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ON HYDROGEN CHEMISORPTION  
ON THE TRANSITION METALS:  
CORRELATION EFFECTS

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## 1. INTRODUCTION

The Anderson model [1] given originally in the context of local moment formation on paramagnetic impurities in a bulk nonmagnetic metallic host, and applied by Edwards and Newns [2] and Grimley [3] to discuss chemisorption allows one to formulate for chemisorption theory some fundamental problems and, at least in part, explain the physics of this phenomenon. However, its further evolution shows that the Anderson model of chemisorption does not contain some important interactions which can lead to qualitative changes in the behaviour of its characteristics [4]. On the other hand, there is necessity of the exact examination of adatom's electron-electron Coulomb interaction. Although this model has been analysed by several authors (see e.g. [5-8] and References there), no complete solution has been found. It is difficult to take into account the correlation effects because the small parameter does not exist in the theory. This means that one has to sum an infinite series of the most divergent diagrams or construct the Green function (GF) with the approximate self-energy operator. This solutions should be, of course, identical with the known exact ones for some special cases. As has already been mentioned, a great number of papers have been devoted to the study of the correlation effects in the chemisorption theory beyond the Hartree-Fock approximation. However, the charge transfer to the adatom (here we consider the hydrogen adatom adsorption on transition metal surfaces) they predict is not compatible with experimental evidence, for example, from the change of the work function [9,10]. Therefore, it is still desirable searching for solutions of the Anderson model which better describe the chemisorption process.

In this paper we study the classical Anderson Hamiltonian using the irreducible Green function method (IGF) introduced by Tsercownikov [14]. Even in the simplest approximation this method allows us to obtain the adatom Green function with correct limits for large and small values of adatom's intra-atomic Coulomb interaction as well as nearly neutral hydrogen adatom chemisorption on transition metal surfaces.

The present paper is organized as follows. In the next section we describe the formalism associated with the irreducible Green function method in computing the adsorbate GF. We give also a short discussion concerning the limiting cases. In section 3, we give the numerical results for the hydrogen adatom charge chemisorbed on transition metal surface compared with the results of calculations performed within a Hartree-Fock approach and results obtained within the theory of Brenig and Schonhammer [5], for comparison.

## 2. THEORY

We consider the adatom-substrate binding from the point of view of the Anderson-Newns model with Hamiltonian of the form:

$$H = \sum_{k\sigma} \varepsilon_k n_{k\sigma} + \sum_{\sigma} E_{\alpha} n_{\alpha\sigma} + U n_{\alpha\sigma} n_{\alpha-\sigma} + \sum_{k\sigma} (V_{\alpha k} a_{\alpha\sigma}^+ a_{k\sigma}^{\dagger} + \text{H.c.}) , \quad (1)$$

where  $a_{\alpha\sigma}$ ,  $a_{k\sigma}^{\dagger}$  ( $a_{\alpha\sigma}^+$ ,  $a_{k\sigma}^{\dagger}$ ) represent annihilation (creation) operators for the adsorbate orbital and  $k$ -th substrate orbital, respectively. Next,  $n_{k\sigma}$  and  $n_{\alpha\sigma}$  are the operators for the number of spin  $\sigma$  electrons in substrate  $k$ -state and adatom orbital, respectively,  $\varepsilon_k$  is the substrate band level,  $E_{\alpha}$  is the adatom level,  $V_{\alpha k}$  measures the interaction between the adatom and substrate and  $U$  is the intra-atomic interaction for the adatom.

In the following we adopt the Green function technique introduced by Tsercownikov [11] and calculate the "adatom" Green function (GF)  $\langle\langle a_{\alpha\sigma} | a_{\alpha\sigma}^{\dagger} \rangle\rangle$  defined as [12]

$$\langle\langle a_{\alpha\sigma}(t) | a_{\alpha\sigma}^{\dagger}(t') \rangle\rangle = -i\theta(t-t') \langle [a_{\alpha\sigma}(t), a_{\alpha\sigma}^{\dagger}(t')] \rangle , \quad (2)$$

where the angular brackets denote the grand canonical ensemble average. In the formalism we used here, in contrast with the usual equation of motion (EM) method, an infinite system of

the Dyson-type equations is constructed for two-time correlation functions and Green functions. In the EM method one has to decouple the higher-order GF and this decoupling process is an approximation the meaning of which is not immediately transparent. Here, one gets the Dyson type equation on each level of hierarchy and a truncation procedure can be motivated, to some extent, on the physical grounds [11].

Let us start with the equation of motion for the  $(N+1)$  component "operator vector"  $A_1^{\sigma}$

$$A_1^{\sigma} = \begin{pmatrix} a_{\alpha\sigma} \\ a_{k\sigma}^{\dagger} \\ \vdots \end{pmatrix} , \quad (3)$$

$$i\dot{A}_1^{\sigma} = W^{\sigma}(1) A_1^{\sigma} + U^{\sigma}(1,2) A_2^{\sigma} , \quad (4)$$

or explicitly

$$i \frac{d}{dt} \begin{pmatrix} a_{\alpha\sigma} \\ a_{k\sigma}^{\dagger} \\ \vdots \end{pmatrix} = \begin{pmatrix} E_{\alpha} & V_{\alpha k} & V_{\alpha k} & \dots \\ V_{\alpha k} & E_{\alpha} & \dots & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix} \begin{pmatrix} a_{\alpha\sigma} \\ a_{k\sigma}^{\dagger} \\ \vdots \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ \vdots \end{pmatrix} (n_{\alpha-\sigma} a_{\alpha\sigma}) . \quad (5)$$

For the matrix GF  $\langle\langle A_1^{\sigma} | A_1^{\sigma\dagger} \rangle\rangle$  we obtain the Dyson equation (for details see the original paper [11] or Ref. [13] with application of this method to the Extended Hubbard Hamiltonian)

$$\langle\langle A_1^{\sigma} | A_1^{\sigma\dagger} \rangle\rangle = \langle\langle A_1^{\sigma} | A_1^{\sigma\dagger} \rangle\rangle^{(0)} + \langle\langle A_1^{\sigma} | A_1^{\sigma\dagger} \rangle\rangle^{(0)} M^{\sigma}(1) \langle\langle A_1^{\sigma} | A_1^{\sigma\dagger} \rangle\rangle . \quad (6)$$

Here,  $\langle\langle A_1^{\sigma} | A_1^{\sigma\dagger} \rangle\rangle^{(0)}$  is the matrix GF calculated in the Hartree-Fock approximation and the self-energy operator  $M^{\sigma}(1)$  satisfies the equation

$$M^{\sigma}(1) = U^{\sigma} I \langle\langle n_{\alpha-\sigma} a_{\alpha\sigma} | n_{\alpha-\sigma} a_{\alpha\sigma}^{\dagger} \rangle\rangle , \quad (7)$$

where the brackets  $\langle\langle \dots \rangle\rangle$  denote the higher-order GF irreducible with regard to  $A_1^{\sigma}$ , i.e., for any operators  $A$  and  $B$  one has (by definition) [11]

$$\langle\langle A | B^+ \rangle\rangle_n = \langle\langle A | B^+ \rangle\rangle_{n-1} + \langle\langle A | B^+ \rangle\rangle_{n-1} \langle\langle A_n | A_n^+ \rangle\rangle_{n-1}^{-1} \langle\langle A_n | B^+ \rangle\rangle_{n-1} \quad (8)$$

with the same definition for irreducible correlation function. The EM for  $M^\sigma(1)$  has a form of the Dyson equation with a "free-like" GF as follows:

$$\begin{aligned} \langle\langle n_{A-\sigma} a_{A\sigma} | n_{A-\sigma} a_{A\sigma}^+ \rangle\rangle_1^{(\sigma)} &= \langle\langle n_{A-\sigma} \rangle\rangle \times \\ &\times (1 - \langle\langle n_{A-\sigma} \rangle\rangle) / [\omega^+ - E_A - U - W^\sigma(2)] , \end{aligned} \quad (9)$$

where  $W^\sigma(2)$ , should be calculated from the equation

$$\begin{aligned} W^\sigma(2) &= U^\sigma(2,3) \langle [A_2^\sigma, A_2^{\sigma+}]_+ \rangle_1 \langle [A_2^\sigma, A_2^{\sigma+}]_+ \rangle_1^{-1} - \\ &- \langle [A_2^\sigma, A_1^{\sigma+}]_+ \rangle \langle [A_1^\sigma, A_1^{\sigma+}]_+ \rangle^{-1} U^\sigma(1,2) , \end{aligned} \quad (10)$$

and  $W^\sigma(2)$ ,  $U^\sigma(2,3)$  can be calculated writing down the corresponding EM for  $A_2^\sigma$  (see Eq. (4)).

The mass operator  $M^\sigma(2)$  in the Dyson-like equation for  $M^\sigma(1)$  is a solution of the next Dyson-like equation and so on. Here, we try to describe the adatom-substrate system by the GF calculated within the continued-fraction-type expansion with one step more in this expansion than the Hartree-Fock approximation, i.e., to approximate the matrix  $\langle\langle A_1^\sigma | A_1^{\sigma+} \rangle\rangle$  by the expression

$$\begin{aligned} \langle\langle A_1^\sigma | A_1^{\sigma+} \rangle\rangle &= \left\{ (\langle\langle A_1^\sigma | A_1^{\sigma+} \rangle\rangle^{(\sigma)})^{-1} - \langle [A_1^\sigma, A_1^{\sigma+}]_+ \rangle^{-1} U^\sigma(1,2) \times \right. \\ &\times \left. \frac{1}{(\langle\langle A_2^\sigma | A_2^{\sigma+} \rangle\rangle^{(\sigma)})^{-1} - R} U^\sigma(2,1) \langle [A_2^\sigma, A_2^{\sigma+}]_+ \rangle^{-1} \right\}^{-1} \quad (11) \end{aligned}$$

where  $R$  the rest part of this expansion is put zero. Finally, in order to obtain  $\langle\langle a_{A\sigma} | a_{A\sigma}^+ \rangle\rangle$  from Eq.(11) we have to calculate  $W^\sigma(2)$ , Eq.(10). This function,  $W^\sigma(2)$ , contains the higher-order correlation function for which, in principle, we would construct a similar system of the coupled Green functions. Instead, we have made a commonly used approximation, namely, the following decoupling procedure was assumed:

$$\langle\langle a_{A-\sigma}^+ a_{K-\sigma}^* n_{A\sigma} \rangle\rangle \approx \langle\langle a_{A-\sigma}^+ a_{K-\sigma}^* \rangle\rangle \langle\langle n_{A\sigma} \rangle\rangle \quad (12)$$

Although this correlation function can be calculated more accurately than in this approximation (see e.g. [9]), we hope it does not introduce significant changes in calculating  $\langle\langle A_1^\sigma | A_1^{\sigma+} \rangle\rangle$  (it is used on a relatively deeper level of calculations). Now the function  $W^\sigma(2)$  reads as

$$\begin{aligned} W^\sigma(2) &= \frac{2 \langle\langle n_{A\sigma} \rangle\rangle - 1}{\langle\langle n_{A\sigma} \rangle\rangle (1 - \langle\langle n_{A\sigma} \rangle\rangle)} \times \\ &\times \sum_K V_{AK} \langle\langle a_{A-\sigma}^+ a_{K-\sigma}^* \rangle\rangle - U \langle\langle n_{A\sigma} \rangle\rangle . \end{aligned} \quad (13)$$

To this end, we present GF  $\langle\langle a_{A\sigma} | a_{A\sigma}^+ \rangle\rangle$  as follows:

$$\begin{aligned} \langle\langle a_{A\sigma} | a_{A\sigma}^+ \rangle\rangle &= \left\{ \omega^+ - E_\sigma - \sum_K \frac{|V_{AK}|^2}{\omega^+ - \epsilon_K} - \right. \\ &\left. \frac{U^2 \langle\langle n_{A\sigma} \rangle\rangle (1 - \langle\langle n_{A\sigma} \rangle\rangle)}{\omega^+ - E_A - U (1 - \langle\langle n_{A\sigma} \rangle\rangle) - \frac{R^\sigma}{\langle\langle n_{A\sigma} \rangle\rangle (1 - \langle\langle n_{A\sigma} \rangle\rangle)}} \right\}^{-1} \end{aligned} \quad (14)$$

$$\begin{aligned} \text{where: } E_\sigma &= E_A + U \langle\langle n_{A\sigma} \rangle\rangle , \\ R^\sigma &= (2 \langle\langle n_{A\sigma} \rangle\rangle - 1) \sum_K V_{AK} \langle\langle a_{A\sigma}^+ a_{K\sigma}^* \rangle\rangle \end{aligned}$$

The correlation function  $\langle\langle a_{A\sigma}^+ a_{K\sigma}^* \rangle\rangle$  is calculated by using GF  $\langle\langle a_{A\sigma} | a_{K\sigma}^+ \rangle\rangle$  extracted from Eq.(6), which can be represented by the equation

$$\begin{aligned} \langle\langle a_{A\sigma} | a_{K\sigma}^+ \rangle\rangle &\approx \langle\langle a_{A\sigma} | a_{K\sigma}^+ \rangle\rangle^{(\sigma)} \times \\ &\times \frac{1}{1 - U^2 \langle\langle n_{A-\sigma} a_{A\sigma}^+ \rangle\rangle^{(\sigma)} \langle\langle a_{A\sigma} | a_{A\sigma}^+ \rangle\rangle^{(\sigma)}} \quad (15) \end{aligned}$$

Note that our adsorbate Green function contains the Hartree-Fock approximation for small  $U$  (independently of the method of calculating  $W^\sigma(2)$ -Eq.(10)) as we can rewrite it in the form

$$\langle\langle a_{A\sigma} | a_{A\sigma}^+ \rangle\rangle = \frac{1}{\omega^+ - E_\sigma - \sum_K \frac{|V_{AK}|^2}{\omega^+ - \epsilon_K} - o(U^2)} , \quad (16)$$

where  $\sigma(U^2)$  immediately follows from (14). The adsorbate Green function (14) has a correct limit for the transfer integral  $V_{AK}$  being zero. In fact, it is similar to the result of Brenig and Schonhammer [5]. We can transform it into their form for the adsorbate Green function with their self-energy as

$$\begin{aligned} m^\sigma(\omega) &= (2 \langle n_{A\sigma} \rangle - 1) \sum_k V_{AK} \langle a_{A-\sigma}^\dagger a_{K-\sigma} \rangle - \\ &- \langle n_{A-\sigma} \rangle (1 - \langle n_{A-\sigma} \rangle) \sum_k \frac{|V_{AK}|^2}{\omega - \epsilon_k}. \end{aligned} \quad (17)$$

The analytical structure of the adatom Green function (14) admits existence of the two localized states (for each spin direction) below and above the substrate density of states (see also [5]). The filling of these states may be calculated from the formula

$$\langle n_{A\sigma} \rangle_L^{(i)} = \frac{E_i - A^\sigma}{(1 - \frac{d}{d\omega} L(\omega))(E - A^\sigma) + \omega - E_\sigma - L(\omega)} \Big|_{\omega=E_i} \quad (18)$$

where  $L(\omega)$  is the real part  $\sum_k \frac{|V_{AK}|^2}{\omega - \epsilon_k}$  and  $i=1,2$ .

$$A^\sigma = U^2 \langle n_{A-\sigma} \rangle (1 - \langle n_{A-\sigma} \rangle),$$

$$B^\sigma = E_A - U (1 - \langle n_{A-\sigma} \rangle) - \frac{R^{-\sigma}}{\langle n_{A-\sigma} \rangle (1 - \langle n_{A-\sigma} \rangle)}$$

and  $E_i$  are solutions of the equation

$$(\omega - E_\sigma - L(\omega))(\omega - A^\sigma) - B^\sigma = 0.$$

Below the bottom of the substrate band  $E_1$ , the localized electron states may occur:

-two states for  $A^\sigma < E_1$  and  $B^\sigma/(E_1 - A^\sigma) < [E_1 - E_\sigma - L(E_1)]$ ,  
-no states for  $A^\sigma > E_1$  and  $B^\sigma/(E_1 - A^\sigma) > [E_1 - E_\sigma - L(E_1)]$   
and one state in the opposite case.

For energies above the top of the substrate energy band  $E_2$ , we have, respectively

-two states for  $A^\sigma > E_2$  and  $B^\sigma/(E_2 - A^\sigma) > [E_2 - E_\sigma - L(E_2)]$ ,

-no states for  $A^\sigma < E_2$  and  $B^\sigma/(E_2 - A^\sigma) > [E_2 - E_\sigma - L(E_2)]$  and one localized state in the opposite case.

### 3. NUMERICAL RESULTS AND CONCLUSION

In order to give a simple and transparent picture of the influence of the on-adatom electronic correlations on some chemisorption characteristics, we have computed (for the temperature  $T=0^\circ\text{K}$ ) the hydrogen adatom electron charge  $q = \langle n_{A\uparrow} \rangle + \langle n_{A\downarrow} \rangle$  on the self-consistent way, Eqs.(14-16), where

$$\langle n_{A\sigma} \rangle = \frac{e_F}{-\infty} \int d\epsilon \left( -\frac{1}{\pi} \right) \text{Im} \langle \langle a_{A\sigma} | a_{A\sigma}^\dagger \rangle \rangle. \quad (19)$$

As a substrate metal we have taken the nickel case with the band density of states (this quantity enters into our equations through the "chemisorption function" in Eq.(14)) calculated for a bulk system according to Ref. [14]. We have also repeated our calculations for a substrate modelled by the Ni(001) surface local density of states which includes the effect of asphericity of the potential at the surface and self-consistent charge transfer [15]. The other parameters needed for calculations were taken from Ref. [2]. However, the difference in the calculated adatom charge was very small for these two cases; so we have shown the results of the first case only, the figure. In this figure we depicted the

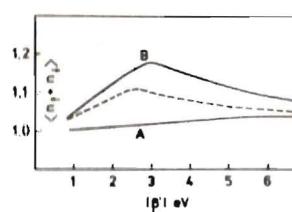


Fig. The electron charge of the hydrogen adatom chemisorbed on the nickel surface vs.  $\beta = |V_{AK}|$ , calculated in this paper - curve A, within a self-consistent Hartree-Fock method - curve B and according to Ref. [5] (for a weak coupling limit) - broken curve.

In conclusion, we have shown that the irreducible Green function method in version given by Tsercovnikov can be very useful in the investigations of the chemisorption processes. Using the simplest possible approximation (beyond the Hartree-Fock level) i.e. retaining only the first two Dyson-type equations (from the infinite system of coupled equations for

correlation functions and Green's functions) one can obtain the adatom Green function with correct limits in some important cases. These are the Hartree-Fock approximation for small  $U$  and the large  $U$  limit. The final result for the adatom Green function is very similar to this one given in Ref.[5] obtained from a certain class of two-particle Green's functions, but with different self-energy function. The charge of the hydrogen atom adsorbed on the transition metal surface calculated within our approach in a self-consistent way indicates rather neutral adsorption. This value is smaller than the Hartree-Fock result or results obtained in Refs [5,9] and this fact can prove that the electronic correlations on the adatom can be better taken into considerations in our approach.

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Таранко Р., Таранко Е., Гавриленко Г.М.  
О хемосорбции водорода на переходных  
металлах: корреляционные эффекты

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Корреляционные эффекты в модели Андерсона рассматриваются в рамках метода неприводимых двухвременных функций Грина. Даже простейшая аппроксимация позволяет нам получить адатомную функцию Грина с правильным поведением в случае больших и малых значений кулоновского взаимодействия на адатоме, а также приводящую к почти нейтральной хемосорбции водорода на переходных металлах.

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On Hydrogen Chemisorption on the Transition  
Metals: Correlation Effects

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A solution of the Anderson model for chemisorption including correlation effects within the irreducible two-time Green function method is presented. Even in the simplest approximation this method allows one to obtain the adatom Green function with correct limits for large and small values of adatom's intra-atomic Coulomb interaction, as well as nearly neutral hydrogen atom chemisorption on transition metal surfaces.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

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