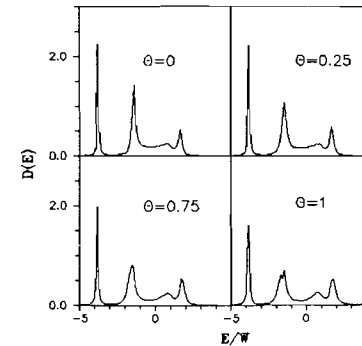


Fig.2- The adatom local density of states for different coverages for titanium substrate with  $V = 4.7eV$



In Figs. (2) and (3) we present the adsorbate density of states for

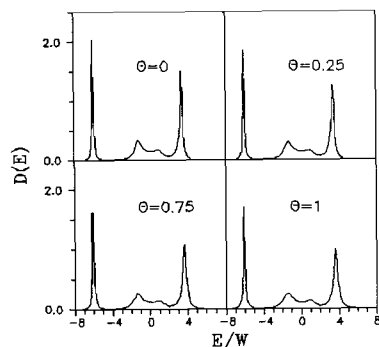


Fig.3- The same as in Fig.2 for nickel substrate and for  $V=3.0\text{eV}$

different coverages for titanium and nickel, respectively. The value of  $V$  was chosen in such a way that it corresponds to the maximum charge transfer between the substrate and an adatom. The  $\theta=0$  results correspond to the single-adatom case and are identical with these ones obtained within method of Ref.[9]. In both cases, i.e. for Ti and Ni substrates we observe at low energies a sharp peak which is unchanged during the covering process. The other two peaks which corresponds in the single adatom case to the bonding and antibonding levels are

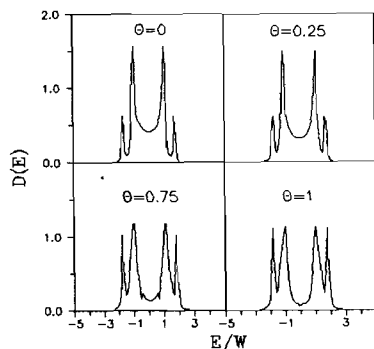


Fig.4- The adatom local density of states for different coverages in the symmetric case for  $V/W=0.9$  and  $U=W$ .

broadened and the density of states between them decreases. At the same time a small shift of the peaks is observed. The broadening of the bonding and antibonding levels with the increasing coverage is due

to the enhancement in the indirect interaction among adatoms mediated by the substrate electrons. A similar situation appears in the symmetric case presented in Fig.4. Here the two peaks located at the edges of the band (they are essentially the same as in the Hartree-Fock description) decrease and the two additional peaks corresponding to the surface molecule states are increased and at the same time they are broadened although their position is unchanged. Roughly speaking we observe for coverage  $\theta=1$  two energy bands originated from the bonding and antibonding states. Similar results can be observed also in Refs.[23-25].

In conclusion, we have developed the theory of the electron correlation effects in the chemisorption theory for the case of finite submonolayer coverages. The electron correlations were included up to second order in  $V$  and the ionic adsorbate correlations within the Bragg-Williams approximation. As a typical example in which the electron correlation is important, the chemisorption of hydrogen atoms on a model transition metal substrate was investigated. The neutralization of the adatoms with increasing coverage was obtained in agreement with the experimental results. We also studied the adatom local density of states in dependence of the coverage. For monolayer coverages the indirect interaction between adatoms through the substrate electrons is so large that can lead, in some cases, to two nearly separated energy bands originated from the adatom bonding and antibonding levels.

Some remarks should be added to the results obtained in this paper. For the charge transfer or magnetic moment on the adatoms results are quite reasonable despite of the fact that we have used a very simple substrate metal density of states. They are integral characteristics and are not very sensible to such details of the calculations. On the other hand, the substrate density of states seems tends to dominate the adatom spectrum [27]. Nevertheless, as we are looking for general trends appearing with increasing coverage, we suppose that the general features obtained by us for the adatom local density of states will be obtained also for more exact (i.e. with correct substrate's surface density of states) calculations.

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Таранко Р. и др. E17-89-570  
Хемосорбция при конечных субмонослойных покрытиях:  
влияние электронных корреляционных эффектов

В рамках обобщенного гамильтониана Андерсона-Ньюнса исследована зависимость от степени покрытия подложки адсорбатов плотности электронных состояний и электрический заряд на адатомах. Электронные корреляционные эффекты на адатоме включены во втором порядке по параметру гибридизации и ионные корреляции в рамках приближения Брэгга-Вильямса. Для модельной системы хемосорбции водорода на поверхности переходных металлов получено, что имеет место постепенная нейтрализация адатома с увеличением степени покрытия, и все значения заряда адатома существенно меньше, чем полученные в рамках приближения Хартри-Фока.

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Taranko R. et al. E17-89-570  
Chemisorption at Finite Submonolayer Coverages:  
Influence of the Electron Correlation Effects

Within the generalized Anderson-Newns Hamiltonian the coverage dependence of the chemisorption characteristics like the adatom charge and adatom local density of states has been calculated. The electron correlation effects on the adatom were included up to second order in  $V$  (the single particle hopping strength between the adatom and the substrate) and the Bragg-Williams approximation for the ionic adsorbate component was used. For a model system of the hydrogen chemisorption on the transition metal surfaces a progressive neutralization of the adatoms with increasing coverage was obtained and all values of the adatom charge are much smaller than the corresponding ones calculated within the Hartree-Fock (or beyond it) approach for general (zero) coverages.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

Communication of the Joint Institute for Nuclear Research. Dubna 1989