

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

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The influence of the dynamic hopping term included in the Newns-Anderson Hamiltonian on the electronic structure of the chemisorbed layer at different coverages rates is investigated. It is shown that this additional interaction can destroy the initial symmetry of the Newns-Anderson model or restore this symmetry in the initial negative asymmetric case. The coverage dependence of the adatom electron charge is also studied for the case of hydrogen chemisorption on a model transition metal surface.

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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 (N-A) Hamiltonian does not take into account many important effects [5]. Recently, a generalized approach was suggested 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 on a base of 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-adatom case and for submonolayer coverages. Even in the simplest version this model shows that along the usual term describing the adatom–substrate charge transfer as in N–A Hamiltonian, so-called dynamic hopping terms may be essential (see also [13, 14]). In Ref. [9] we have shown that including this additional interactions to N–A model (in the one-adatom 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 generalized to submonolayer coverages with the dynamic hopping terms included. The electron correlation effects will be included within the second-order (with respect to the electron adatom–substrate coupling) perturbation approach of Brenig and Schönhammer [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 [18].

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]:

$$\begin{aligned}
 H = & \sum_{k,\sigma} \varepsilon_k n_{k\sigma} + \sum_{\alpha\sigma} N_\alpha \left\{ E_\alpha n_{\alpha\sigma} + \frac{U}{2} n_{\alpha\sigma} n_{\alpha-\sigma} \right. \\
 & \left. + \sum_k [(V_{\alpha k} - V_{\alpha\alpha k} n_{\alpha-\sigma}) a_{\alpha\sigma}^\dagger a_{k\sigma} + \text{h.c.}] \right\} \\
 & + \sum_{\substack{\alpha \neq \beta \\ \alpha, \beta, \sigma}} N_\alpha N_\beta a_{\alpha\sigma}^\dagger a_{\beta\sigma} a_{\beta\sigma} E_{\alpha\beta} + H_{\text{rest}}.
 \end{aligned} \tag{1}$$

All symbols have a 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]. The model (1) can be viewed as a generalization of the N–A Hamiltonian to the case of many adatoms chemisorbed on the metal surface. The operator  $N_\alpha$  has eigenvalues equal to 1 or 0 if the adatom is present or not in the corresponding adsorption site  $\alpha$ , respectively. 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  $\langle N_\alpha \rangle \equiv \theta$  (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 four first terms of the Hamiltonian (1) form the usual N–A model but generalized to the case of many adatoms chemisorbed on the substrate surface. The fifth term is absent in N–A model and describes the so-called dynamic hopping (compare [13, 14]). 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 which describes the metallization of the chemisorbed layer caused by enveloping of the adatom valence orbitals at the neighboring adsorption centers.  $H_{\text{rest}}$  contains other terms of less importance — for details see Ref. [6]. In the following we adopt for the matrix elements  $V_{\alpha\alpha k}$  a rather good approximation (for details see [7, 8])

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

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:

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

### 3. Numerical results and discussion

The electron correlation effects will be included into considerations within the matrix self-energy approach of Brenig and Schönhammer [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 the 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 centers in a perfectly random way. This paper can be viewed as a generalization of that from Ref. [15]

to general coverages or 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  $\langle N_\alpha a_{\alpha\sigma} | a_{\alpha\sigma}^\dagger \rangle$ . The Green function is given by the formula:

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

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

$$\begin{aligned} D_{11} &= \Lambda(E)(1 - \zeta)^2 \left[ n_{-\sigma}(1 - \theta n_{-\sigma}) + \frac{1}{2} \right] + \theta n_{-\sigma}^2 P_q(E) - \mathcal{X}_1, \\ D_{12} &= \Lambda(E)(1 - \zeta) \left[ -\frac{\theta}{4} - \frac{1}{2} \right] + \theta n_{-\sigma}^2 P_q(E) + \mathcal{X}_2, \\ D_{22} &= \Lambda(E) \left[ 1 - n_{-\sigma} - \theta(1 - n_{-\sigma})^2 + \frac{1}{2} \right] + \theta(1 - n_{-\sigma})^2 P_q(E) - \mathcal{X}_1, \\ \mathcal{X}_1 &= \frac{1}{2} \sum_k |V_{\alpha k}|^2 \left\{ (1 - \zeta)^2 \frac{f(\varepsilon_k) - f(E_\alpha + U)}{\varepsilon_k - E_\alpha - U} - \frac{f(\varepsilon_k) - f(E_\alpha)}{\varepsilon_k - E_\alpha} \right\}, \\ \mathcal{X}_2 &= \frac{1}{2} \sum_k |V_{\alpha k}|^2 (1 - \zeta) \left\{ \frac{f(\varepsilon_k) - f(E_\alpha)}{\varepsilon_k - E_\alpha} - \frac{f(\varepsilon_k) - f(E_\alpha + U)}{\varepsilon_k - E_\alpha - U} \right\}, \end{aligned} \quad (5)$$

and  $\Lambda(E)$ ,  $P_q(E)$  are given below. Here  $q$  denotes a two-dimensional wave vector lying in the first Brillouin zone of the reciprocal lattice corresponding to the adsorption centers.

In the following, in order to study the quantitative features of the chemisorption characteristics, we shall use as a substrate the (100) surface of a cubic crystal lattice described in the 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 to simulate the finite lifetime of the substrate electron states. The chemisorption function is calculated as follows:

$$\Lambda(E) = \frac{2V^2}{N_{\parallel}N_{\perp}} \sum_k \frac{\sin^2(ak_z)}{E + \frac{1}{3}(\cos(ak_x) + \cos(ak_y) + \cos(ak_z))} \quad (7)$$

and

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

where the zero energy point is taken as the band center and the band extends in limits  $(-1, +1)$ . Let us 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  $\Lambda(E)$ .

First, 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 value of the adatom energy level and the hopping strength. One has

$$E_{\sigma} = E_{\alpha} + \frac{U \langle N_{\alpha} n_{\alpha-\sigma} \rangle}{\theta} - \zeta \sum_k \left[ \frac{V_{\alpha k} \langle N_{\alpha} a_{\alpha\sigma}^{\dagger} a_{k\sigma} \rangle}{\theta} + \text{h.c.} \right],$$

$$V_{\alpha k}^{\sigma} = \left( 1 - \frac{\zeta \langle N_{\alpha} n_{\alpha-\sigma} \rangle}{\theta} \right) V_{\alpha k}. \quad (9)$$

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 levels 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), respectively. In all figures the front, middle and back panels correspond to  $\zeta = 0, 0.3$  and  $0.5$ , respectively. As should be expected, at small values of  $V$  we obtain almost coverage independent adatom density of states. 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  $V$ , Figs. 2 and 3, we observe additional peaks outside the

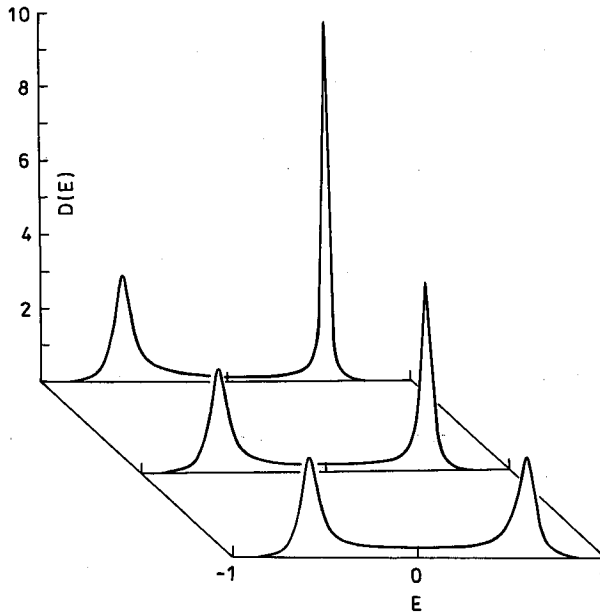


Fig. 1. The adatom density of states for the symmetrical N-A model ( $E_\alpha = -0.5$ ,  $V = 0.15$ ,  $U = 1.0$ ,  $E_F = 0$ ) for  $\zeta = 0$ , front panel;  $\zeta = 0.3$ , middle panel and  $\zeta = 0.5$ , back panel. There are no differences for various coverage rates.

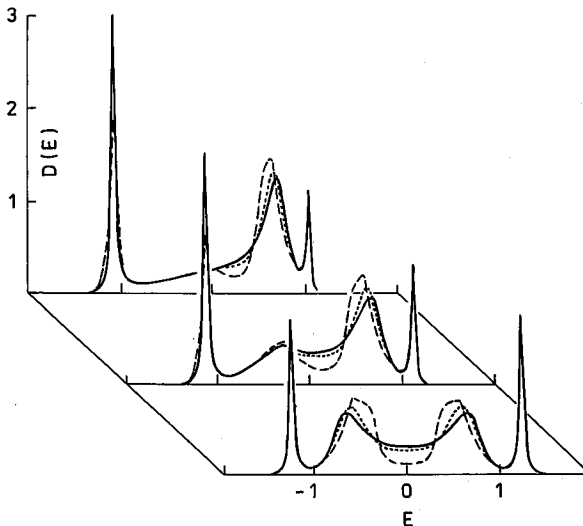


Fig. 2. The same as in Fig. 1 but for  $V = 0.6$ . The full, dotted and broken lines correspond to the coverage rate equal to 0, 0.5 and 1.0, respectively.

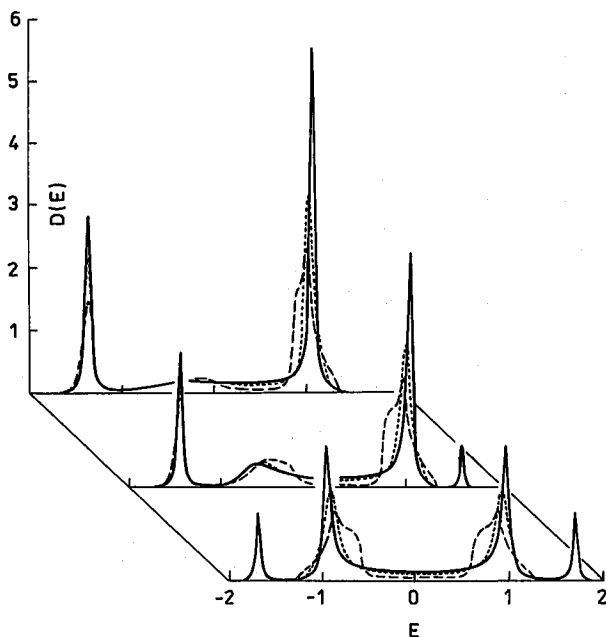


Fig. 3. The same as in Fig. 1 but for  $V = 0.9$ .

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. 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 unchanged 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 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  $V$  or, in most cases, for greater values of  $\zeta$ . Especially it is seen clearly in Fig. 8.

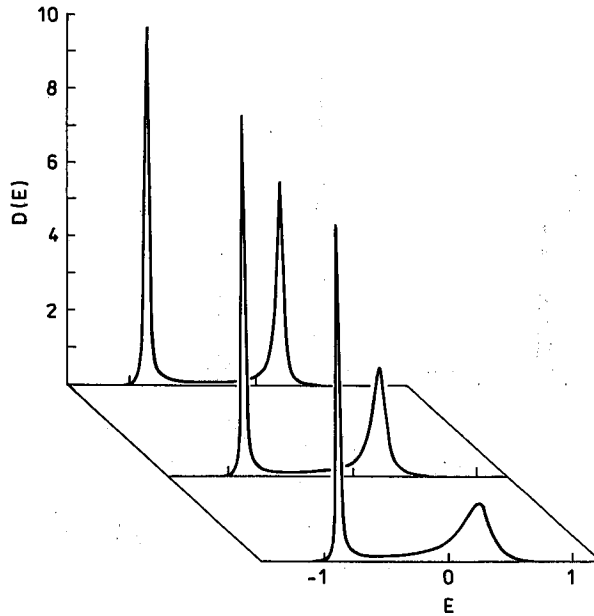


Fig. 4. The same as in Fig. 1 but for the negative asymmetry of N-A model ( $E_\alpha = -0.8$ ,  $V = 0.15$ ,  $U = 2.0$ ,  $E_F = 0$ ).

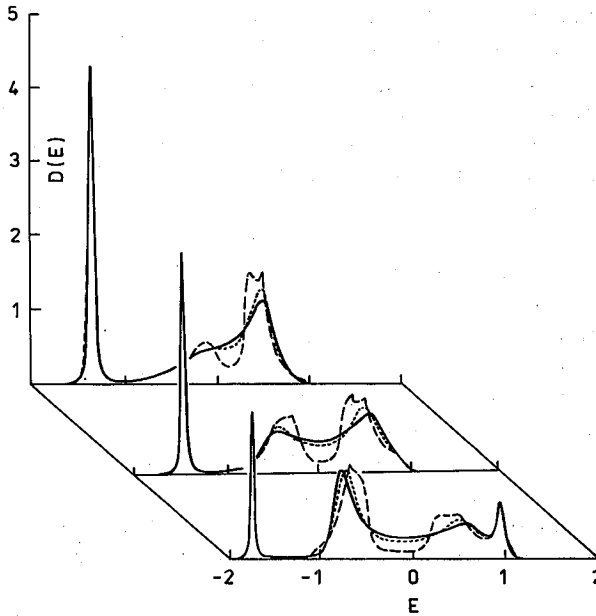


Fig. 5. The same as in Fig. 4 but for  $V = 0.6$ .



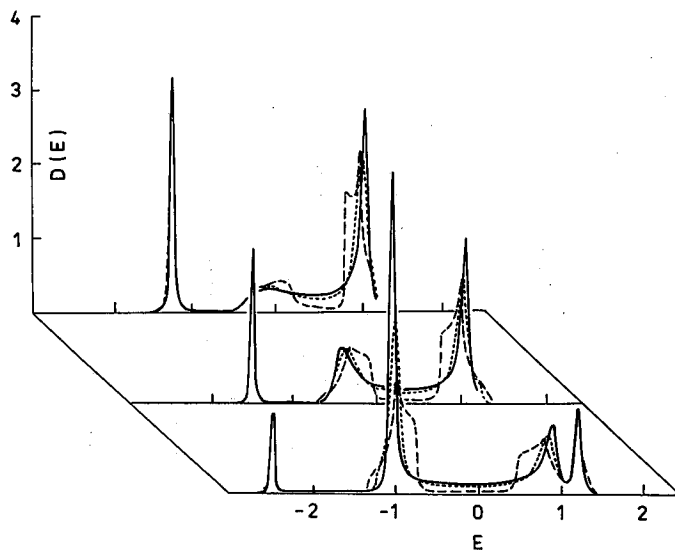


Fig. 6. The same as in Fig. 4 but for  $V = 0.9$ .

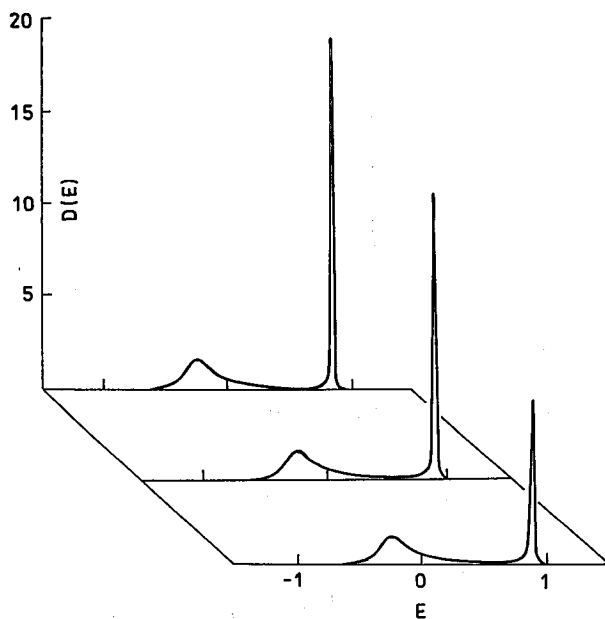


Fig. 7. The same as in Fig. 1 but for the positive asymmetry of N-A model ( $E_\alpha = -0.2$ ,  $V = 0.15$ ,  $U = 1.0$ ,  $E_F = 0$ ).

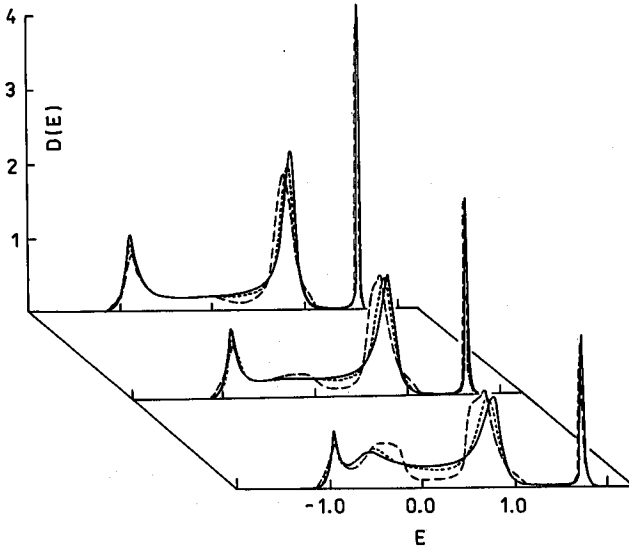


Fig. 8. The same as in Fig. 7 but for  $V = 0.6$ .

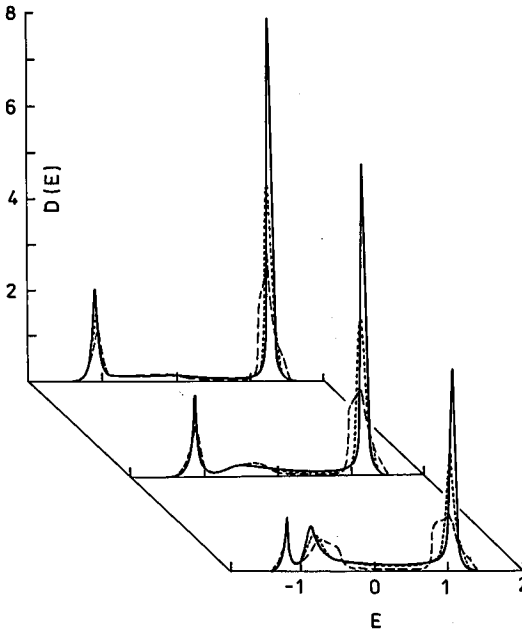


Fig. 9. The same as in Fig. 7 but for  $V = 0.9$ .

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 Figs. 10 and 11 the HF results for the symmetric and negative asymmetric cases, respectively. The transition from the symmetric case to more and more positive asymmetric case is shown in Fig. 10 and in Fig. 11 from the negative asymmetric case through "symmetric" case to positive asymmetric case. It should be noted

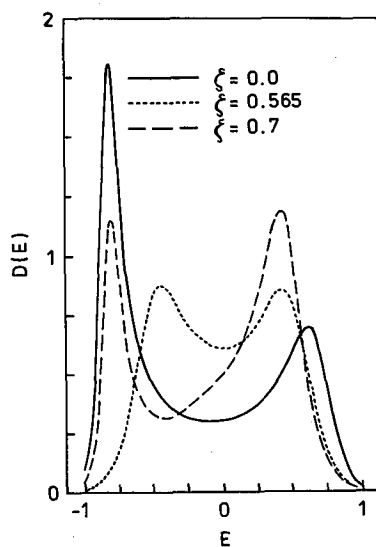
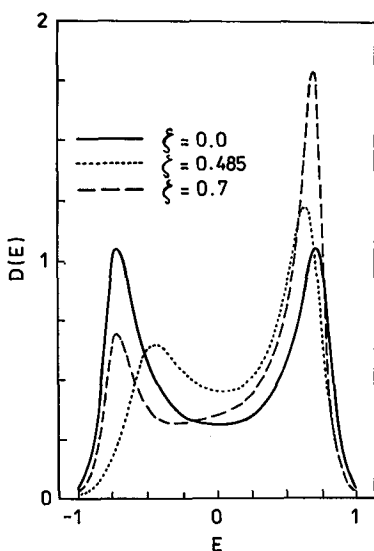


Fig. 10. The adatom density of states for the symmetrical N-A model ( $E_\alpha = -0.5$ ,  $V = 0.6$ ,  $U = 1.0$ ,  $E_F = 0$ ) for  $\zeta = 0$ , 0.485, and 0.7.

Fig. 11. The adatom density of states for the negative asymmetry of the N-A model ( $E_\alpha = -0.8$ ,  $V = 0.6$ ,  $U = 1.0$ ,  $E_F = 0$ ) for  $\zeta = 0$ , 0.565, and 0.7.

that despite of the symmetrical density of states for  $\zeta = 0.565$  in Fig. 11, this case does not correspond to the vanishing value of the parameter  $\eta$  describing the asymmetry in N-A model. One can find, however, such renormalized values of these parameters that the resulting Hamiltonian ( $\zeta = 0$ ) will possess a desired symmetry. It can be checked that the Hamiltonian (3) with the 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 the parameters  $E_\alpha = -0.20841$ ,  $V = 0.42913$ ,  $U = 0.41682$ ,  $E_F = 0$  and  $\zeta = 0$ . From the mathematical point of view such a general trend of transition from negative asymmetry case to positive one can be understood looking at formula (9), if we take into account the fact 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. For the construction of the chemisorption function we take the cubium (100) surface density of states and the other parameters are chosen from the Newns paper [4]. In Fig. 12 we have depicted the electron charge localized on the hydrogen adatom as a function of  $V$  (in eV), for different coverage rates and for the following values of  $\zeta$ ;  $\zeta = 0.0, 0.3, 0.5, 0.7$  — panels (a), (b), (c) and (d) respectively. The neutralization

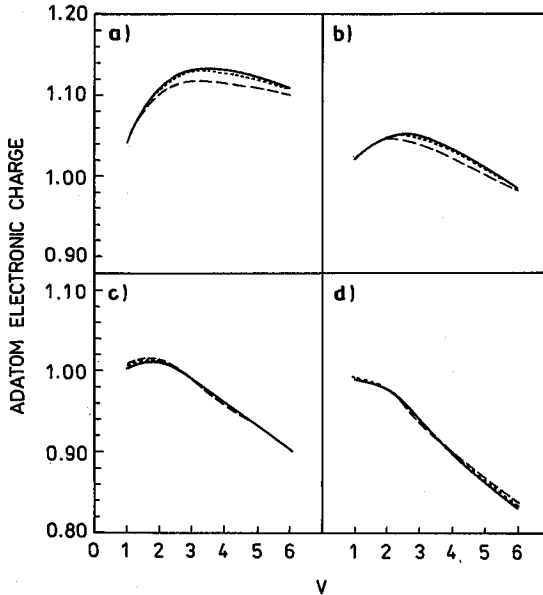


Fig. 12. The hydrogen adatom (on the chromium substrate) electronic charge vs. the hopping strength  $V$  at different coverages  $\theta$  obtained for model (3) for parameters  $\zeta$  equal to 0, 0.3, 0.5, and 0.7 — panels (a), (b), (c) and (d), respectively. The full, dotted and broken curves correspond to  $\theta = 0, 0.5$  and 1, respectively.

of the chemisorbed layer is seen only for the N-A model without the additional dynamic hopping interaction (or for small values of  $\zeta$ , only). For increasing values of  $\zeta$  the results become 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 smaller to greater values of  $\zeta$ . In general, the hydrogen chemisorbed on transition metals is observed in nearly neutral state, so we can conclude that the generalized N-A model with the dynamic hopping terms included ( $\zeta \approx 0.3 \div 0.5$  and for  $V$  corresponding to the hydrogen adatoms on transition metal substrates [4]) should better describe this chemisorption system. The small or vanishing dependence of the adatom charge on the coverage rate is also confirmed by the first principles calculations [19]. We emphasize that neutralization with increasing coverage rate is somewhat model dependent, more exactly, it may depend on the function  $P_q(E)$ . 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-like 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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