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Electron Correlation Effects in Chemisorption Theory

1. INTRODUCTION

The model Hamiltonian most frequently used in literature for description of the chemisorption phenomenon is the Hamiltonian introduced by Anderson [1] and used by Newns [2] and Edwards and Newns [3] - so called Newns-Anderson (NA) Hamiltonian. The Anderson model has first been introduced to describe a magnetic impurity in a metal but also is very useful to formulate fundamental microscopic foundations of the chemisorption theory. However, the NA model does not take into account many important effects which may lead to considerable qualitative differences in some chemisorption characteristics [4]. The model considered by us in this paper is a direct generalization of the Newns-Anderson model to the case of final

coverages of randomly arranged adatoms [5]. The problem of constructing more realistic model of chemisorption has thoroughly been studied by us for the case of one admixture in Ref. [6]. At present, the microscopic theories of the chemisorption systems can be roughly divided into three classes depending on methods used for the calculations of various chemisorption characteristics. In the first class we can place the methods using the local density functional method (LDF). Apparently, the description of the coverage dependence of the properties of the chemisorbed overlayers was for the first time realized within LDF [7]. In the framework of this scheme the adsorbate ion cores were modelled by a thin jellium slab adsorbed on a jellium surface. In the next step there appeared extensions of this approach, see, for example Refs. [8, 9], where an approximate description of the metallic substrate by either a semi-infinite jellium system or by including the substrate structure within first-order perturbation theory for jellium plus adatom system was used. In Refs. [10-13] the alkali-metal adsorption on metal surfaces (the alkali-metal-overlayer-jellium system) was investigated and a fully self-consistent electronic structure was obtained. In Ref. [14] a further improvement was achieved, i.e. a coverage dependence of the electronic structure of alkali-metal adatoms on a metal surface was studied treating both the adatom and substrate as discrete atoms. Although the "ab initio" method give very useful information, it involves a large amount of computer calculations and all the calculations must be repeated for new sets of an input data (for example, for a value of the coverage rate). In addition, these calculations rather reproduce the experimentally observed features and not explain it. The second class of methods consists essentially of the quantum chemistry approaches (see, e.g. cluster methods [15]) and the third class comprises the model Hamiltonian methods (see e.g. [4]). Especially, the method of model Hamiltonians can be well suited for better understanding and not only for reproducing of the experimental results. It is to be noted that model approach is wide open to

criticism. However, in comparison with the "ab initio" calculations it is an indispensable tool for explanation of basic mechanism of physical processes, which essentially promotes their understanding.

In the present paper we consider the problem of many adatoms simultaneously existing on the metal surface within the model Hamiltonian method. The model Hamiltonian used here was recently obtained by us generalizes the Newns-Anderson Hamiltonian. The electron correlation effects are included within the second-order self-energy matrix formalism of Brenig and Schönhammer [16]. We also discuss here general solutions obtained within the equation of motion method for a case of submonolayer coverages.

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 and compare this model with others known from the literature. In the section 3 we present shortly some methods which incorporate the electron-electron interaction (on the adsorbate atom) and generalise the Hartree-Fock solutions.

2. THE BASIC MODEL HAMILTONIAN. ONE ADATOM CASE

Recently, we have obtained from the microscopic considerations the Hamiltonian intended to describe the system of adatoms located on the metal surface [5]. The system adatom plus metal surface is described by the Hamiltonian (we consider the hydrogen adatom in the 1 s ground state):

$$H = \sum_{i=1}^{N+1} \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i \neq j}^{N+1} V(\vec{x}_i - \vec{x}_j) - \sum_{i=1}^{N+1} V(\vec{R}_A - \vec{x}_i) - \sum_{i=1}^{N+1} P(\vec{x}_i) + U_0. \quad (1)$$

Here the potential $V(\vec{x} - \vec{y})$ describes the Coulomb interaction between electrons placed at the positions \vec{x} and \vec{y} , $P(\vec{x})$ is the electrostatic interaction of electrons with the electric fields of the metallic substrate. The constant U_0 represents the energy of electrostatic interaction between ions of the metal

substrate and between these ions and the proton of the adatom. After performing the second quantization procedure (for details see Ref. [5]) we obtain:

$$\begin{aligned}
 H = & \sum_{\vec{k}} E_{A\vec{k}} n_{A\vec{k}} + U n_{A\uparrow} n_{A\downarrow} + \sum_{\vec{k}, \vec{k}'} \epsilon_{\vec{k}} n_{\vec{k}\vec{\sigma}} + \sum_{\vec{k}, \vec{k}', \vec{\sigma}, \vec{\sigma}'} V_{A\vec{k}\vec{k}'} n_{A\vec{\sigma}} a_{\vec{k}\vec{\sigma}}^{\dagger} a_{\vec{k}'\vec{\sigma}'} - \\
 & - \sum_{\vec{k}, \vec{k}'} V_{\vec{k}\vec{k}'} (A) a_{\vec{k}\vec{\sigma}}^{\dagger} a_{\vec{k}'\vec{\sigma}'} + \sum_{\vec{k}, \vec{k}'} (V_{A\vec{k}\vec{k}'} a_{A\vec{\sigma}}^{\dagger} a_{\vec{k}\vec{\sigma}} + \text{h.c.}) - \\
 & - \sum_{\vec{k}, \vec{k}'} (V_{AA\vec{k}\vec{k}'} n_{A-\vec{\sigma}} a_{A\vec{\sigma}}^{\dagger} a_{\vec{k}\vec{\sigma}} + \text{h.c.}) + \sum_{\vec{k}, \vec{k}', \vec{k}''\vec{\sigma}, \vec{\sigma}'} (V_{A\vec{k}\vec{k}'\vec{k}''} a_{A\vec{\sigma}}^{\dagger} a_{\vec{k}\vec{\sigma}}^{\dagger} a_{\vec{k}'\vec{\sigma}'} a_{\vec{k}''\vec{\sigma}'} + \\
 & + \text{h.c.}) + \frac{1}{2} \sum_{\vec{k}, \vec{k}, \vec{k}'} (V_{AA\vec{k}\vec{k}'} a_{A\vec{\sigma}}^{\dagger} a_{A-\vec{\sigma}}^{\dagger} a_{\vec{k}-\vec{\sigma}} a_{\vec{k}'\vec{\sigma}} + \text{h.c.}) + \\
 & + \sum_{\vec{k}, \vec{k}', \vec{\sigma}, \vec{\sigma}'} V_{A\vec{k}\vec{k}'} a_{A\vec{\sigma}}^{\dagger} a_{\vec{k}\vec{\sigma}}^{\dagger} a_{\vec{k}'\vec{\sigma}'} a_{A\vec{\sigma}} + \\
 & + \frac{1}{2} \sum_{\vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_4, \vec{\sigma}, \vec{\sigma}'} V_{\vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_4} a_{\vec{k}_1\vec{\sigma}}^{\dagger} a_{\vec{k}_2\vec{\sigma}'}^{\dagger} a_{\vec{k}_3\vec{\sigma}} a_{\vec{k}_4\vec{\sigma}'} - \sum_{\vec{k}} n_{A\vec{k}} P_A + U_0. \quad (2)
 \end{aligned}$$

Here, the functions $V_{\vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_4}$, $V_{A\vec{k}_1, \vec{k}_2, \vec{k}_3}$ are the matrix elements calculated for the Coulomb interaction $V(\vec{x}-\vec{y})$ between states described by the substrate electron wave functions $\phi_{\vec{k}_1}^{\dagger}$, $\phi_{\vec{k}_2}^{\dagger}$, $\phi_{\vec{k}_3}^{\dagger}$, $\phi_{\vec{k}_4}^{\dagger}$ and adatom electron function ϕ_A and $\phi_{\vec{k}_1}^{\dagger}$, $\phi_{\vec{k}_2}^{\dagger}$, $\phi_{\vec{k}_3}^{\dagger}$, respectively. Other abbreviations have their usual meaning (see, also [5]). Very similar model Hamiltonian, although without some terms present in (2) was obtained by Doyen [17] and Doyen and Ertl [18, 19]. Starting with the Newns-Anderson Hamiltonian and adding additional self-consistent fields arising from electron-electron interactions they obtained parametrized model Hamiltonian which treats the interaction between adsorbate and metal electrons in some details. In our case we have started from very general physical description - Eq.(1), and as a result we have obtained the Newns-Anderson

Hamiltonian plus many other terms describing in detail the chemisorption process. To some extent, we can give a very rough physical interpretation for terms in the Hamiltonian - Eq. (2) (for comparison, see. Ref. [17]). For example, the fourth term describes repulsion between electrons localized on adatom and substrate electrons, the next term corresponds to the attraction of metal electrons by the positive ion core of the adatom and so on. Very important for our further considerations is the seventh term which can be interpreted as an interaction of overlap charge with electrons on adatom. In other words, this term describes the influence of the fractional occupation of the surface impurity resonance on the electron transfer between the adatom and substrate metal. It is also important to note that for a consistent treatment of the polarization properties of the metal substrate it is insufficient to characterize its electronic properties by the parameter $\epsilon_{\vec{k}}$ (the energy spectrum of the substrate electron band), but it is necessary to introduce a long range part of the Coulomb interaction between substrate electrons $V_{\vec{k}_1 \vec{k}_2 \vec{k}_3 \vec{k}_4}$ [20], or introduce plasmons [21]. Corresponding term is present in our Hamiltonian.

In the following we confine ourselves to the model in which together with the standard interactions present in the NA model we include only effects connected with the influence of the adatom orbital occupation on the charge transfer between an adatom and a metal substrate. In this case the Hamiltonian reads as [5, 6]:

$$H = \sum_{\vec{k}G} \epsilon_{\vec{k}} n_{\vec{k}G} + \sum_G E_A n_{AG} + U n_{A\uparrow} n_{A\downarrow} + \sum_{\vec{k}G} \left[(V_{A\vec{k}} - V_{AA\vec{k}} n_{A-G}) a_{A-G}^\dagger a_{\vec{k}G} + \text{h.c.} \right] \quad (3)$$

The last term can be simplified as for $|\vec{R}_A| \gg 0.5 \text{ \AA}$ we obtain $V_{AA\vec{k}} \sim \alpha V_{A\vec{k}}$, where the parameter α depends on the distance between the adatom and the metal surface ($0 \leq \alpha \leq 1$). We have checked in Ref. [6] that this approximation works relatively good. In Ref. [5] we have performed the self-consistent

calculations of the adatom electron charge and chemisorption energy in the framework of the Hartree-Fock approximation, i.e. for Hamiltonian :

$$\begin{aligned}
 H = & \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} n_{\vec{k}\sigma} + \sum_{\sigma} (E_A + U \langle n_{A-\sigma} \rangle - \alpha \sum_{\vec{k}} (V_{A\vec{k}} \langle a_{A-\sigma}^+ a_{\vec{k}-\sigma} \rangle \\
 & + \text{h.c.})) n_{A\sigma} + \sum_{\vec{k}\sigma} [V_{A\vec{k}} (1 - \alpha \langle n_{A-\sigma} \rangle) a_{A\sigma}^+ a_{\vec{k}\sigma} + \text{h.c.}] - \\
 & - U \langle n_{A\uparrow} \rangle \langle n_{A\downarrow} \rangle + \alpha \sum_{\vec{k}\sigma} (V_{A\vec{k}} \langle n_{A-\sigma} \rangle \langle a_{A\sigma}^+ a_{\vec{k}\sigma} \rangle + \text{h.c.}) .
 \end{aligned} \quad (4)$$

The calculations were performed for parameters modelling the hydrogen chemisorption on transition metal surfaces. The results indicate that the charge transfer to the adatom is considerably damped with increasing value of the parameter α . This means that the additional term $-V_{AA\vec{k}} n_{A-\sigma} a_{A\sigma}^+ a_{\vec{k}\sigma}$ in NA Hamiltonian, which in a Hartree-Fock approximation leads to spin dependent effective hopping matrix element and renormalizes in special way the energy of an electron moving in the field of the adparticle ion core, plays an essential role in description of the adsorption system. Note, that the semiempirical one-particle Hamiltonian obtained for description of the chemisorption process in Ref.[19] leads to some difficulties. In this paper Doyen and Ertl checked that reasonable agreement with experiment could be only achieved if the hopping matrix element for different spins were allowed to differ. In this case it becomes obvious that the corresponding Hamiltonian is not the Hartree-Fock operator of a proper many-particle Hamiltonian. In order to improve this situation one has to add to the Hamiltonian the term like $n_{A\sigma} \langle a_{A-\sigma}^+ a_{\vec{k}-\sigma} \rangle + \text{h.c.}$, which was absent in model explored in Ref.[19]. In our formulation this term is present in the Hartree-Fock Hamiltonian from very beginning. It is contained in the second term in Eq.(4) leading to additional spin-dependence of the effective adatom energy level position (through the correlation function $\langle a_{A\sigma}^+ a_{\vec{k}\sigma} \rangle$).

In the analysis we have performed above, the electron-electron interaction was treated in the framework of the Hartree-Fock approximation. It is difficult to take into account the correlation effects because the small parameter does not exist in the theory. This means that one has to sum an infinite series of the most divergent diagrams or construct the Green Function with the approximate self-energy operator. This solution should be, of course, identical with the known ones for some special case. A great number of papers have been devoted to the study of the correlation effects in the chemisorption theory beyond the Hartree-Fock approximation. Here we mention merely few of them. First of all we have works by Brenig and Schönhammer [16], Yosida and Yamada [22], Anda, Majlis and Grempel [23], Sebastian and Rangarajan [24], Bell and Madhukar [25], Lacroix [26] and by Munoz et al. [27]. Especially two of them are interesting. First, it is work by Brenig and Schönhammer [16] in which the correlation effects on an adatom are treated within so called second order (in V - the single particle hopping strength between the adatom and the substrate atom) self-energy matrix formalism. This method was also transferred with success by Schönhammer [28] to considerations of the electron correlation effects in the standard many-body Hubbard Hamiltonian. Second work is the one by Munoz et al. [27]. In this case the self-energy expression interpolates between two opposite cases, i.e. between the second-order perturbation formula and formula for strong correlation limit. Here we use the second-order self-energy matrix formalism described in [16] to consider the electron correlation effects within our generalized NA Hamiltonian, i.e. with the term

$$- \sum_{\vec{k}\sigma} V_{AAK} \eta_{A-\sigma} a_{A\sigma}^+ a_{\vec{k}\sigma} + \text{h.c.}, \quad (5)$$

included. Using the double-time retarded Green functions [29] build up from the operators $n_{A-\sigma} a_{A\sigma}$ and $a_{A\sigma} (1 - n_{A-\sigma})$ we can try to solve the Dyson equation for this Green function

up to second order in powers of V_{Ak} (here we used $V_{AAk} \approx \alpha V_{Ak}$ [6]). As a result for the self-energy expression we obtain [30]

$$M^{\epsilon}(E) = \begin{pmatrix} \langle n_{A-\epsilon} \rangle & 0 \\ 0 & 1 - \langle n_{A-\epsilon} \rangle \end{pmatrix} (A^{\epsilon} + B^{\epsilon}) \begin{pmatrix} \langle n_{A-\epsilon} \rangle & 0 \\ 0 & 1 - \langle n_{A-\epsilon} \rangle \end{pmatrix}^{-1}, \quad (6)$$

where

$$A^{\epsilon} = \begin{pmatrix} (1-\alpha)^2 \langle n_{A-\epsilon} \rangle \Lambda(E) + (1-\alpha)^2 C^{\epsilon} + D^{\epsilon}, & -(1-\alpha)(C^{\epsilon} + D^{\epsilon}) \\ -(1-\alpha)(C^{\epsilon} + D^{\epsilon}), & (1 - \langle n_{A-\epsilon} \rangle) \Lambda(E) + C^{\epsilon} + (1-\alpha)^2 D^{\epsilon} \end{pmatrix},$$

$$D^{\epsilon} = \langle n_{A\epsilon} n_{A-\epsilon} \rangle \Lambda(-E + 2E_A + U) + \langle 1 - n_{A\epsilon} - n_{A-\epsilon} \rangle R(-E + 2E_A + U),$$

$$R(E) = \sum_{\vec{k}} |V_{A\vec{k}}|^2 f(\epsilon_{\vec{k}}) (E - \epsilon_{\vec{k}})^{-1}; \quad B^{\epsilon} = \begin{pmatrix} B_{11}^{\epsilon} & B_{12}^{\epsilon} \\ B_{21}^{\epsilon} & B_{22}^{\epsilon} \end{pmatrix};$$

$$\Lambda(E) = \sum_{\vec{k}} |V_{A\vec{k}}|^2 (E - \epsilon_{\vec{k}})^{-1}; \quad B_{21}^{\epsilon} = -B_{12}^{\epsilon}, \quad B_{22}^{\epsilon} = -B_{11}^{\epsilon},$$

$$C^{\epsilon} = \langle n_{A-\epsilon} \rangle \langle 1 - n_{A-\epsilon} \rangle \Lambda(E) + (\langle n_{A-\epsilon} \rangle - \langle n_{A\epsilon} \rangle) R(E),$$

$$B_{11}^{\epsilon} = \sum_{\vec{k}} |V_{A\vec{k}}|^2 \left\{ (1-\alpha)^2 \langle n_{A-\epsilon} \rangle \frac{f(\epsilon_{\vec{k}}) - f(E_A + U)}{\epsilon_{\vec{k}} - E_A - U} - \langle 1 - n_{A-\epsilon} \rangle \frac{f(\epsilon_{\vec{k}}) - f(E_A)}{\epsilon_{\vec{k}} - E_A} \right\},$$

$$B_{12}^{\epsilon} = - \sum_{\vec{k}} |V_{A\vec{k}}|^2 (1-\alpha) \left\{ \langle 1 - n_{A-\epsilon} \rangle \frac{f(\epsilon_{\vec{k}}) - f(E_A)}{\epsilon_{\vec{k}} - E_A - U} \right\},$$

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

In Ref. [30] we have performed the self-consistent numerical calculations of the adatom charge for model hydrogen on titanium surface chemisorption system for different values of the parameter α . The parameters for calculations were taken from Ref. [2]. The effect obtained after introduction of the self-energy corrections can be described as follows. For small values of α we have much smaller values of the adatom electronic charge comparing with the results obtained for standard NA model. For moderate values of α , i.e. for $\alpha \sim 0.5$ (we remember that α and distance between the adatom and substrate's surface depend on each other) the results obtained in Hartree-Fock approximation, as well as beyond this approximation are comparable. For greater values of α the charge transfer "stabilizes" around the neutral adatom case more and more positive charged.

On the other hand, we expect on physical grounds, that for a large separation distance (for large α) the hydrogen adatom should be in a nearly neutral state. Thus we can say, that the generalized NA Hamiltonian (i.e., NA Hamiltonian plus correction expressed by Eq. (5)) better describes this chemisorption system. This description is sufficiently good for moderate values of α even in the Hartree-Fock approximation. From the comparison with results obtained for whole range of the parameter α it appears that generalized NA model combined with the self-energy corrections obtained within the method of Brenig and Schonhammer can be helpful in understanding of the chemisorption process.

3. CHEMISORPTION AT FINITE SUBMONOLAYER COVERAGES

The extension of the one-adatom chemisorption case to the submonolayer coverage can be described in analogous way as follows [31]:

$$H = \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} n_{\vec{k}\sigma} + \sum_{\alpha\sigma} N_{\alpha} \left\{ \epsilon_{\alpha} n_{\alpha\sigma} + \frac{U}{2} n_{\alpha\sigma} n_{\alpha-\sigma} - \sum_{\vec{k}} \left[(V_{\alpha\alpha\alpha\vec{k}} n_{\alpha-\sigma} - V_{\alpha\vec{k}}) a_{\alpha\sigma}^{\dagger} a_{\vec{k}\sigma} + \text{h.c.} \right] \right\} + \sum_{\substack{\alpha \neq \beta \\ \alpha\beta k k'\sigma\sigma'}} V_{\alpha\beta k} N_{\alpha} N_{\beta} a_{\alpha\sigma}^{\dagger} a_{\vec{k}\sigma'}^{\dagger} a_{\beta\sigma} a_{\vec{k}'\sigma} + R. \quad (7)$$

The Hamiltonian in the form presented here 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 describing the correlations between adatom charge fluctuations and the redistributed substrate charge density and others effects of much higher order (for details see Refs [5, 31]). Having in mind such complicated system as a chemisorbed layer on the metal surface we restrict ourselves in the first step to the simplest case, i.e. we consider the model described by the Hamiltonian:

$$H = \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} n_{\vec{k}\sigma} + \sum_{\alpha\sigma} \epsilon_{\alpha} N_{\alpha} n_{\alpha\sigma} + \frac{U}{2} \sum_{\alpha\sigma} N_{\alpha} n_{\alpha\sigma} n_{\alpha-\sigma} + \sum_{\vec{k}\alpha\sigma} V_{\alpha\vec{k}} N_{\alpha} a_{\alpha\sigma}^{\dagger} a_{\vec{k}\sigma} + \text{h.c.} \quad (8)$$

Model (8) is a generalization of the well-known NA Hamiltonian to the case of a stochastic arrangement of adatoms on the metal surface. The sum over α is carried out over all the adsorption centres. The operator $N_{\alpha} = C_{\alpha}^{\dagger} C_{\alpha}$ has eigenvalues equal to 0 or 1, and the operators C_{α}^{\dagger} and C_{α} are the Fermi amplitudes of the creation and annihilation of an adsorbed ion (adion) at the adsorption center α . We consider only the case when there is no more than one adatom ion in each adsorption center. At complete

monolayer coverage the adatoms form a two-dimensional lattice with the periodicity commensurate with that of the substrate surface. For the coverage 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.

In the following we are going to consider the electron-electron correlation effects within the method of Brenig and Schonhammer [16] and the adatoms properties related with its position on the substrate surface are involved in correlators of the Ising type $\langle N_\alpha N_\beta n_{\alpha-\sigma} n_{\beta-\sigma} \rangle$. 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 concerns the Ising type correlators and here we proceed as follows :

$$\langle N_\alpha N_\beta \rangle \approx \delta_{\alpha\beta} \langle N_\alpha \rangle + (1 - \delta_{\alpha\beta}) \langle N_\alpha \rangle \langle N_\beta \rangle . \quad (9)$$

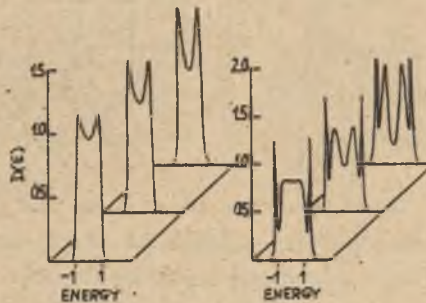


Fig.1. The adatom local density of states for different coverages (first curve in each panel corresponds to $\theta=0$, second for $\theta=0.5$ and last for $\theta=1.0$) in the symmetric case for $U/W=0.15$ (left panel) and $U/W=0.3$ (right panel). Energy in units of the substrate half bandwidth and $\theta = \langle N_\alpha \rangle$.

The second approximation can be understood as neglecting 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 substrate surface. In this way our

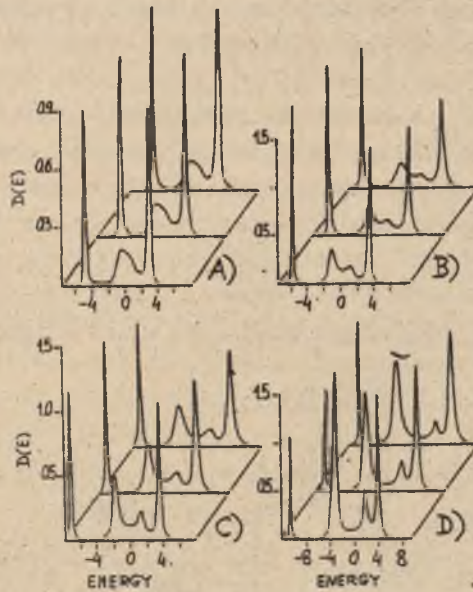


Fig.2. The adatom local density of states for nickel substrate for V equal 2 eV, 3 eV, 5 eV and 6 eV for panels A, B, C and D, respectively. The first curve in each panel corresponds to coverage $\theta=0$, second for $\theta=0.5$ and last for $\theta=1$, respectively.

calculations can be comparable with those done, for example, within the single-site coherent potential approximation [35,37]. The second approximation is fully justified for our system, as it corresponds to neglecting the interatomic electron correlations in Hubbard type Hamiltonian. The

numerical calculations have been performed for the electron charge of the hydrogen chemisorbed on the model substrates intended to describe nickel and titanium metals (for details see Ref. [34]). For all coverages the value of $q = \langle n_{\uparrow} \rangle + \langle n_{\downarrow} \rangle$ is significantly lower than results of Hartree-Fock calculations for the same set of parameters. The neutralization of the adatoms with increasing coverage was obtained in

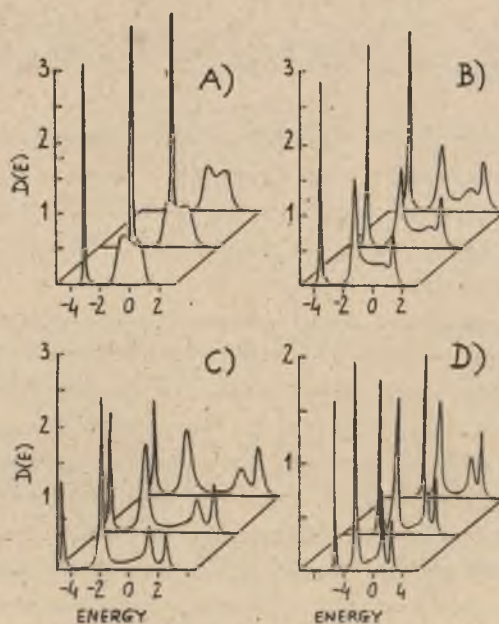


Fig.3. The same as in Fig.1 except for titanium substrate for V equal 2 eV, 4 eV, 7 eV and 8 eV, respectively.

agreement with the experimental results. The adatom local density of states depends on the coverage, too. For monolayer coverages the indirect interaction between adatoms through the substrate electrons is so large that can lead to two nearly separated energy bands. In Figs. 1-3 we have presented the adatom local density of states for three cases. Fig. 1 presents results for symmetric case, Fig. 2 for nickel substrate case

and Fig. 3 for titanium substrate case, respectively. In all cases a similar situation appears, i.e., for large coverages ($\theta = 1$ corresponds to one monolayer coverage) and for greater V one can observe appearance of a two electron subbands - effect very visible in Fig. 1. It can be understood as a result of the indirect interaction between adatoms through the substrate electrons which for large V and θ is extremely strong.

4. GENERALIZED HARTREE-FOCK SOLUTIONS

The model Hamiltonians considered in preceding sections have an unusual structure. They have the form of the Ising model with respect to ion variables N_α but with the operator coefficients consisting of Fermi amplitudes [31]. It seems that the electronic properties described by correlators like $\langle N_\alpha \rangle$, $\langle N_\alpha N_\beta \rangle$, ... can be computed simultaneously within the same Green function "machinery" within equation of motion method. In the equation of motion method one obtains, in successive steps, the sequence of coupled equations for higher and higher order Green functions and the decoupling process usually applied in such situations is an approximation, the meaning of which is not immediately transparent. For that reason, if the decouplings of the higher order Green functions into lower ones are made on a sufficiently high level of the hierarchy of equations or we take into considerations infinite series of the Green functions belonging to some classes, than we may believe that these approximations can be justified.

Here we are going to calculate the Green function $\langle\langle N_\alpha a_{\alpha\sigma} | N_\beta a_{\beta\sigma}^+ \rangle\rangle$ within the equation of motion method. Let us write equation of motion for this function:

$$\begin{aligned} (E - \epsilon_\alpha) \langle\langle N_\alpha a_{\alpha\sigma} | N_\beta a_{\beta\sigma}^+ \rangle\rangle &= \delta_{\alpha\beta} \langle N_\alpha N_\beta \rangle + \\ + U \langle\langle N_\alpha a_{\alpha\sigma} n_{\alpha-\sigma} | \dots \rangle\rangle &+ \sum_{\vec{k}} V_{\alpha\vec{k}} \langle\langle N_\alpha a_{\vec{k}\sigma} | \dots \rangle\rangle, \end{aligned} \quad (10)$$

where $|\dots\rangle$ on the right-hand-side of the Green functions denotes $|N_{\alpha} a_{\beta\sigma}^{\dagger}\rangle$. Writing the equations for the Green functions appeared in (10) and for new Green functions in next equations we obtain:

$$(E - \epsilon_k^{\dagger}) \langle\langle N_{\alpha} a_{k\sigma}^{\dagger} | \dots \rangle\rangle = \sum_{\alpha_1} V_{\alpha_1 k}^{\dagger} \langle\langle N_{\alpha} N_{\alpha_1} a_{\alpha_1\sigma} | \dots \rangle\rangle, \quad (11)$$

$$(E - \epsilon_{\alpha_1}) \langle\langle N_{\alpha} N_{\alpha_1} a_{\alpha_1\sigma} | \dots \rangle\rangle = \delta_{\alpha\beta} \langle N_{\alpha} N_{\alpha_1} N_{\beta} \rangle + \\ + U \langle\langle N_{\alpha} N_{\alpha_1} a_{\alpha_1\sigma} n_{\alpha_1-\sigma} | \dots \rangle\rangle + \sum_k V_{\alpha_1 k} \langle\langle N_{\alpha} N_{\alpha_1} a_{k\sigma}^{\dagger} | \dots \rangle\rangle, \quad (12)$$

$$(E - \epsilon_k^{\dagger}) \langle\langle N_{\alpha} N_{\alpha_1} a_{k\sigma}^{\dagger} | \dots \rangle\rangle = \sum_{\alpha_2} V_{\alpha_2 k}^{\dagger} \langle\langle N_{\alpha} N_{\alpha_1} N_{\alpha_2} a_{\alpha_2\sigma} | \dots \rangle\rangle, \quad (13)$$

$$(E - \epsilon_{\alpha_2}) \langle\langle N_{\alpha} N_{\alpha_1} N_{\alpha_2} a_{\alpha_2\sigma} | \dots \rangle\rangle = \delta_{\alpha_2\beta} \langle N_{\alpha} N_{\alpha_1} N_{\alpha_2} N_{\beta} \rangle + \\ + U \langle\langle N_{\alpha} N_{\alpha_1} N_{\alpha_2} a_{\alpha_2\sigma} n_{\alpha_2-\sigma} | \dots \rangle\rangle + \sum_k V_{\alpha_2 k} \langle\langle N_{\alpha} N_{\alpha_1} N_{\alpha_2} a_{k\sigma}^{\dagger} | \dots \rangle\rangle, \quad (14)$$

$$(E - \epsilon_{\alpha_i}) \langle\langle N_{\alpha} N_{\alpha_1} \dots N_{\alpha_i} a_{\alpha_i\sigma} | \dots \rangle\rangle = \delta_{\alpha\beta} \langle N_{\alpha} \prod_{n=1}^i N_{\alpha_n} N_{\beta} \rangle + \\ + U \langle\langle N_{\alpha} \prod_{n=1}^i N_{\alpha_n} a_{\alpha_i\sigma} n_{\alpha_i-\sigma} | \dots \rangle\rangle + \sum_k V_{\alpha_i k} \langle\langle N_{\alpha} \prod_{n=1}^i N_{\alpha_n} a_{k\sigma}^{\dagger} | \dots \rangle\rangle. \quad (15)$$

Having in hand Eqs. (10-15) we can obtain exact equation for the Green function $\langle\langle N_{\alpha} a_{\alpha\sigma} | N_{\beta} a_{\beta\sigma}^{\dagger} \rangle\rangle$ in terms of ionic correlators $\langle N_{\alpha} N_{\alpha_1} \dots N_{\beta} \rangle$ and the Green function belonging to the specific class of higher order Green functions, namely to the class of

functions $\langle N_{\alpha} N_{\alpha_1} \dots N_{\alpha_n} a_{\alpha_1-\sigma} | \dots \rangle$:

$$\begin{aligned}
 (E - \epsilon_{\alpha}) \langle N_{\alpha} Q_{\alpha\sigma} | N_{\beta} Q_{\beta\sigma}^+ \rangle &= \delta_{\alpha\beta} \langle N_{\alpha} N_{\beta} \rangle + \\
 + \sum_{n=1}^{\infty} \sum_{\alpha_1 \alpha_2 \dots \alpha_n} \frac{P_{\alpha\alpha_1}(E) \dots P_{\alpha\alpha_n}(E)}{(E - \epsilon_{\alpha_1}) \dots (E - \epsilon_{\alpha_n})} \langle N_{\alpha} \dots N_{\alpha_n} N_{\beta} \rangle &\delta_{\alpha_n\beta} + \\
 + U \langle N_{\alpha} Q_{\alpha\sigma} | \eta_{\alpha-\sigma} | \dots \rangle + \\
 + \sum_{n=1}^{\infty} \sum_{\alpha_1 \dots \alpha_n} \frac{P_{\alpha\alpha_1}(E) \dots P_{\alpha\alpha_n}(E)}{(E - \epsilon_{\alpha_1}) \dots (E - \epsilon_{\alpha_n})} \langle N_{\alpha} \dots N_{\alpha_n} Q_{\alpha_n\sigma} \eta_{\alpha_n-\sigma} | \dots \rangle
 \end{aligned} \tag{16}$$

where $P_{\alpha\beta}(E) = \frac{1}{N} \sum_{\vec{k}} \frac{V_{\alpha\vec{k}} V_{\vec{k}\beta}}{E - \epsilon_{\vec{k}}}$.

Let us introduce some approximations in further treatment of this equation. First of all we approximate the higher-order Ising-type correlators in the spirit of the Kirkwood superposition formula:

$$\langle N_{\alpha} N_{\alpha_1} \dots N_{\alpha_n} \rangle \approx \langle N_{\alpha} N_{\alpha_1} \rangle \dots \langle N_{\alpha_{n-1}} N_{\alpha_n} \rangle \langle N_{\alpha_n} N_{\alpha} \rangle / \langle N_{\alpha} \rangle^n \tag{17}$$

which was first used by Bethe [32] and Peierls [33] in the theory of lattices [38]. In this case the second term on the right hand side of Eq. (16) can be summed up exactly and reads as:

$$\langle N_{\alpha} N_{\beta} \rangle \frac{1}{N} \sum_{\vec{q}} e^{i\vec{q} \cdot (\alpha - \beta)} \frac{1}{1 - \overline{P}_{\vec{q}}(E)} \tag{18}$$

where $\overline{P}_{\vec{q}}(E)$ is a Fourier transform of the $\overline{P}_{\alpha\beta}(E)$:

$$\overline{P}_{\alpha\beta}(E) = \frac{P_{\alpha\beta}(E) \langle N_{\alpha} N_{\beta} \rangle}{(E - \epsilon_{\alpha}) \langle N_{\alpha} \rangle} \tag{19}$$

It should be remarked that in our notation \vec{q} -vectors are two-dimensional vectors corresponding to the array of the adsorption centres in the adlayer and \vec{k} -vectors are

three-dimensional. In a second step we neglect the last term of Eq. (16) containing the higher order Green functions and the third term decouple within an usual scheme. Note, that neglecting of the last term does not mean that we do not work with the infinite system of the equations for higher-and-higher order Green functions. This denotes simply that we removed from our considerations only special kind of higher order Green functions, namely, such as $\langle\langle N_\alpha N_{\alpha_1} \dots N_{\alpha_n} a_{\alpha_n-\sigma} | N_\beta a_{\beta\sigma}^+ \rangle\rangle$, and all others present in Eqs. (10-15) up to infinite degree of hierarchy of this equations are present in our calculations. To this end, for the single-site Green function ($\alpha=\beta$) we obtain:

$$\langle\langle N_\alpha a_{\alpha\sigma} | a_{\alpha\sigma}^+ \rangle\rangle = \frac{1}{N} \sum_{\vec{q}} \left[E - \epsilon_\alpha - \frac{U \langle N_\alpha n_{\alpha-\sigma} \rangle}{\theta} - (1-\theta) \Lambda'_\sigma(E) - \theta P'_\sigma(\vec{q}, E) \right]^{-1} \quad (20)$$

where we have used approximation (9). Here, $\Lambda'_\sigma(E)$ and $P'_\sigma(\vec{q}, E)$ are as follows

$$\begin{aligned} \Lambda'_\sigma(E) &= \Lambda(E) \left(1 - U \frac{\langle N_\alpha n_{\alpha-\sigma} \rangle}{\theta(E - \epsilon_\alpha)} \right), \\ P'_\sigma(\vec{q}, E) &= P_{\vec{q}}(E) \left(1 - \frac{U \langle N_\alpha n_{\alpha-\sigma} \rangle}{\theta(E - \epsilon_\alpha)} \right), \quad \theta \equiv \langle N_\alpha \rangle \end{aligned} \quad (21)$$

The Green function in the form represented in Eq. (20) generalizes the Hartree-Fock result in which $\Lambda'_\sigma(E)$ and $P'_\sigma(\vec{q}, E)$ are replaced by $\Lambda(E)$ and $P(\vec{q}, E)$ [38].

As an another treatment of the system of equations (10-11) we take into consideration all the higher order Green functions which were omitted in our previous calculations. Unfortunately, we are not able to obtain an exact solution, of course. For that reason we have to do some additional approximations. We decouple the higher order Green functions as follows (it is

generalization of usually used decouplings):

$$\begin{aligned} \langle\langle N_\alpha N_{\alpha_1} \dots N_{\alpha_n} a_{\alpha_n-\sigma} | \dots \rangle\rangle &\approx \frac{\langle N_\alpha N_{\alpha_1} \dots N_{\alpha_n} \rangle}{\theta} \times \\ \langle\langle N_{\alpha_n} a_{\alpha_n-\sigma} n_{\alpha_n-\sigma} | \dots \rangle\rangle &\approx \frac{\langle N_\alpha N_{\alpha_1} \rangle}{\theta} \dots \frac{\langle N_{\alpha_{n-1}} N_{\alpha_n} \rangle}{\theta} \times \\ \frac{\langle N_{\alpha_n} N_\alpha \rangle}{\theta} \frac{\langle N_{\alpha_n} n_{\alpha_n-\sigma} \rangle}{\theta} G_{\alpha_n \beta}^\sigma(E). \end{aligned} \quad (21)$$

Using Eq.21 we can rewrite two last parts of Eq.(16) in the form:

$$\frac{U \langle N_\alpha n_{\alpha-\sigma} \rangle}{\theta} \frac{1}{N} \sum_{\vec{q}} e^{i\vec{q}(\alpha-\beta)} \frac{G_{\vec{q}}^\sigma(E)}{1 - \overline{P_{\vec{q}}}(E)}. \quad (22)$$

After straightforward calculations we obtain:

$$\begin{aligned} (E - \epsilon_\alpha) G_{\alpha\alpha}^\sigma(E) &= \theta \frac{1}{N} \sum_{\vec{q}} \frac{1}{1 - \overline{P_{\vec{q}}}(E)} + \\ &+ \frac{U \langle N_\alpha n_{\alpha-\sigma} \rangle}{\theta} \frac{1}{N} \sum_{\vec{q}} \frac{B_{\vec{q}}(E)}{\left(1 - \overline{P_{\vec{q}}}(E)\right) \left(E - \epsilon_\alpha - \frac{U \langle N_\alpha n_{\alpha-\sigma} \rangle}{\theta} \frac{1}{1 - \overline{P_{\vec{q}}}(E)}\right)} \end{aligned} \quad (23)$$

$$B_{\vec{q}}(E) = \frac{1}{N^2} \sum_{\alpha\beta\vec{q}_1} e^{-i(\vec{q}-\vec{q}_1)(\alpha-\beta)} \frac{\langle N_\alpha N_\beta \rangle}{1 - \overline{P_{\vec{q}}}(E)}$$

Using the Bragg-Williams approximation for calculation of $\overline{P_{\vec{q}}}(E)$ and $B_{\vec{q}}(E)$ we have the final result:

$$\begin{aligned} G_{\alpha\alpha}^\sigma(E) &= G_{\alpha\alpha}^{\sigma \text{ HF}(U=0)}(E) \left[1 + \frac{U \langle N_\alpha n_{\alpha-\sigma} \rangle}{\theta} (1-\theta) G_{\alpha\alpha}^{\sigma \text{ HF}}(E) \right] + \\ &+ U \langle N_\alpha n_{\alpha-\sigma} \rangle \frac{1}{N} \sum_{\vec{q}} G_{\vec{q}}^{\sigma \text{ HF}(U=0)}(E) \left(E_\sigma^{\text{HF}}(\vec{q}, E) \right)^{-1} \end{aligned} \quad (24)$$

where

$$G_{\alpha\alpha}^{\sigma HF(U=0)}(E) = \frac{1}{N} \sum_{\vec{q}} [E - \epsilon_{\alpha} - (1-\theta)\Lambda(E) - \theta P_{\vec{q}}(E)]^{-1} \equiv \\ \equiv \frac{1}{N} \sum_{\vec{q}} G_{\vec{q}}^{\sigma HF(U=0)}(E) ,$$

$$E_{\vec{q}}^{\sigma HF}(\vec{q}, E) = E - \epsilon_{\alpha} - \frac{U \langle N_{\alpha} n_{\alpha-\sigma} \rangle}{\theta} - (1-\theta)\Lambda(E) - \theta P_{\vec{q}}(E) .$$

This formula stands for generalization of the Hartree-Fock result for final coverages. All the higher-order Green functions appearing in the equation of motion for $\langle\langle N_{\alpha} a_{\alpha\sigma} | N_{\beta} a_{\beta\sigma}^{\dagger} \rangle\rangle$ enter through two first terms in Eq. (16).

Corresponding correlators are decoupled along the Kirkwood superposition formula, and all other Green functions belonging to the class of functions of a type $\langle\langle N_{\alpha} N_{\alpha'} \dots N_{\alpha_l} a_{\alpha_l\sigma} n_{\alpha_l-\sigma} | N_{\beta} a_{\beta\sigma}^{\dagger} \rangle\rangle$ are decoupled within the same method, i.e., Kirkwood superposition formula combined with Hartree-Fock type decouplings.

5. CONCLUSIONS AND REMARKS

We have investigated the generalized Newns-Anderson Hamiltonian intended to describe the hydrogen atom or hydrogen overlayer chemisorbed on the metal surface. This Hamiltonian was obtained from more general one derived from microscopic considerations and can be served as "ab initio" derivation of the chemisorption model Hamiltonian. We have retained only this terms which are important for our specific systems. In this case we have obtained the standard Newns-Anderson Hamiltonian supplemented by the additional terms describing the influence of the fractional occupation of the adatom induced resonances

on the charge transfer between the adatom and substrate surface. The electron correlation effects have been considered beyond the Hartree-Fock approximation along the second-order self-energy matrix formalism of Ref. [16]. We have used model in which the nonorthogonality of the adatom and substrate wave functions is not taken into account, but in Ref. [4] has been shown that overlap effects nearly do not influence the adatom charge. On the other hand, the overlap effects may be essential for the calculation of the binding energy. For that reason we do not calculate the binding energy. The Hartree-Fock calculations performed for standard Hamiltonian predict the charge transfer to the adatom not compatible with experimental evidence. In our case results for generalized Hamiltonian are much better. Even in the Hartree-Fock description calculated adatom electron charge is more realistic and after introduction of the correlation effects the results are much better. In a next step we have considered a submonolayer coverages within another variant of a general Hamiltonian. Now, having in mind such complicated system we restricted ourselves to NA model with possibility of simultaneous occupation of the adsorption centres by the adatoms. Using the equation of motion for appropriate Green functions and Bragg-Williams approximation for Ising type correlators we were able to take into account the stochastic arrangement of the adatoms within the overlayer. The nature of such approximation (in treatment of the overlayer) should be comparable with the coherent potential approximation but is much simpler in practical calculations. The variation of the electron charge localized on hydrogen adatom with increasing coverage is rather small, although leads to progressive neutralization. This electron charge is too large, of course, irrespective of the improved method along which the correlation effects were introduced. But this fact is rather result of the simple model Hamiltonian (without additional term $-\sum_{\alpha} N V_{\alpha\alpha\alpha\alpha} n_{\alpha\sigma} a_{\alpha\sigma} a_{k\sigma}^{\dagger} + \text{h.c.}$) which was used. Taking into consideration this term we should obtain improved results similarly as in the one-adatom case [30]. From the other hand,

these relatively small changing of the adatom electron charge vs. coverage are in good agreement with recently published results of the " ab initio " calculations [14]. Additionally, we have also analyzed the adatom density of states for various coverages of randomly arranged adatoms. Generally one can say, that with increasing coverage a some sort of metallization of the overlayer can occur. In last section we derived the general expression for the one-particle Green function $\langle N_a | N_a \rangle$ for final coverages of the metal surfaces. We hope this general formula, Eq. (24), better describes the problem under consideration as it takes into account all contributions although calculated in approximate manner. The analysis of the presented results calculated on the basis of the generalized Hamiltonian and the results given in Refs. [5,30,34] show that there is a satisfactory description of the chemisorption process. Thus, this Hamiltonian can serve as a model more efficient in describing the chemisorption process.

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