

ОБЪЕДИНЕННЫЙ
ИНСТИТУТ
ЯДЕРНЫХ
ИССЛЕДОВАНИЙ
ДУБНА

G27

E17-87-758

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**ON HYDROGEN CHEMISORPTION
ON METALS**

Submitted to "Surface Science"

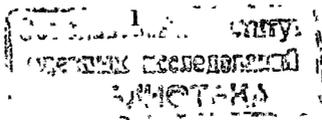
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I. Introduction

In recent years there has been a considerable amount of works dealing with semiphenomenological calculations in chemisorption theory by means of the model Hamiltonian method [1], and especially on the basis of the Newns-Anderson Hamiltonian [2]. The Anderson model has first been introduced to describe a magnetic impurity in a metal but also allows one to formulate fundamental microscopic foundations of the chemisorption theory [3-5] and is very useful for interpretation of the spectroscopic experimental results. However, despite a remarkable success in obtaining a relatively good description of the chemisorption process, it was shown that the Newns-Anderson model Hamiltonian does not take into consideration many important effects, which may lead to considerable qualitative differences in some chemisorption characteristics [6]. Moreover, if we treat this model as a semiphenomenological one, i.e. we define its parameters by comparing with experimental data, it is very difficult to find a connection between these parameters and the results of non-phenomenological calculations, for example, obtained in the local-density-functional approximation [7] or in other methods [8].

Therefore, it would be particularly useful to set up a theoretical framework for a microscopic derivation of the Anderson model for a relatively simple physical situation and analyze interactions which are inherent in it.

In this paper we present a microscopic derivation of the model Hamiltonian that is intended to describe chemisorption of



a single hydrogen atom in a ground state on a substrate of a simple metal. In this case we have a relatively simple and clear-cut microscopic picture and our approach has the advantages of giving a clear physical insight into the physics involved in this problem.

The organization of this paper is as follows. In the next section we present the fundamental microscopic description of the chemisorption process and make a second quantization procedure of this starting microscopic model. Section III describes various quantum mechanical models which are obtained after quantization of our problem. In Sec. IV, we discuss the effect of the partially occupied surface resonances induced by adatom on the hybridization, and hence, on the chemisorption binding between the adatom and substrate. In Sec. V, we present derivation of the self-consistent Hartree-Fock equations for main characteristics of the chemisorption process with the effects described in Sec. IV, included. In Sec. VI, we give the results of the numerical calculations for chemisorption energy, charge transfer between the adatom and the substrate, as well as we present the adatom local density of states for some parameters describing the chemisorption process. In conclusion we briefly discuss the obtained results.

II. The Basic Model and Second Quantization Procedure

Let us consider, from many-body point of view, the interaction of the hydrogen adatom being in the 1S - ground state with the surface of a simple metal substrate [4]. When adatom is located at the adsorption centre \vec{R}_A then the wave function of its valence electron overlaps with the substrate electron wave functions, and as a result, we have collectivization of electrons in a whole adsorbate plus adsorbent system. Thus, this complex system is described by a Hamiltonian of the form [10]:

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

Here we neglect the kinetic energy of the proton vibration (ion of the hydrogen adatom) around the equilibrium position at the adsorption centre \vec{R}_A . The potential $V(\vec{x}-\vec{y})$ describes the electrostatic Coulomb interaction between unit charges (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 latter involves also the boundary conditions on the surface between the solid state and vacuum [11]. Usually, in first-principle calculations of a free-electron like metal substrate, the jellium one of $P(\vec{x})$ is successful when the ion-core pseudopotentials are taken into account in first-order perturbation theory [12]. The constant U_0 represents the energy of the electrostatic interaction between ions of the substrate metal, and also between these ions and the proton of the adatom. Owing to the charge neutrality of the system we have removed from second and third terms of the Hamiltonian (1) the energy which represents the electron interaction with its Hartree field and included it into the energy $\sum P(\vec{x})$ and U_0 , respectively. So, we have:

$$V(\vec{x}) = \frac{1}{\Omega} \sum_{q \neq 0} v(\vec{q}) \exp(i\vec{x} \cdot \vec{q}) ; \quad v(\vec{q}) = \frac{4\pi e^2}{q^2} \quad (2)$$

where Ω is the volume of the system and N is a number of electrons in the substrate. The interaction $P(\vec{x})$ and the localization of the hydrogen atom \vec{R}_A are the parameters of our model.

Now we are in a good position to begin the second quantization procedure for the system described by the Hamiltonian (1) [13]. For that reason, it is necessary to introduce the quasi-particle description of the adatom-substrate system. This step is achieved by introducing an appropriate single-electron basis of functions. For one-particle states we choose the wave functions of electrons in the clean metal substrate $\langle \varphi_{\vec{k}}(\vec{x}) \rangle$. These basis functions are the Bloch-like wave functions describing the delocalized electron states in the metal. Here, vector \vec{k} stands for the electron quasi-momentum. In the case of the existence of surface states this index represents these surface states too which may be marked $\vec{k} = \langle \vec{k}, \gamma \rangle$, where the coordinates \vec{x}, \vec{y} lie in the surface plane [14]. However, in the case of simple me-

tal substrates we do not consider the role of these surface states in a chemisorption process. The influence of these states on chemisorption is discussed in [15]. Thus, the electron quasi-momentum \vec{k} stands for continuum states only and will be contained within the inverse site with the additional condition $k_x > 0$. For simplicity, we will consider the metal substrate with a single electron band only assuming that its contribution to the chemisorption process is an essential one. For the description of the localized electron states on the adatom we add to the basis functions $\langle \rho_{\vec{k}}(\vec{x}) \rangle$ the orthogonalized Anderson extra-orbital which is chosen as 1S-hydrogen atom wave function: $\rho_{\vec{k}}(\vec{x}) = \rho(\vec{k}_A - \vec{x})$.

The functions $\langle \rho_{\vec{k}}(\vec{x}) \rangle$ and $\rho_{\vec{k}}(\vec{x})$ satisfy the following equations:

$$\begin{aligned} \left(-\frac{\hbar^2}{2m} \nabla_{\vec{x}}^2 - P(\vec{x}) \right) \rho_{\vec{k}}(\vec{x}) &= \epsilon_{\vec{k}} \rho_{\vec{k}}(\vec{x}); \\ \left(-\frac{\hbar^2}{2m} \nabla_{\vec{x}}^2 - V(\vec{k}_A - \vec{x}) \right) \rho_{\vec{k}}(\vec{x}) &= E_A \rho_{\vec{k}}(\vec{x}), \end{aligned} \quad (3)$$

where $\epsilon_{\vec{k}}$ is the energy spectrum of the substrate electron band, E_A is the 1S-level or the ionization potential of the adatom. Note that because of the lack of the translational symmetry in the direction perpendicular to the surface, the methods of solution of the Schrödinger equation for $\rho_{\vec{k}}(\vec{x})$ are different from those for "bulk"-problems. In the paper [11], it was shown how to construct the functions $\rho_{\vec{k}}(\vec{x})$ having in hand solutions of the appropriate "bulk"-problem.

In the following we introduce the operator functions for the electron fields $\Psi^{\dagger}(\mathbf{X})$, $\Psi(\mathbf{X})$ in the form:

$$\begin{aligned} \Psi^{\dagger}(\mathbf{X}) &= \sum_{\vec{k}, \sigma} a_{\vec{k}\sigma}^{\dagger} \rho_{\vec{k}\sigma}^{\dagger}(\mathbf{X}) + \sum_{\sigma} a_{\sigma}^{\dagger} \rho_{\sigma}^{\dagger}(\mathbf{X}); \\ \Psi(\mathbf{X}) &= \sum_{\vec{k}, \sigma} a_{\vec{k}\sigma} \rho_{\vec{k}\sigma}(\mathbf{X}) + \sum_{\sigma} a_{\sigma} \rho_{\sigma}(\mathbf{X}), \end{aligned} \quad (4)$$

where $\rho_{\vec{k}\sigma}(\mathbf{X}) = \rho_{\vec{k}}(\vec{x}) \Delta_{\sigma}$; $\rho_{\sigma}(\mathbf{X}) = \rho_{\vec{k}}(\vec{x}) \Delta_{\sigma}$. The

Kronecker symbol Δ_{σ} is introduced for description of electron's spin state, σ is the spin variable, $\sigma = \pm 1$, $\mathbf{X} \equiv (\vec{x}, \sigma)$ and $a_{\vec{k}\sigma}^{\dagger}$, $a_{\vec{k}\sigma}$, a_{σ}^{\dagger} , a_{σ} are the Fermi operators for creation and annihilation of the substrate and adatom electrons, respectively. Finally, the Hamiltonian (1) in second quantization representation built up from the operator field $\Psi^{\dagger}(\mathbf{X})$, $\Psi(\mathbf{X})$ has the form:

$$\begin{aligned} H &= \int d\mathbf{X} \Psi^{\dagger}(\mathbf{X}) \left[-\frac{\hbar^2}{2m} \nabla_{\vec{x}}^2 - P(\vec{x}) \right] \Psi(\mathbf{X}) + \\ &+ \frac{1}{2} \int d\mathbf{X} d\mathbf{X}' \Psi^{\dagger}(\mathbf{X}) \Psi^{\dagger}(\mathbf{X}') \Psi(\mathbf{X}') \Psi(\mathbf{X}) V(\vec{x} - \vec{x}') - \\ &- \int d\mathbf{X} \Psi^{\dagger}(\mathbf{X}) \Psi(\mathbf{X}) V(\vec{k}_A - \vec{x}) + U. \end{aligned} \quad (5)$$

Here, we have used the notation $\int d\mathbf{X} = \sum_{\sigma=\pm 1} \int d\vec{x}$. Note that for performing the second quantization procedure we must work with the complete and orthogonalized basis functions, and our set of basis functions does not fulfil these conditions. However, as for nonorthogonality, we can use instead of an additional Anderson orbital $\rho_{\vec{k}}(\vec{x})$ an atomic-like function $\psi_{\vec{k}}(\vec{x})$ which will be orthogonal to the electron states of the substrate $\rho_{\vec{k}}(\vec{x})$:

$$\rho_{\vec{k}}(\vec{x}) \Rightarrow \psi_{\vec{k}}(\vec{x}); \quad \psi_{\vec{k}} = B^{-1} \left[\rho_{\vec{k}}(\vec{x}) - \sum_{\vec{k}'|\mathbf{A}} \langle \vec{k}'|\mathbf{A} \rangle \rho_{\vec{k}'}(\vec{x}) \right], \quad (6)$$

where

$$B = \left[1 - \sum_{\vec{k}'|\mathbf{A}} |\langle \vec{k}'|\mathbf{A} \rangle|^2 \right]^{-\frac{1}{2}}, \quad \langle \vec{k}'|\mathbf{A} \rangle = \int d\vec{x} \rho_{\vec{k}'}^{\dagger}(\vec{x}) \rho_{\vec{k}}(\vec{x}).$$

In the paper [16] it was shown that this substitution is equivalent to transition in the Hartree-Fock approximation of the Hamiltonian of the Anderson model to its unitary nonequivalent representation. In addition, there was given a detailed consideration concerning the influence of the nonorthogonality of the basis functions on the analytical structure of Green's

function. In further consideration the overlap parameter $\langle \vec{k} | \vec{A} \rangle$ of the wave functions will be neglected. As for incompleteness of the bases set functions, it has been shown by N.N. Bogolubov [9] that this does not effect the formal second quantization scheme, however, it changes the original problem for some approximate one in the spirit of variational Ritz problem. Therefore, if the initial set of basis functions is chosen in a sufficiently rich form, from physical point of view, then we may hope to obtain a good description of our problem. In the opposite cases, we must include into consideration additional physically essential states.

In our case, we include into the basis set functions the substrate electron wave functions belonging to the one energy band, most important one for chemisorption, and the wave function of the 1S-state of the hydrogen atom. This basis is appropriate for chemisorption of the hydrogen on a simple metal. The remaining effects may be considered in perturbation theory. However, for better understanding of the chemisorption on the transition metal substrates the effects of the band degeneracy must be necessarily taken into consideration. Sometimes the contribution of the states of continuous spectrum which spreads outside the region of action of the self-consistent potential $P(\vec{x})$ of the metal substrate [17], the contribution of exciting levels of the adsorbed atom [18] and other effects are important.

IV. Quantum Mechanical Models of Chemisorption

Using the representation of the electron operator fields Ψ^\dagger, Ψ and Eq. (3), the Hamiltonian (5) can be written in the form:

$$H = \sum_{k\sigma} \epsilon_k n_{k\sigma} + \sum_{\sigma} E_A n_{A\sigma} + U n_{A\uparrow} n_{A\downarrow} - \sum_{k,\sigma} [c_{V_{AAA\vec{k}}} n_{A-\sigma} - V_{A\vec{k}}] \times \\ \times a_{A\sigma}^\dagger a_{k\sigma} + \text{H.c.}] + H_{\text{rest.}} + U. \quad (7)$$

where

$$H_{\text{rest.}} = \frac{1}{2} \sum_{\substack{k_1 k_2 k_3 k_4 \\ \sigma_1 \sigma_2 \sigma_3 \sigma_4}} V_{\vec{k}_1 \vec{k}_2 \vec{k}_3 \vec{k}_4} a_{\vec{k}_1 \sigma_1}^\dagger a_{\vec{k}_2 \sigma_2}^\dagger a_{\vec{k}_3 \sigma_3} a_{\vec{k}_4 \sigma_4} - \sum_{\sigma} n_{A\sigma} P_A - \\ - \sum_{k'k\sigma} V_{\vec{k}'\vec{k}\sigma} a_{k'\sigma}^\dagger a_{k\sigma} + \sum_{kk'\sigma\sigma'} V_{\vec{k}\vec{k}'\sigma\sigma'} n_{A\sigma} a_{k\sigma}^\dagger a_{k'\sigma'} + \\ + \sum_{kk'\sigma\sigma'} V_{\vec{k}\vec{k}'\sigma\sigma'} a_{k\sigma}^\dagger a_{k'\sigma'} a_{A\sigma} a_{k\sigma} + \sum_{kk'k''\sigma\sigma'} (V_{\vec{k}\vec{k}'\vec{k}''} a_{A\sigma}^\dagger a_{k\sigma}^\dagger \times \\ \times a_{k'\sigma'} a_{k''\sigma''} + \text{H.c.}) + \frac{1}{2} \sum_{kk'\sigma} (V_{\vec{k}\vec{k}'\sigma} a_{A-\sigma}^\dagger a_{k-\sigma}^\dagger a_{k'\sigma} a_{k\sigma} + \text{H.c.}).$$

Here we have introduced the parameters:

$$U = \int d\vec{x} d\vec{y} |\varphi_A(\vec{x})|^2 |\varphi_A(\vec{y})|^2 V(\vec{x}-\vec{y}); \quad V_{A\vec{k}} = - \int d\vec{x} V(\vec{k}-\vec{x}) \times \\ \times \varphi_A^*(\vec{x}) \varphi_{\vec{k}}(\vec{x}); \quad V_{AAA\vec{k}} = - \int d\vec{x} d\vec{y} \varphi_A^*(\vec{x}) \varphi_{\vec{k}}(\vec{x}) |\varphi_A(\vec{y})|^2 V(\vec{x}-\vec{y}); \\ P_A = \int d\vec{x} |\varphi_A(\vec{x})|^2 P(\vec{x}); \quad V_{\vec{k}\vec{k}'\sigma}(\sigma) = \int d\vec{x} \varphi_{\vec{k}}^*(\vec{x}) \varphi_{\vec{k}'}(\vec{x}) V(\vec{k}-\vec{x}).$$

Other interaction parameters of the type $V_{\vec{k}_1 \vec{k}_2 \vec{k}_3 \vec{k}_4}$; $V_{\vec{k}_1 \vec{k}_2 \vec{k}_3}$, ...etc. are the matrix elements calculated for the Coulomb interaction $V(\vec{x}-\vec{y})$ between electron states described by the functions $\varphi_{\vec{k}_1}, \varphi_{\vec{k}_2}, \varphi_{\vec{k}_3}, \varphi_{\vec{k}_4}$; $\varphi_A, \varphi_{\vec{k}_2}, \varphi_{\vec{k}_3}, \varphi_{\vec{k}_4}, \dots$, respectively.

In the Hamiltonian (7) the well-known Anderson model is written out in an explicit form with the additional term of the form: $-\sum_{k\sigma} V_{\vec{k}\sigma} n_{A-\sigma} a_{k\sigma}^\dagger + \text{H.c.}$. This term describes the influence of the adsorbat level occupation on the hybridization of the electron states. This effect will be discussed in detail in a further part of this work.

Other parameters entering into Eq. (7), i.e. $\epsilon_{\vec{k}}, E_A, U, V_{A\vec{k}}$ have their usual meaning [2,5].

The term $H_{\text{rest.}}$ in Eq. (7) involves the interactions which

are not usually considered in the simple chemisorption models [6] and it generalizes the Anderson Hamiltonian. Let us briefly discuss the physical interpretation of various terms appearing in H_{res} . First of all we consider the terms of the form:

$$-\sum_{\sigma} n_{A\sigma} P_A - \sum_{k'k\sigma} V_{k'k}^{+}(\Lambda) a_{k\sigma}^{\dagger} a_{k'\sigma} + \sum_{kk'\sigma\sigma'} V_{kk'\sigma\sigma'} V_{Akk'}^{+} n_{A\sigma} a_{k\sigma}^{\dagger} a_{k'\sigma} \quad (8)$$

Let us rewrite these formulas in an identical form as:

$$\begin{aligned} & - \sum_{kk'\sigma} (V_{k'k}^{+}(\Lambda) - V_{Akk'}^{+} \langle \sum_{\sigma'} n_{A\sigma'} \rangle) a_{k\sigma}^{\dagger} a_{k'\sigma} - \sum_{\sigma} n_{A\sigma} (P_A - \\ & - \sum_{kk'\sigma\sigma'} V_{Akk'}^{+} \langle a_{k\sigma}^{\dagger} a_{k'\sigma'} \rangle) + \sum_{kk'\sigma\sigma'} V_{Akk'}^{+} [n_{A\sigma} - \langle n_{A\sigma} \rangle] \times \\ & \times [a_{k\sigma}^{\dagger} a_{k'\sigma'} - \langle a_{k\sigma}^{\dagger} a_{k'\sigma'} \rangle] - \sum_{kk'\sigma\sigma'} V_{Akk'}^{+} \langle n_{A\sigma} \rangle \langle a_{k\sigma}^{\dagger} a_{k'\sigma'} \rangle. \end{aligned} \quad (9)$$

The matrix element $V_{Akk'}^{+}$ can be written as:

$$\begin{aligned} V_{Akk'}^{+} &= \int d\vec{x} d\vec{y} \rho_A^{*}(\vec{x}) \rho_R^{*}(\vec{y}) \rho_R(\vec{y}) \rho_A(\vec{x}) V(\vec{x}-\vec{y}) = \int d\vec{y} \frac{e^2}{|\vec{R}_A - \vec{y}|} \times \\ & \times \langle 1 - (1 + \frac{|\vec{R}_A - \vec{y}|}{b}) \exp[-2 \frac{|\vec{R}_A - \vec{y}|}{b}] \rangle \rho_R^{*}(\vec{y}) \rho_R(\vec{y}) = \quad (10) \\ & = V_{k'k}^{+}(\Lambda) - \int d\vec{y} (1 + \frac{|\vec{R}_A - \vec{y}|}{b}) \exp[-2 \frac{|\vec{R}_A - \vec{y}|}{b}] \rho_R^{*}(\vec{y}) \rho_R(\vec{y}). \end{aligned}$$

Here, we have used explicit form for the Coulomb interaction and for the hydrogen 1S-electron wave function and $\langle \dots \rangle$ denotes the quantum statistical average. The atomic length b equals $\frac{\hbar^2}{m_0 e^2} \cong 0.5 \text{ \AA}$. If the separation between the adatom and substrate's surface is much greater than b , then the second term in Eq.(10) can be neglected and we obtain as a result $V_{Akk'}^{+} \cong V_{k'k}^{+}(\Lambda)$. So, the first term of Eq.(9) can be rewritten

in the form:

$$\sum_{kk'\sigma} (V_{k'k}^{+}(\Lambda) - V_{Akk'}^{+} \langle \sum_{\sigma'} n_{A\sigma'} \rangle) a_{k\sigma}^{\dagger} a_{k'\sigma} \cong \sum_{kk'\sigma} V_{k'k}^{+}(\Lambda) q a_{k\sigma}^{\dagger} a_{k'\sigma}, \quad (11)$$

where $q = 1 - \sum_{\sigma} \langle n_{A\sigma} \rangle$ is the charge on a hydrogen adatom measured in units of electron charge e . Consequently, the contribution to the Hamiltonian of the form displayed in Eq.(11) describes the scattering of the substrate electrons on the additional charge of the adsorbed atom. In the case of the neutral chemisorption, i.e. when there is no charge transfer between the adatom and substrate metal, these contributions to the Hamiltonian may be neglected. Applying a similar method, the second term in Eq.(9) becomes:

$$\begin{aligned} & - \sum_{\sigma} n_{A\sigma} (P_A - \sum_{kk'\sigma\sigma'} V_{Akk'}^{+} \langle a_{k\sigma}^{\dagger} a_{k'\sigma'} \rangle) \cong \sum_{\sigma} n_{A\sigma} A_A + \\ & + \sum_{\sigma} n_{A\sigma} \int d\vec{x} V(\vec{R}_A - \vec{y}) \delta\rho(\vec{x}), \end{aligned} \quad (12)$$

where the first part describes the interaction of the adatom electron with double electric layer of the clean metal surface, and A_A is the energy needed for an electron to go across this layer [14,19]. The second part in Eq.(12) describes the interaction of the valence adatom electron with the redistributed charge cloud in the substrate metal induced by the adatom electrons themselves, i.e. this part of the Hamiltonian includes the so-called static image potential problem [12]. It is important to note that for a consistent treating of these polarization properties of the metal substrate in chemisorption theory, it is insufficient to characterize its electronic properties by the spectral parameter ϵ_R^* . It is necessary to introduce at least the long range part of the Coulomb interaction between substrate electrons $V_{k_1 k_2 k_3 k_4}$ [10], or introduce plasmons [18]. The third part of Eq.(9) describes effects connected with the correlations between the adatom charge fluctuations and the redistribution of the charge

density of the substrate metal induced by the adatom. It describes the dynamical effects of the image potential or the so-called relaxation shift problem discussed in detail in the review paper [12]. Usually, in the Hartree-Fock calculations these effects are neglected. The last term in Eq. (9) is a constant value which must be included in order to evaluate correctly the ground state energy of the adatom plus substrate system. In conclusion, the part of the Hamiltonian (7) displayed in Eq. (8) describes the polarization effects in adatom and substrate metal.

The next contribution to H_{rest} of the form:

$$\sum_{kk', oo'} V_{AAkAk'} a_{AO}^+ a_{RO}^+ a_{AO'} a_{R'O'} \quad (13)$$

involves the exchange-type correlations between the adatom and substrate metal. These contributions, together with effects connected with the dipole moment induced on the adatom, for which the description of the excited p - states of hydrogen is needed [10], are important for an accurate description of the interaction between the substrate metal and adatom placed at large distance from the metal surface. These effects lead to the weak Van der Waals forces and are important for the description of the physisorption [20].

Finally, the remaining terms in H_{rest} involve effects of the interaction between an adatom and a substrate and are of much higher order, for example, two-electron hopping and others.

V. Influence of Partial Occupation of the Adsorbate Resonances on the Hybridization of Electron States.

In the following we confine ourselves to the model in which together with the standard interactions present in the Anderson model [2] we include only effects connected with the influence of the adatom orbital occupation on the charge transfer between an adatom and a metal substrate. Such a model is described by the Hamiltonian:

$$H = \sum_{kO} \epsilon_k^+ n_{kO}^+ + \sum_O E_A n_{AO} + U n_{AO} n_{A-O} + \sum_{kO'} (V_{AR}^+ - n_{A-O} V_{AAAR}^+) a_{AO}^+ a_{RO}^+ + \text{H.c.} \quad (14)$$

In accordance with Eq. (10), the matrix element V_{AAAR}^+ can be represented in the form:

$$V_{AAAR}^+ = - \int d\vec{x} d\vec{y} \phi_A^*(\vec{x}) \phi_A^*(\vec{y}) \phi_A(\vec{y}) \phi_R(\vec{x}) V(\vec{x}-\vec{y}) = - \int d\vec{x} \phi_A^*(\vec{x}) \times \\ \times \phi_R(\vec{x}) \left[1 - \left(1 + \frac{|\vec{R}_A - \vec{x}|}{b} \right) \exp \left[-2 \frac{|\vec{R}_A - \vec{x}|}{b} \right] \right] \frac{e^2}{|\vec{R}_A - \vec{x}|} = \\ = V_{AR}^+ + \int d\vec{x} \phi_A^*(\vec{x}) \phi_R(\vec{x}) \left(1 + \frac{|\vec{R}_A - \vec{x}|}{b} \right) \times \\ \times \exp \left[-2 \frac{|\vec{R}_A - \vec{x}|}{b} \right] V(\vec{R}_A - \vec{x}), \quad (15)$$

and for $|\vec{R}_A| \gg b$ we obtain $V_{AAAR}^+ \approx V_{AR}^+$, and the Hamiltonian (14) may be written as:

$$H = \sum_{kO} \epsilon_k^+ n_{kO}^+ + \sum_O E_A n_{AO} + U n_{AO} n_{A-O} + \sum_{kO'} (1 - n_{A-O}) \times \\ \times (V_{AR}^+ a_{AO}^+ a_{RO}^+ + \text{H.c.}) \quad (16)$$

Note that in accordance with the paper [21], the distance between the adsorbed layer of hydrogen atoms and the substrate surface layer for chemisorption on (111)-plane of nickel reads as 1.17 Å and is much larger than the atomic unit length b . In general, the typical distance between adsorbed atoms and the substrate surface layer lies in the interval 0.9 - 2.9 Å [12].

The introduction of the additional term $-\sum_{kO'} n_{A-O} V_{AAAR}^+ \times$

$a_{A\sigma}^+ a_{A\sigma} + \text{H.c.}$ into the Anderson model has a considerable influence on the hybridization between the adatom orbital wave function and substrate wave functions and on the charge transfer between the adatom and the substrate, respectively. We demonstrate this by the example of the model Hamiltonian (16) neglecting the second part of the expression in Eq.(15) (distance from the metal surface is greater comparing with atomic unit b). For that reason, let us consider the operators \hat{P}_A^+ , \hat{P}_A^0 , \hat{P}_A^- of the form:

$$\begin{aligned}\hat{P}_A^+ &= 1 - \sum_{\sigma} n_{A\sigma} + n_{A\uparrow} n_{A\downarrow}; \\ \hat{P}_A^0 &= \sum_{\sigma} n_{A\sigma} (1 - n_{A-\sigma}); \\ \hat{P}_A^- &= n_{A\uparrow} n_{A\downarrow}.\end{aligned}\quad (17)$$

It is easy to show that these are projection operators on the states of the system described by the Hamiltonian (16), when on the adatom orbital there are no electrons, there is only one electron and there are two electrons, respectively. The first and third states describe the charged state of the adatom with $q = 1$ and $q = -1$, respectively, and the second is neutral $q = 0$. In the following, these states will be denoted by $|q = \pm 1, 0; \xi\rangle$ where the parameter ξ represents the set of other quantum numbers needed for the description of the system. The operators \hat{P}_A^+ , \hat{P}_A^0 , \hat{P}_A^- do not commute with the Anderson Hamiltonian (2). This means that, in general, the ground state eigenfunction of the Anderson Hamiltonian would be a composition of these three types of states [22]. In addition, as it is known from the Hartree-Fock calculations, the Anderson model gives much larger charge transfer from the substrate to the adatom than it is observed in experiments [5]. This means that there is an overestimated contribution of the functions $|q = -1, \xi\rangle$ to the ground state of the Anderson Hamiltonian. In order to restore this situation, in papers [23,24] the valence bound method, the analog of the Heitler - London theory for molecules, was introduced in which the role of the charged states is suppressed in an

artificial way. In the case of the model (16), the projection operator \hat{P}_A^- commutes with the Hamiltonian and this Hamiltonian is diagonal in the subspace $\hat{P}_A^- \mathcal{S}$ of the state space \mathcal{S} . This means that the ground state of the Hamiltonian (16) must be constructed as the linear combination of the states $|q = 1; \xi\rangle$, $|q = 0; \xi\rangle$ and the state $|q = -1; \xi\rangle$ does not mix with them. Moreover, for $E_A + U > e_F$, this is always satisfied for a hydrogen chemisorbed on metals, the state $|q = -1; \xi\rangle$ does not contribute at all to a chemisorption bond. In other words, the charge transfer from the substrate to the adatom is suppressed for Hamiltonian (16) in comparison with the predictions obtained in the Anderson model. A similar effect will be observed for a model (15). However, the situation mentioned above will be destroyed depending on the adatom-substrate separation d . Having in mind the smoothing of the functions $\phi_R^{(\pm)}$ outside the substrate surface, we can approximate the matrix element V_{AAAR} as αV_{AR} ; $\alpha \leq 1$. For a large adatom-surface separation we have $\alpha \cong 1$ and the charge transfer is possible from the adatom to the substrate only. When the adatom moves towards the surface then the parameter α decreases and the contributions of the states $|q = -1; \xi\rangle$ to the ground state of a system increase. In a further part of this work we will investigate the influence of the parameter α on the main characteristics of the chemisorption process.

VI. Hartree-Fock Description of the Chemisorption

In this chapter we introduce the equations for main chemisorption characteristics in the Hartree-Fock approximation for a model described by the Hamiltonian:

$$\begin{aligned}H &= \sum_{k\sigma} \epsilon_k^{\sigma} n_{k\sigma} + \sum_{\sigma} E_A n_{A\sigma} + U n_{A\uparrow} n_{A\downarrow} + \sum_{k\sigma} (1 - \alpha n_{A-\sigma}) \\ &\times (V_{AR}^{\sigma} a_{A\sigma}^+ a_{k\sigma} + \text{H.c.}).\end{aligned}\quad (18)$$

The Hartree-Fock approximation for a system described by

Eq.(18) is equivalent to considering of the approximate Hamiltonian of the form:

$$H = \sum_{k\sigma} \epsilon_k^\sigma n_{k\sigma} + \sum_{\sigma} E_{\sigma} n_{A\sigma} + \sum_{k\sigma} (V_{A\bar{k}}^{\sigma} a_{A\sigma}^{\dagger} a_{k\sigma} + \text{H.c.}) + C \quad (19)$$

where

$$E_{\sigma} = E_A + U \langle n_{A-\sigma} \rangle - \alpha \sum_k (V_{A\bar{k}} \langle a_{A-\sigma}^{\dagger} a_{k-\sigma} \rangle + \text{H.c.});$$

$$V_{A\bar{k}}^{\sigma} = (1 - \alpha \langle n_{A-\sigma} \rangle) V_{A\bar{k}};$$

$$C = -U \langle n_{A\uparrow} \rangle \langle n_{A\downarrow} \rangle + \alpha \sum_{k\sigma} (V_{A\bar{k}} \langle n_{A-\sigma} \rangle \langle a_{A\sigma}^{\dagger} a_{k\sigma} \rangle + \text{H.c.}).$$

Note that in contrast with the Hartree-Fock description of the standard Anderson model [5], here the quantity $V_{A\bar{k}}^{\sigma}$, which determines the electron transfer between adatom and substrate, depends on the occupation of adatom's orbital. The constant C has the same meaning as in Eq.(9).

Using the Green function technique [25], one can obtain the following set of nonlinear integral equations for an average number of electrons $\langle n_{A\sigma} \rangle$; $\sigma = \uparrow, \downarrow$ on adatom orbital (for temperature $\theta = 0 \text{ K}^\circ$):

$$\langle n_{A\sigma} \rangle = \int_{-\infty}^{e_F} d\omega D_{\sigma}(\omega); \quad (20)$$

$$\xi_{\sigma} = \frac{2\alpha}{1 - \alpha \langle n_{A-\sigma} \rangle} \int_{-\infty}^{e_F} d\omega D_{\sigma}(\omega) (\omega - E_{\sigma}),$$

where

$$D_{\sigma}(\omega) = \frac{1}{\pi} \frac{\Delta_{\sigma}(\omega)}{[\omega - E_{\sigma} - \Lambda_{\sigma}(\omega)]^2 + \Delta_{\sigma}^2(\omega)}$$

and

$$\Lambda_{\sigma}(\omega) = \frac{1}{\pi} \int dx \frac{\Delta_{\sigma}(x)}{(\omega - x)}$$

is the Hilbert transform of the so-called chemisorption

function $\Delta_{\sigma}(\omega)$ which for the model (19) reads as:

$$\Delta_{\sigma}(\omega) = (1 - \alpha \langle n_{A-\sigma} \rangle) \sum_k |V_{A\bar{k}}|^2 \delta(\omega - \epsilon_k^\sigma). \quad (21)$$

Here ξ_{σ} denotes:

$$\xi_{\sigma} = \alpha \sum_k (V_{A\bar{k}} \langle a_{A\sigma}^{\dagger} a_{k\sigma} \rangle + \text{H.c.}), \quad (22)$$

so that $E_{\sigma} = E_A + U \langle n_{A-\sigma} \rangle - \xi_{-\sigma}$.

In an analogous way, one can obtain expressions for the chemisorption energy ΔE and the adatom charge q [5]:

$$\Delta E = \sum_{\sigma} \left\{ E_{L\sigma} + \frac{1}{\pi} \int_{e_0}^{e_F} d\omega \tan^{-1} \left[\frac{\Delta_{\sigma}(\omega)}{\omega - E_{\sigma} - \Lambda_{\sigma}(\omega)} \right] \right\} - \quad (23)$$

$$- E_A + C; \quad q = e (1 - \sum_{\sigma} \langle n_{A\sigma} \rangle),$$

where e_0 - the bottom of the energy band which is present in forming the chemisorption bond, $E_{L\sigma}$ - the energy of the localized electron state ($E_{L\sigma} \leq e_0$) which may be obtained from following equation:

$$E_{L\sigma} - E_{\sigma} - \Lambda_{\sigma}(E_{L\sigma}) = 0. \quad (24)$$

In Eq.(23) the energy zero is placed at e_F . In the absence of the occupied localized state, we discard the term $E_{L\sigma}$ in Eq.(23) and take $-\pi < \arctg < 0$ (if an occupied localized state exists, then $0 < \arctg < \pi$). For $\alpha \Rightarrow 0$ we obtain the well-known Hartree-Fock self-consistent description of the chemisorption process [5].

VII. Numerical Results and Conclusions

The above presented microscopic consideration is adopted to

the hydrogen chemisorption on the simple metal substrates. However, the models described by Hamiltonians (14) and (18) can be useful for description of the chemisorption on the transition metal substrates, which is more interesting from practical point of view. Therefore, we make the self-consistent calculations of the basis chemisorption parameters for this case in the spirit of work [5]. In the following, according to Newns [5], we take the chemisorption function in the form:

$$\Delta_{\sigma}(\omega) = (1 - \alpha \langle n_{A-\sigma} \rangle)^2 2\beta'^2 (1 - \omega^2)^{1/2}; \quad |\omega| < 1,$$

$$\Delta_{\sigma}(\omega) = 0; \quad |\omega| > 1,$$

(25)

where we use β' as it has been introduced by Newns [5], and zero energy is located at the middle of the band. Half bandwidth is taken as an energy unit. For numerical calculations of the charge transfer and chemisorption energy of a hydrogen chemisorption on transition metal surfaces - in the H-F approximation for Hamiltonian (18) - we take Ti, Cr and Ni metals. The parameters: the band width W , Fermi energy e_F and work function, the hydrogen ionization potential and Coulomb integral for hydrogen adatom were taken from the work by Newns [5].

In Fig.1 we displayed the charge on adatom's orbital for different values of the parameters α for Ti, Cr and Ni, respectively, as a function of β' parameter. The value $\alpha = 0$

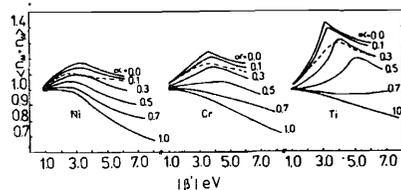


Fig.1. The hydrogen adatom charge in units of e versus β' and α for the metal substrates Ni, Cr and Ti, respectively. The curves with $\alpha = 0.0$ correspond to the standart H-F results of Newns [5] and broken ones for the results of Brenig and Schönhammer [26]. The parameters describing the metal substrates are taken from [5].

on chemisorption beyond the Hartree-Fock approximation. We briefly discuss some general features of our results. It is easy to observe that the charge transfer to the adatom decreases with increasing value of the parameter α . Moreover, beginning from some value of α the charge transfer direction is from the adatom to substrate metal. These results confirm the damping of the charge transfer from a substrate to adatom when the influence of the adatom orbital occupancy on the hybridization of the electron states is included. Sometimes the adatom-substrate separation can be sufficiently large and the parameter α differs considerably from zero and in this manner this situation corresponds to a strong damped charge transfer from substrate to adatom, which is really observed for hydrogen chemisorption on transition metals.

In Fig.2 we display the chemisorption energy curves for Ti, Cr

and Ni, respectively, for different values of the parameter α .

In Fig.3 we present, for illustration, the influence of the parameter α on the adatom projected density of states for hydrogen on Ti for $\beta' = 4.0$. For $\alpha = 0$ (standard result) and for $\alpha = 0.1$ we have paramagnetic cases only, and for other values of α we have ferromagnetic solutions, too. We

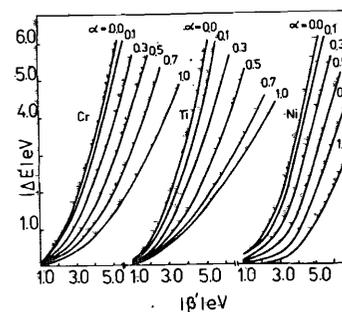
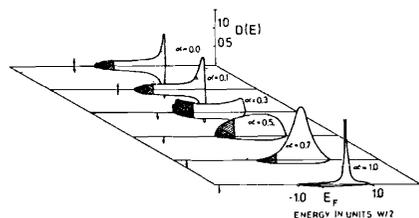


Fig.2. Self-consistent H-F chemisorption energy versus hopping integral β' and the parameter α for hydrogen chemisorption on transition metals Cr, Ti and Ni, respectively.

can observe very large changes in the shape of the adatom density of states as well as in the localization of the occupied localized states.

In conclusion, we have presented a microscopic approach to the chemisorption of a single adatom on a metal substrate, and as a result, a generalized Newns-Anderson Hamiltonian was obtained. The consideration of the particular cases of chemisorption of the hydrogen adatom does not restrict its generality. The main merit of the expounded procedure lies in the

possibility of the explicit and straightforward account of the influence of the adatom orbital occupancy on the hybridization of the substrate and adatom orbital electron wave functions. For a



sufficiently large adatom-substrate separation, one can take the parameter α approximately close to 1.0. This leads to significant quantitative changes of the adatom orbital occupancy and electron adatom structure

Fig.3. The adatom projected density of states (for spin - up and spin - down) for the hydrogen chemisorbed on Ti for $\beta' = 4$ eV as a function of energy and parameter α . The arrows indicate the localized electron states and shaded areas denote filled electron states.

comparing with the standard result [5]. Unfortunately, the problem of the largeness of the parameter α is unresolved for the time being. It is interesting to note that the charge transfer damping obtained by Brenig and Schönhammer [26] as typical correlation effect may be obtained in our approach within the Hartree-Fock approximation at $\alpha \cong 0.2 - 0.3$.

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Received by Publishing Department
on October 21, 1987.