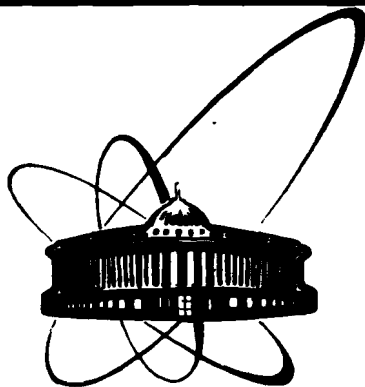


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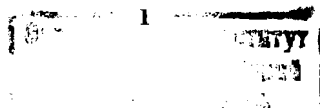
ELECTRON CORRELATIONS
IN THE CHEMISORPTION THEORY:
SELF-CONSISTENT CALCULATIONS
OF THE ADATOM CHARGE

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1. Introduction

The Newns-Anderson (N-A) model Hamiltonian has been used by many authors to study the chemisorption on transition or on free-electron-like metals. The Hartree-Fock (H-F) approximation for the electron-electron (on the adatom) interaction was probably the most widely accepted approach in studying the chemisorption phenomena (see e.g. [1-6]). But it is well-known that H-F description of the correlation effects in chemisorption fails to provide a satisfactory explanation of the observed phenomena. On the other hand, it is impossible till now to solve the full many-body problem and approximations must be tolerated. The great number of papers have been devoted to the study of the correlation effects in the chemisorption theory based on the N-A Hamiltonian beyond the H-F approximation (see e.g. [7-16]). The N-A model allows one to formulate fundamental microscopic foundations of the chemisorption theory and is useful for interpretation of the spectroscopic experimental results. However, it is well-known that the N-A model does not take into account many effects which may lead to considerable qualitative differences in some chemisorption characteristics [6,17]. For that reason, recently, we set up a theoretical framework for a microscopic derivation of the N-A model for a relatively simple physical situation [17]. There it has been shown that along the usual term describing the electron transfer in the N-A model



$$G_{\alpha\beta}^{\sigma}(\omega) = G_{\alpha\beta}^{(0)\sigma}(\omega) + \sum_{\gamma\delta} G_{\alpha\gamma}^{(0)\sigma}(\omega) M_{\gamma\delta}^{\sigma}(\omega) G_{\delta\beta}^{\sigma}(\omega) \quad (7)$$

and it can be shown that even a very simple expression for $M_{\gamma\delta}^{\sigma}$ leads to a correct behaviour of the GF $G_{\alpha\sigma}(\omega)$ in the large U limit [7]. Here, $G_{\alpha\beta}^{(0)\sigma}(\omega)$ denotes the GF calculated for $U=0$. The conditional operators (5) do not obey the simple anticommutation rules and we can't use the usual perturbational diagrammatic expansion. For that reason, in the BS approach one tries to solve the equation of motion for $G_{\alpha\beta}^{\sigma}(\omega)$ up to second order in powers of V . In the first step, using the equation of motion obtained after the differentiation over the left-hand side time argument we have

$$(E I - h) G^{\sigma}(E) = A^{\sigma} + \langle \varphi_{\sigma} | \psi_{\sigma}^{+} \rangle \quad (8)$$

where

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

$$\varphi_{\sigma} = \begin{pmatrix} \varphi_{+, \sigma} \\ \varphi_{-, \sigma} \end{pmatrix}, \quad \psi_{\sigma} = \begin{pmatrix} \psi_{+, \sigma} \\ \psi_{-, \sigma} \end{pmatrix}$$

and

$$\varphi_{+, \sigma} = \sum_{\vec{k}\sigma}^3 \varphi_{+, \sigma}^{(1)} = \sum_{\vec{k}\sigma} V_{\Lambda\vec{k}} (1 - \xi) a_{\vec{k}\sigma}^{\dagger} n_{\Lambda-\sigma} + \quad (9)$$

$$+ \sum_{\vec{k}\sigma} V_{\Lambda\vec{k}} (1 - \xi) a_{\Lambda\sigma} a_{\Lambda-\sigma}^{\dagger} a_{\vec{k}\sigma}^{\dagger} - \sum_{\vec{k}\sigma} V_{\vec{k}\Lambda} (1 - \xi) a_{\vec{k}\sigma}^{\dagger} a_{\Lambda-\sigma}^{\dagger} a_{\Lambda\sigma},$$

$$\varphi_{-, \sigma} = \sum_{\vec{k}\sigma}^3 \varphi_{-, \sigma}^{(1)} = \sum_{\vec{k}\sigma} V_{\Lambda\vec{k}} (1 - n_{\Lambda-\sigma}) a_{\vec{k}\sigma} - \quad (10)$$

$$- \sum_{\vec{k}\sigma} V_{\Lambda\vec{k}} a_{\Lambda\sigma} a_{\Lambda-\sigma}^{\dagger} a_{\vec{k}\sigma} + \sum_{\vec{k}\sigma} V_{\vec{k}\Lambda} (1 - \xi) a_{\vec{k}\sigma}^{\dagger} a_{\Lambda-\sigma} a_{\Lambda\sigma}.$$

In the second step, using Eq.(8) and equation of motion (obtained after the differentiation over the right-hand side time argument) combined with Eq.(7) we obtain (for details see BS [7]):

$$M_{\alpha\beta}^{\sigma}(E) = A_{\alpha\alpha}^{\sigma-1} \langle \langle \varphi_{\alpha\sigma} | \varphi_{\beta\sigma}^{+} \rangle \rangle + \langle [\varphi_{\alpha\sigma}, \psi_{\beta\sigma}^{+}]_{+} \rangle A_{\beta\beta}^{\sigma-1} \quad (11)$$

In the following we confine ourselves to the weak scattering case and after BS approach one can obtain (up to an order of V^2):

$$\langle \langle \varphi_{\alpha\sigma}^{(1)}, \varphi_{\beta\sigma}^{(1)+} \rangle \rangle = 0, \quad i \neq j \quad (12)$$

$$\langle \langle \varphi_{\alpha\sigma}^{(1)}, \varphi_{\beta\sigma}^{(1)+} \rangle \rangle = f^{\alpha\beta}(\xi) \Gamma(z) \delta_{\alpha\beta} \langle n_{\alpha\sigma} \rangle \quad (13)$$

$$\langle \langle \varphi_{\alpha\sigma}^{(2)}, \varphi_{\beta\sigma}^{(2)+} \rangle \rangle = \alpha\beta f^{\alpha\beta}(\xi) \{ \langle n_{\Lambda-\sigma} \rangle (1 - n_{\Lambda\sigma}) \Gamma(z) + \langle n_{\Lambda\sigma} \rangle - \langle n_{\Lambda-\sigma} \rangle \} R(z) \quad (14)$$

$$\langle \langle \varphi_{\alpha\sigma}^{(3)}, \varphi_{\beta\sigma}^{(3)+} \rangle \rangle = \alpha\beta f^{-\alpha-\beta}(\xi) \{ \langle n_{\Lambda\sigma} n_{\Lambda-\sigma} \rangle \Gamma(-z + 2\epsilon_{\Lambda} + U) + \langle 1 - n_{\Lambda\sigma} - n_{\Lambda-\sigma} \rangle R(-z + 2\epsilon_{\Lambda} + U) \} \quad (15)$$

where

$$\Gamma(z) = \sum_{\vec{k}} |V_{\Lambda\vec{k}}|^2 (z - \epsilon_{\vec{k}})^{-1},$$

$$R(z) = \sum_{\vec{k}} |V_{\Lambda\vec{k}}|^2 f(\epsilon_{\vec{k}}) (z - \epsilon_{\vec{k}})^{-1},$$

$$f^{\alpha\beta}(\xi) = \begin{cases} (1-\xi)^2 & \text{for } (\alpha, \beta) = (+, +), \\ (1-\xi) & \text{for } (\alpha, \beta) = (+, -), (-, +); \\ 1 & \text{for } (\alpha, \beta) = (-, -), \end{cases}$$

and $f^{\alpha\beta}(\xi)$ is a Fermi function. Similarly, for the expectation value of the anticommutator in Eq.(11) one obtains

$$\langle [\varphi_{\alpha\sigma}, \psi_{\beta\sigma}^\dagger]_+ \rangle = \alpha \sum_{\vec{K}} |V_{\lambda\vec{K}}|^2 \left(f^{\alpha\beta}(\xi) \langle n_{\beta-\sigma} \rangle \frac{f(\epsilon_{\vec{K}}) - f(\epsilon_{-\beta})}{\epsilon_{\vec{K}} - \epsilon_{-\beta}} - f^{-\alpha-\beta}(\xi) \langle n_{\beta-\sigma} \rangle \frac{f(\epsilon_{\vec{K}}) - f(\epsilon_{-\beta})}{\epsilon_{\vec{K}} - \epsilon_{-\beta}} \right) \quad (16)$$

where $\epsilon_+ = \epsilon_A + U$, $\epsilon_- = \epsilon_A$.

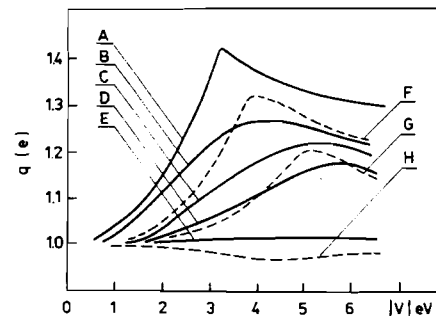
Having in hands formulas (7,11-16) we can calculate various chemisorption characteristics in the model described by the generalized Hamiltonian (4).

3. Results and discussion

The microscopic considerations presented in the previous section are adopted to the hydrogen chemisorption on the transition metal substrate, namely on Ti surface. In order to calculate the chemisorption function $\Gamma(E)$ we assume the semielliptical density of states for the substrate electron band (with small imaginary part in argument to simulate a finite lifetime for the metal electron states - see e.g. [7]). All other parameters needed for calculations were taken from the work by Newns [1]. In this paper we give the results of self-consistent (weak coupling case) calculations for the expectation value $q = \langle n_{A\downarrow} \rangle + \langle n_{A\uparrow} \rangle$ of the adatom charge as a function of the coupling strength V for different values of the parameter ξ . The value of this adatom charge is a very important chemisorption quantity which, for example, significantly influences the changes in a work-function. The H-F calculations performed by Newns [1] predict the charge transfer to the adatom not compatible with experimental evidence (see e.g. 9,19), which indicates rather an neutral or low charged hydrogen chemisorption. Furthermore, the correlation

effects included along the way presented in this paper. but for N-A Hamiltonian lead to decreasing of the adatom electron charge but still this effect is too small. Our results are depicted in Fig.1. The curve labelled by A denotes the adatom charge calculated in H-F approximation for the N-A model vs. the coupling strength V , and the curve B denotes the same but calculated along BS approach. The next curves C, D, E represent the adatom electron charge calculated for the generalized Hamiltonian (3) along BS

Fig. 1. The total electron charge on the hydrogen adatom on Ti surface vs. hopping strength V for different values of ξ . The curve labelled: A(B) - N-A model in H-F approximation, (B-S approach). C,D, E - generalized N-A model in BS approach for $\xi=0.3, 0.5$ and 0.7 , respectively. F,G,H-generalized N-A model in H-F approximation for $\xi=0.3, 0.5$ and 0.7 , respectively.



approach for increasing values of the parameter ξ . For comparison, the broken curves F, G and H represent the results obtained for the generalized Hamiltonian (3) but in the H-F approximation (see also [17]). One can observe a charge transfer from the adatom to the substrate in the H-F approximation for generalized N-A model for relatively large values of the parameter ξ ($\xi \geq 0.7$). This is a case also for nickel and chromium substrates as has been

shown in [17]. The effect obtained after introduction of the self-energy corrections can be described as follows. For small values of ξ we have much smaller values of q , i.e., for this distance between the adatom and substrate's surface (we remember that ξ and this distance depend on each other) we obtain further decreasing of the charge transfer to the adatom. For moderate values of ξ , i.e., for $\xi \approx 0.5$, the results obtained in H-F, as well as in the improved scheme are comparable. For greater values of ξ the charge transfer "stabilizes" around the neutral adatom case while in the HF approach the adatom becomes more and more positive charged. On the other hand, we expect on physical grounds that for a large separation distance, i.e., for large ξ , the hydrogen adatom should be in a nearly neutral state. Thus, the self-energy corrections improve the H-F results in a clear way. In summary, the self-energy corrections give much more realistic values of the hydrogen adatom charge for small value of ξ (for small distance adatom-substrate), give results comparable with those calculated in H-F approximation for moderate values of ξ and indicate rather a neutral adsorption for large adatom-substrate distances. The analysis of the presented results calculated on a basis of the generalized Hamiltonian and the results given in papers [2,17] show that there is a satisfactory description of the charged, spectroscopic and chemisorption heat experimental data. Thus, this Hamiltonian can serve as a model more efficient in describing the chemisorption process.

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