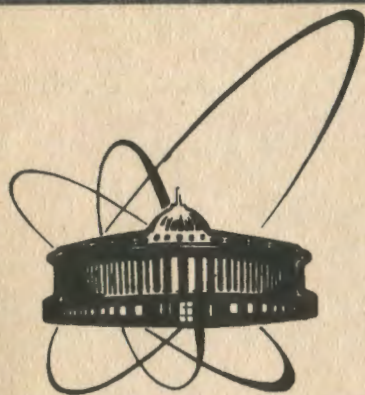


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CHEMISORPTION THEORY  
AT SUBMONOLAYER COVERAGES:  
INFLUENCE OF THE DYNAMIC HOPPING  
ON THE ELECTRONIC CHARACTERISTICS

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## 1. Introduction

The Anderson model /1/ given in the context of the local moment formation on impurities in a bulk metallic host was used with success by Edwards and Newns /2/, Grimley /3/ and by Newns /4/ to the description of the chemisorption process. Despite a remarkable success in obtaining a relatively good description of this phenomena it is now well known that so-called Newns-Anderson (NA) Hamiltonian does not take into account many important effects /5/. Recently, a generalized approach was suggested to be applied to a self-consistent microscopic description of the electronic and thermodynamic properties of atomic submonolayers adsorbed on solid state substrates /6/. The generalized Hamiltonian describing the chemisorption process was constructed based on the microscopic considerations. This model was carefully investigated in our recent works /7-12/ in the context of the mean-field (Hartree-Fock (HF)) approximation, as well as beyond HF approximation for the one-atom case, and for submonolayer coverages. Even in the simplest version this model shows that along the usual term describing the electron atom-substrate transfer as in N-A Hamiltonian, essential may be so-called dynamic hopping terms (see also /13,14/). In Ref./9/ we have shown that by including of this additional interactions to N-A model (in the one-atom case) one may improve the description of the chemisorption characteristics.

At present considerable efforts are made to describe the properties of atomic submonolayer coverages of solid crystal surfaces. These investigations have a great practical importance as they deepen our understanding of processes taking place in catalysis, corrosion and other practical domains of surface science (see, for example /16/).

In this paper we are going to investigate the N-A model with dynamic hopping terms included generalized to submonolayer coverages. The electron correlation effects will be included within the second-order with respect to the electron adatom-substrate coupling perturbation approach of Brenig and Schonhammer /15/. The adatom distribution over the substrate surface is assumed to be completely uncorrelated and will be treated within a method equivalent to the coherent potential approximation.

The description of the model is given in Sec. 2 and the results of its numerical investigations with remarks and conclusions are presented in Sec. 3.

## 2. Hamiltonian

The Hamiltonian which may describe the chemisorbed hydrogen-like overlayer on metal surfaces can be written as follows /6,7/

$$H = \sum_{k\sigma} \epsilon_k n_{k\sigma} + \sum_{\alpha\sigma} N_{\alpha} \left\{ E_{\alpha} n_{\alpha\sigma} + \frac{U}{2} n_{\alpha\sigma} n_{\alpha-\sigma} - \sum_k \left[ (V_{\alpha\alpha k} n_{\alpha-\sigma} - V_{\alpha k}) a_{\alpha\sigma}^+ a_{k\sigma} + \text{h.c.} \right] \right\} + \sum_{\substack{\alpha \neq \beta \\ \sigma}} N_{\alpha} N_{\beta} a_{\alpha\sigma}^+ a_{\beta\sigma} E_{\alpha\beta} + H_{\text{rest.}} \quad (1)$$

All symbols have usual meaning like in the N-A model and others, not present in N-A model, were explained in Ref. /6/ and in our recent papers /7-12/. Model (1) can be viewed as a generalization of the N-A Hamiltonian to the case of a stochastic arrangement of adatoms on the metal surface. The operator  $N_{\alpha}$  has eigenvalues equal to 1 or 0 depending on the adatom is present or not in the corresponding adsorption site  $\alpha$ . For that reason the sum over  $\alpha$  is carried out over all adsorption centers (not only over filled up with adatoms). The electronic properties of the chemisorption system are described by the correlation functions of the type  $\langle n_{k\sigma} \rangle$ ,  $\langle N_{\alpha} n_{\alpha\sigma} \rangle$ ,  $\langle N_{\alpha} a_{\alpha\sigma}^+ a_{k\sigma} \rangle$ , ..., and the ionic

(adatoms) properties by the functions like  $\langle N_\alpha \rangle \cong \theta$  (number of chemisorbed adatoms/number of adsorption sites) - the coverage of the substrate surface,  $\langle N_\alpha N_\beta \rangle$ ,  $\langle N_\alpha N_\beta N_\gamma \rangle$ , ... . The correlation functions describing the electronic properties can be calculated through the corresponding Green Functions (GF) of the type  $\langle\langle a_{k\sigma} | a_{k\sigma}^+ \rangle\rangle$ ,  $\langle\langle N_\alpha a_{k\sigma} | a_{k\sigma}^+ \rangle\rangle$ ,  $\langle\langle N_\alpha a_{\alpha\sigma} | a_{k\sigma}^+ \rangle\rangle$ , ... , (the retarded, double-time GF introduced by Zubarev /17/). The correlation functions describing the ionic correlators are obtainable from the knowledge of the GF  $\langle\langle c_\alpha | c_\alpha^+ \rangle\rangle$ ,  $\langle\langle N_\alpha | N_\beta \rangle\rangle$ , ... , where  $N_\alpha = c_\alpha^+ c_\alpha$ .

The first four terms of the Hamiltonian (1) form the usual N-A model but generalized to the stochastic arrangement of adatoms on the substrate surface. The fifth term is absent in N-A model and describes so-called dynamic hopping (compare /13,1/). This additional term results from very general treatment of the microscopic Hamiltonian within the second quantization procedure described in Ref./6/. The sixth term in (1) represents in a very concise form that part of the general Hamiltonian and describes the metallization of the chemisorbed layer caused by enveloping the adatom valence orbitals at the neighboring adsorption centres.  $H_{rest}$  contains others; of less importance terms - see Ref. /6/. In the following we adopt for the matrix elements  $V_{\alpha\alpha\alpha k}$  a rather good approximation (for details see /7,8/)

$$V_{\alpha\alpha\alpha k} \approx \zeta V_{\alpha k}, \quad 0 \leq \zeta \leq 1 \quad (2)$$

and reject the two last terms in the Hamiltonian (1). The term describing the direct interaction between the hydrogen adatoms should not introduce a qualitative changes in the chemisorption characteristics. The atomic radius of these adatoms is sufficiently small in comparison with the substrate lattice constant and, as a first approximation, the direct adatom-adatom interaction can be neglected. Finally, the following Hamiltonian will be taken for further considerations

$$H = \sum_{k\sigma} \epsilon_k n_{k\sigma} + \sum_{\alpha\sigma} N_{\alpha} \left( E_{\alpha} n_{\alpha\sigma} + \frac{U}{2} n_{\alpha\sigma} n_{\alpha-\sigma} \right) + \sum_{\alpha k \sigma} N_{\alpha} V_{\alpha k} \left( 1 - \zeta n_{\alpha-\sigma} \right) a_{\alpha\sigma}^{+} a_{k\sigma} + \text{h.c.} \quad (3)$$

### 3. Numerical results and discussion

The electron correlation effects will be included into considerations within the matrix self-energy approach of Brenig and Schonhammer /15/. Recently we have used this formalism in the case of one adatom chemisorbed on the metal surface /9/. From the other hand, the model described by Hamiltonian like (1) but without dynamic hopping was investigated by us in Ref./10/. In this case the Green Functions involving the electron and ionic operators were decoupled to yield results which treat the adatom distribution on the adsorption centres in a perfectly random way. This paper can be viewed as a generalization of that from Ref./15/ to general coverages or of that from Ref./10/ generalized to a model described by Hamiltonian (3). Here we do not repeat the calculations given in the mentioned papers but give only final expressions for the required GF  $\langle\langle N_{\alpha} a_{\alpha\sigma} | a_{\alpha\sigma}^{+} \rangle\rangle$ . This Green Function is given by the formula

$$\begin{aligned} \langle\langle N_{\alpha} a_{\alpha\sigma} | a_{\alpha\sigma}^{+} \rangle\rangle = \frac{\theta}{N_{\parallel}} \sum_{\sigma} \left\{ 2n_{-\sigma}(1-n_{-\sigma})D_{12} + n_{-\sigma}^2 \left[ (E-E_{\alpha})(1-n_{-\sigma})-D_{22} \right] + \right. \\ \left. + (1-n_{-\sigma})^2 \left[ (E-E_{\alpha}-U)n_{-\sigma}-D_{11} \right] \right\} \left\{ \left[ (E-E_{\alpha}-U)n_{-\sigma}-D_{11} \right] \times \right. \\ \left. \times \left[ (E-E_{\alpha})(1-n_{-\sigma})-D_{22} \right] - D_{12}^2 \right\}^{-1} \quad (4) \end{aligned}$$

where  $D_{ik}$  ( $i, k=1, 2$ ) read as

$$D_{11} = \Lambda(E)(1-\zeta)^2 \left[ n_{-\sigma}(1-\theta n_{-\sigma}) + \frac{1}{2} \right] + \theta n_{-\sigma}^2 P_{\sigma}(E) - \mathcal{X}_1$$

$$D_{12} = \Lambda(E)(1-\zeta) \left[ -\frac{\theta}{4} - \frac{1}{2} \right] + \theta n_{-\sigma}^2 P_{\sigma}(E) + \mathcal{X}_2$$

$$D_{22} = \Lambda(E) \left[ 1 - n_{-\sigma} - \theta(1-n_{-\sigma})^2 + \frac{1}{2} \right] + \theta(1-n_{-\sigma})^2 P_{\sigma}(E) - \mathcal{X}_1$$

$$\begin{aligned} \mathcal{X}_1 &= \frac{1}{2} \sum_k |V_{\mathbf{A}k}|^2 \left\{ (1-\zeta)^2 \frac{f(\varepsilon_k) - f(E_{\mathbf{A}} + U)}{\varepsilon_k - E_{\mathbf{A}} - U} - \frac{f(\varepsilon_k) - f(E_{\mathbf{A}})}{\varepsilon_k - E_{\mathbf{A}}} \right\}, \\ \mathcal{X}_2 &= \frac{1}{2} \sum_k |V_{\mathbf{A}k}|^2 (1-\zeta) \left\{ \frac{f(\varepsilon_k) - f(E_{\mathbf{A}})}{\varepsilon_k - E_{\mathbf{A}}} - \frac{f(\varepsilon_k) - f(E_{\mathbf{A}} + U)}{\varepsilon_k - E_{\mathbf{A}} - U} \right\}, \end{aligned} \quad (5)$$

and  $\Lambda(E)$ ,  $P_g(E)$  are given below.

In following, in order to study the quantitative features of the chemisorption characteristics, we shall use as a substrate the (100) surface of a cubium (a crystal with simple cubic lattice described in the s-tight-binding approximation). The adatoms are assumed to lie just on the top of the surface atoms. The hopping integral between the adatom and the metal is written as

$$V_{\alpha k} = \sqrt{\frac{2}{N_{\parallel} N_{\perp}}} V e^{ik_{\parallel} R_{\parallel}} \sin k_z a \quad (6)$$

i.e. we have assumed the translational symmetry in the plane of the substrate surface. Similarly as in our previous works and in Ref./15/ we have added a small broadening of the substrate density of states curve to simulate the finite lifetime of the substrate electron states. The chemisorption function is calculated as follows

$$\Lambda(E) = \frac{2V^2}{N_{\parallel} N_{\perp}} \sum_k \frac{\sin^2 \alpha k_z}{E + (\cos \alpha k_x + \cos \alpha k_y + \cos \alpha k_z)/3 + i\tau} \quad (7)$$

and

$$P_g(E) = \frac{1}{N_{\parallel}} \sum_{\alpha\beta k} \frac{V_{\alpha k} V_{k\beta} e^{-iq(\alpha-\beta)}}{E - \varepsilon_k + i\tau} \quad (8)$$

where the zero energy point is taken as the band center and the band extends in limits  $(-1, +1)$ . The  $g$ -dependence enters into formula (6) only through the function  $E_g = (\cos \alpha k_x + \cos \alpha k_y)/3$  so we can transform the two-dimensional

integrals simply into a one-dimensional one using the two-dimensional density of states  $\rho_{2D}(\tilde{E})$ , i.e. (compare with /18/)

$$\sum_q f(q) \rightarrow \int dE \rho_{2D}(E) f(E). \quad (9)$$

Note, that the chemisorption function (7) is expressed through the first layer density of states for cubium substrate, i.e. for assumed symmetry of the substrate metal it represents the best approximation for  $\Lambda(E)$ .

As a first step we are going to consider the influence of the dynamic hopping on the problem of breaking and restoring of the symmetry of the N-A model. It is clear, especially in the HF approximation, that the dynamic hopping renormalizes the values of the adatoms energy level and the hopping strength. One has

$$E_\sigma = E_\alpha + U \langle N_\alpha n_{\alpha-\sigma} \rangle / \theta - \zeta \left[ \sum_k \left[ V_{\alpha k} \langle N_\alpha a_{\alpha\sigma}^+ a_{k\sigma} \rangle / \theta + h.c. \right] \right] \quad (10)$$

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

To study the general trends in breaking and restoring of the symmetry in N-A model we introduce a frequently used parameter  $\eta = 2(E_\alpha - E_f) + U$  which characterizes the position of the adatom level  $E_\alpha$  and the energy level  $E_\alpha + U$  with respect to the Fermi level. The case with  $\eta = 0$  corresponds to the so-called symmetrical Anderson model with both level at equal distance on different sides of  $E_f$ . The two remaining cases correspond to a broken symmetry. In general, beyond the HF approximation, one should also observe a some kind of "transition" from a negative asymmetric case through  $\eta = 0$  symmetric case to a positive asymmetric case with increasing value of the parameter  $\zeta$  - this parameter "measures" the strength of the dynamic hopping in our model (3).

In Figs. 1-3 we have shown the adatom density of states for increasing values of the hopping strength  $V$ ,  $V = 0.15, 0.60$  and  $0.90$  (in units of the half band width),

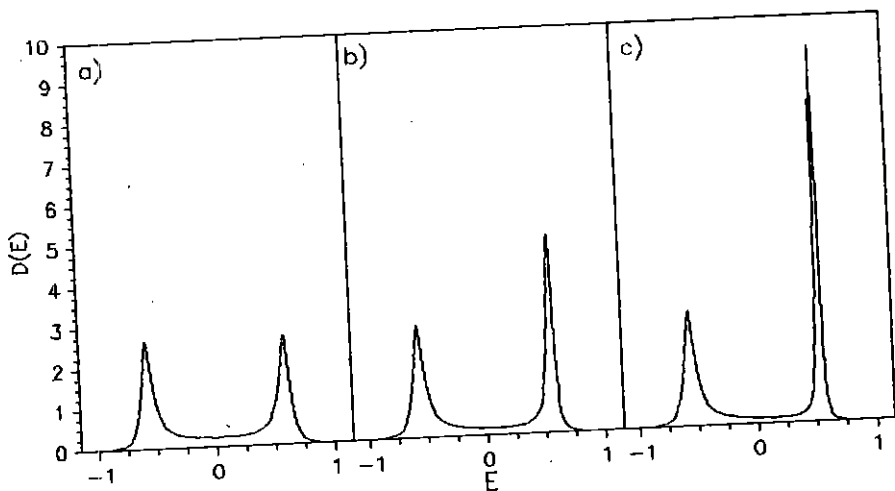


Fig.1.-The adatom density of states calculated for the symmetric case with  $V=0.15$ ,  $U=1.0$ ,  $E_{\alpha}=-0.5$ , for  $\zeta=0.0$ ,  $0.3$  and  $0.5$  (panels a), b) and c) respectively).

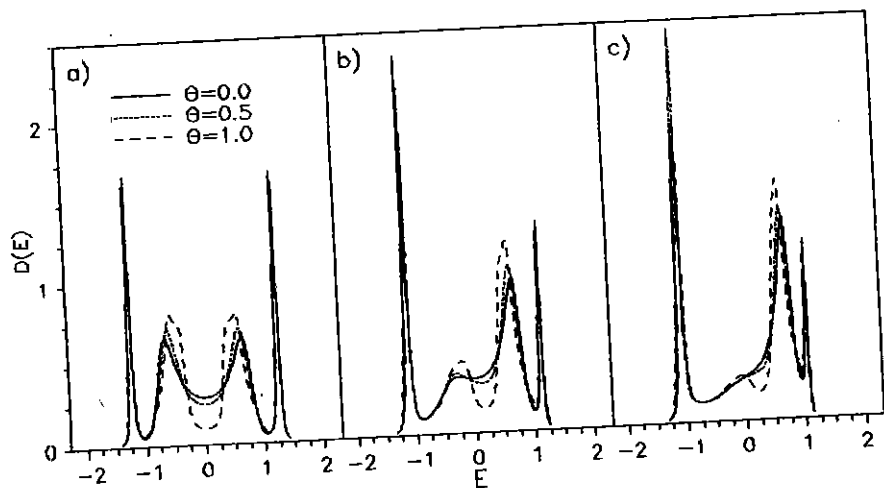


Fig.2.-The adatom density of states calculated for the symmetric case with  $V=0.60$ ,  $U=1.0$ ,  $E_{\alpha}=-0.5$ , for  $\zeta=0.0$ ,  $0.3$  and  $0.5$  (panels a), b) and c) respectively).



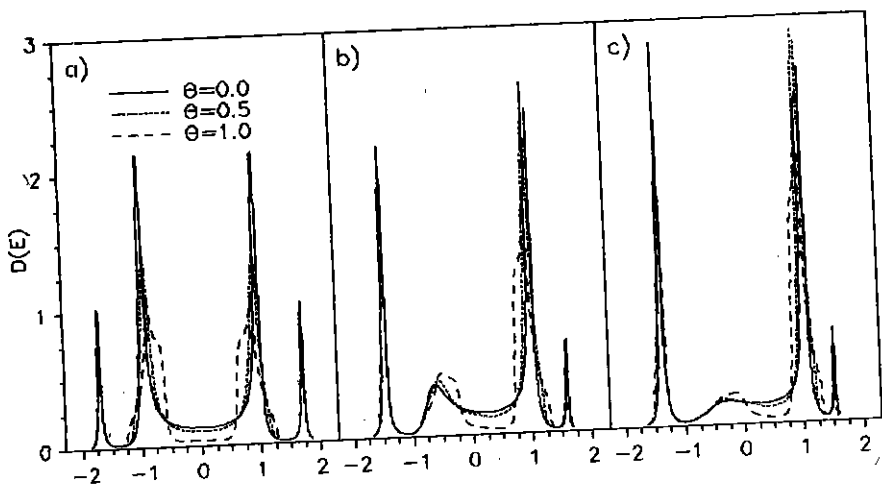


Fig.3.-The adatom density of states calculated for the symmetric case with  $V=0.90$ ,  $U=1.0$ ,  $E_{\alpha}=-0.5$ , for  $\xi=0.0$ ,  $0.3$  and  $0.5$  (panels a), b) and c) respectively).

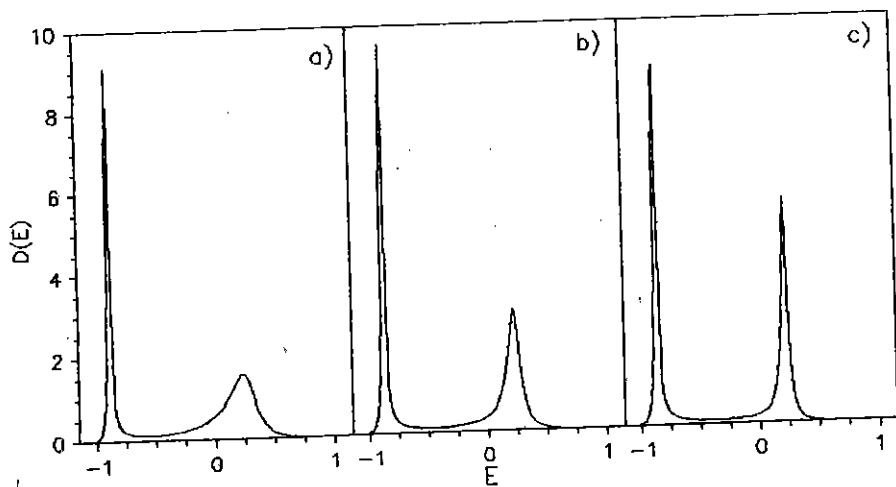


Fig.4.-The adatom density of states calculated for the asymmetric case with  $V=0.15$ ,  $U=1.0$ ,  $E_{\alpha}=-0.8$ , for  $\xi=0.0$ ,  $0.3$  and  $0.5$  (panels a), b) and c) respectively).

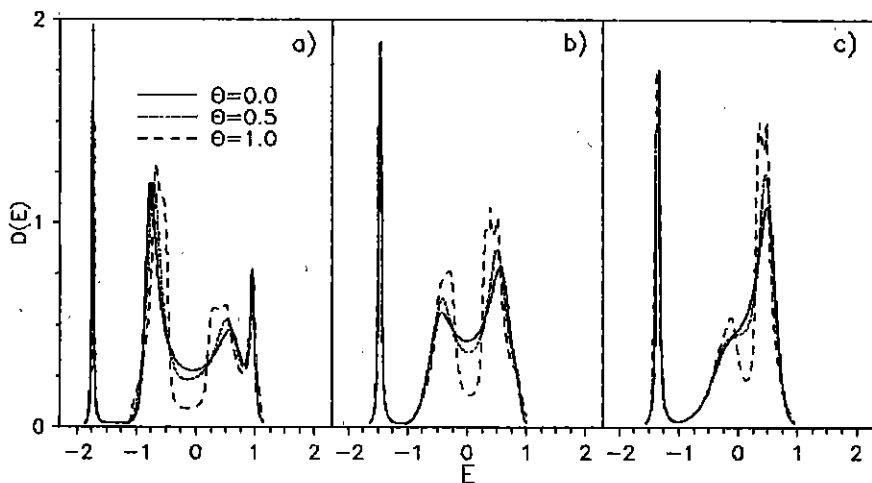


Fig.5.-The adatom density of states calculated for the asymmetric case with  $V=0.60$ ,  $U=1.0$ ,  $E_{\alpha}=-0.8$ , for  $\zeta=0.0$ ,  $0.3$  and  $0.5$  (panels a), b) and c) respectively).

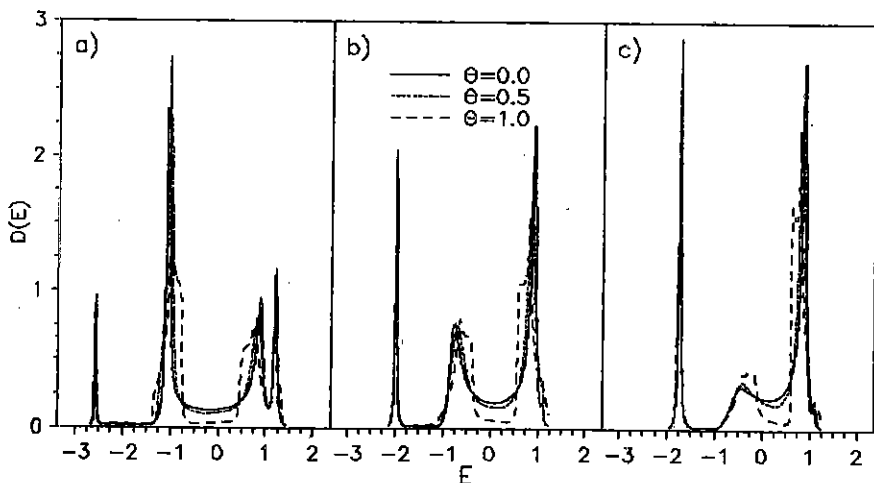


Fig.6.-The adatom density of states calculated for the asymmetric case with  $V=0.90$ ,  $U=1.0$ ,  $E_{\alpha}=-0.8$ , for  $\zeta=0.0$ ,  $0.3$  and  $0.5$  (panels a), b) and c) respectively).

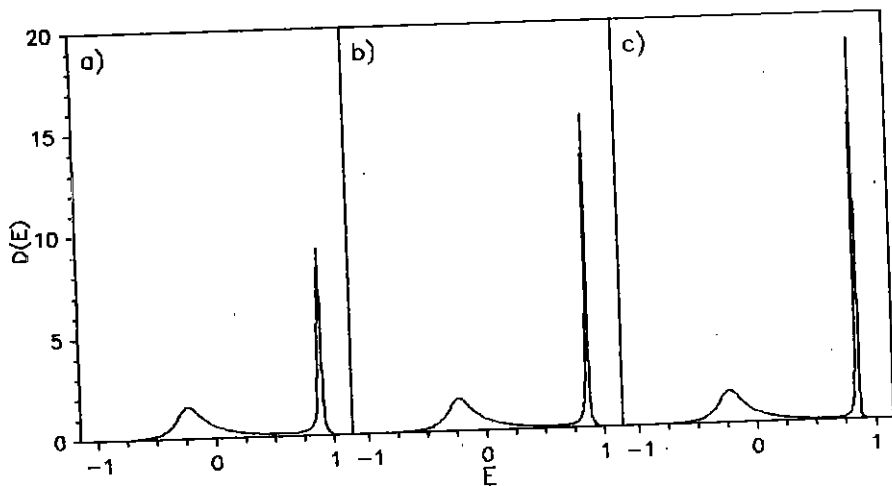


Fig.7.-The adatom density of states calculated for the asymmetric case with  $V=0.15$ ,  $U=1.0$ ,  $E_{\alpha}=-0.2$ , for  $\zeta=0.0$ ,  $0.3$  and  $0.5$  (panels a), b) and c) respectively).

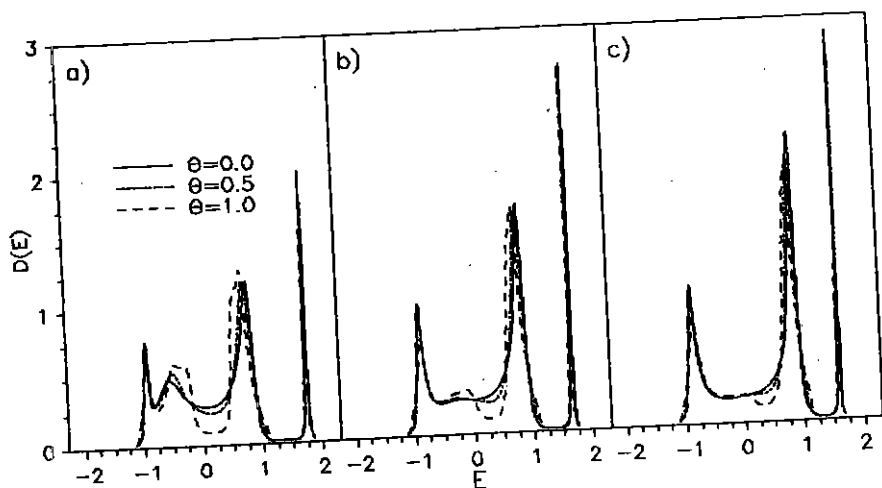


Fig.8.-The adatom density of states calculated for the asymmetric case with  $V=0.60$ ,  $U=1.0$ ,  $E_{\alpha}=-0.2$ , for  $\zeta=0.0$ ,  $0.3$  and  $0.5$  (panels a), b) and c) respectively).

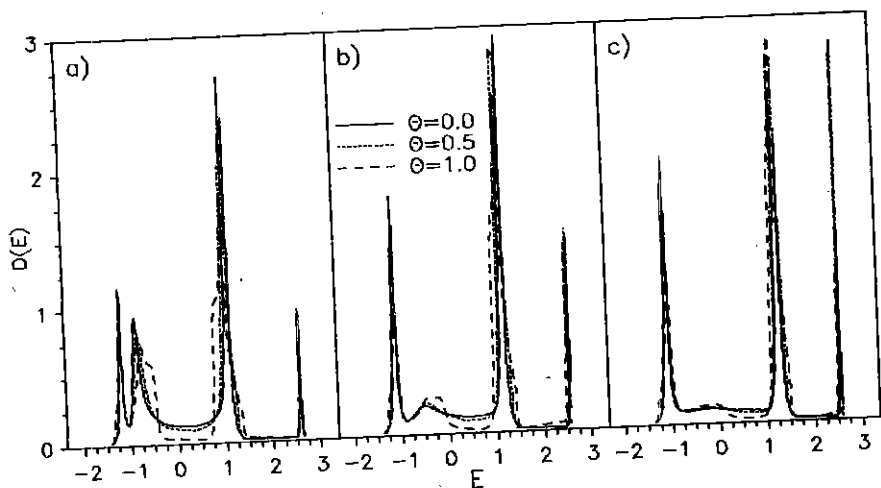


Fig.9.-The adatom density of states calculated for the asymmetric case with  $V=0.90$ ,  $U=1.0$ ,  $E_{\alpha}=-0.2$ , for  $\zeta=0.0$ ,  $0.3$  and  $0.5$  (panels a), b) and c) respectively).

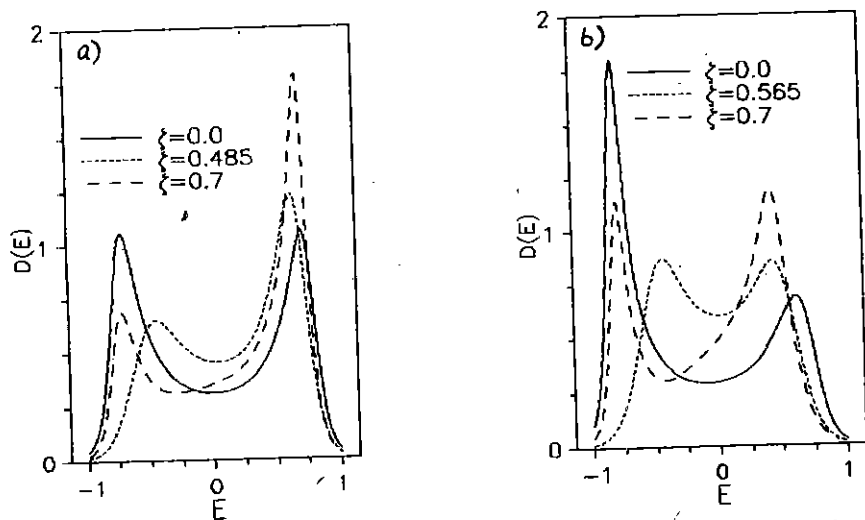


Fig.10-The adatom density of states calculated for  $\theta=0$  and different values of  $\zeta$  for the hamiltonian parameters:  
a)  $E_{\alpha}=-0.5$ ,  $U=1.0$ ,  $V=0.6$  ( $\eta=0$ ).  
b)  $E_{\alpha}=-0.8$ ,  $U=1.0$ ,  $V=0.6$  ( $\eta < 0$ ).

respectively. In all figures the left middle and right panels correspond to  $\zeta=0, 0.3$  and  $0.5$ , respectively. As could be expected, at small value of  $V$  we see almost coverage independent adatom density of states curves. With increasing value of  $\zeta$ , the initial symmetry case goes into an asymmetric one with increasing height of the right peak. At the same time the left peak shifts slightly inwards. For greater values of  $V$  in Figs. 2 and 3 we observe additional peaks outside the substrate energy band (compare /10,15/). Now the differences for various values of  $\zeta$  are more visible. With increasing  $\zeta$  the spectrum changes from four-peaked structure to three-peaked structure with decreasing of the highest energy peak. The peak lying at the lower edge of the substrate energy band disappears but at the same time the peak centered at the upper edge of the band increases. The increasing of  $\zeta$  tends to reduce the influence of the increasing value of the coverage and this suggests decreasing of the effective adatom-substrate interaction - see Eq.(8). It is also consistent with our previous discussion concerning the parameter  $\zeta$  /7,8/. It is important to note, that the dynamic hopping renormalizes not only the hopping strength, as in this case the symmetry of the adatom density of states should remain symmetric also for nonzero values of  $\zeta$ , but also renormalizes the adatom level position and the correlation strength.

In Figs. 4-6 we have displayed results for the negative asymmetric case. The behavior is essentially the same and increasing dynamic hopping tends to restore the symmetry of the adatom density of states. For the positive asymmetric case shown in Figs. 7-9 we see that the greater values of  $\zeta$  lead to increasing of the mentioned asymmetry. Thus we can say that in most cases the role of the dynamic hopping is to change the adatom density of states suggesting a transition from the negative asymmetric case to the positive one.

The adatom density of states is almost coverage independent for small values of  $V$  and/or in most cases for greater values of  $\zeta$ . It is especially clear seen in Fig.8. With

increasing  $\zeta$  the relative changes of these curves with increasing coverage are smaller. We can understand this fact if we remember that the increasing value of  $\zeta$  corresponds to the increasing distance between adatom and the substrate surface. In such a case one may expect a decreasing of the effective coupling between adatoms and substrate.

In order to better represent this changing of the symmetry with  $\zeta$  we show in Fig. 10 the HF results for the symmetric and negative asymmetric cases, respectively. The transition from the symmetry to more and more positive asymmetry is shown in Fig. 10a and in Fig. 10b from the negative asymmetry through "symmetric" case to positive asymmetry case. It should be noted, that despite of the symmetrical density of states for  $\zeta=0.565$  in Fig. 10b, this case does not represent the symmetric Anderson model, as the values of  $E_\alpha$ ,  $U$  and  $E_f$  does not fulfilled the condition of vanishing  $\eta$ . One can find, however, such renormalized values of these parameters that the resulting Hamiltonian ( $\zeta=0$ ) will possess desired symmetry. It can be checked the Hamiltonian (3) with parameters  $E_\alpha=-0.8$ ,  $V=0.6$ ,  $U=1.0$ ,  $E_f=0.0$  and  $\zeta=0.565$  is equivalent to the symmetrical model with parameters  $E_\alpha=-0.20841$ ,  $V=0.42913$ ,  $U=0.41682$ ,  $E_f=0$  and  $\zeta=0$ . From mathematical point of view such a general trend of transition from negative asymmetry case to positive one can be understood by looking at formula (10), if we take into account that the sum over  $k$  in the last term of this formula is a negative quantity (a result of the numerical calculations).

The last problem we want to discuss is the adatom electron charge. Here we consider the hydrogen chemisorbed on chromium substrate. As the chemisorption function we take the cubium (100) surface density of states and the other parameters are chosen from the Newns paper /19/. The electron correlation effects were included up to second order in  $V$  within the self-energy matrix formalism of Brenig and Schonhammer /15/. In Fig.11 we have depicted the electron charge localized on the hydrogen adatom as a function of  $V$ , for different coverage rates and for the

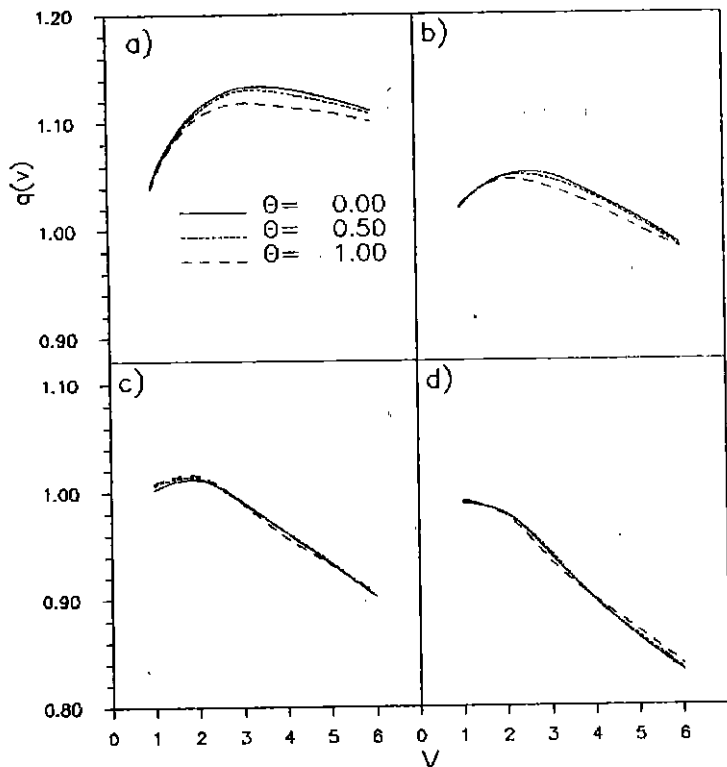


Fig.11-The adatom charge as a function of  $\theta$ ,  $V$  and  $\zeta$  for parameters values chosen to describe Cr substrate:  $E_{\alpha}^{\circ} = -9.05$  eV,  $U = 12.9$  eV,  $E_f^{\circ} = 0.69$  eV and  $\Gamma = 3.05$  eV. All energies are given with respect to the band center.

following values of  $\zeta$ ;  $\zeta = 0.0, 0.3, 0.5, 0.7$  -panels a), b), c) and d) respectively. The neutralization of the chemisorbed layer is seen only for the N-A model without additional dynamic hopping interaction. For increasing values of  $\zeta$  the results becomes less sensitive (within the range of numerical errors) to the coverage rate. On the other hand, the electron charge is depressed when one is going from 0 to greater values of  $\zeta$ . In general, the

hydrogen chemisorption on transition metals is in nearly neutral state, so we can conclude that the generalized N-A model with dynamic hopping terms included ( $\approx 0.3-0.5$ ) should better describe this chemisorption system. The small or vanishing dependence of the adatom charge on the coverage rate is also confirmed by first principles calculations /20/. We lay stress on that neutralization with increasing coverage rate is somewhat model dependent, more exactly it may depend on the  $P_g(E)$  function calculation. In any case, however, we observe a small or vanishing coverage dependence of the electron charge localized on adatoms.

In summary, we have investigated the influence of the dynamic hopping on the electronic structure of the hydrogen adatoms chemisorbed on transition metal substrates. The additional interactions present in the generalized N-A Hamiltonian change the initial symmetry of the Hamiltonian and renormalize the effective adatom energy level and the adatom-substrate coupling strength. The increasing value of the dynamic hopping leads also to a relatively smaller coverage dependence of the adatom density of states, as well as to a more neutral chemisorption.

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