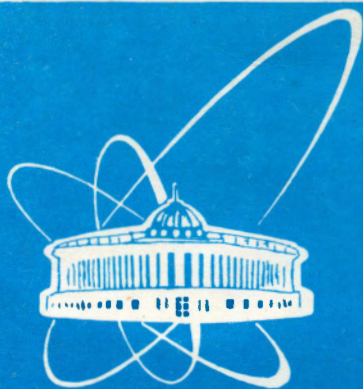


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**THEORY OF CHEMISORPTION ON METALS
AT FINITE COVERAGES:
Adsorption Isotherms**

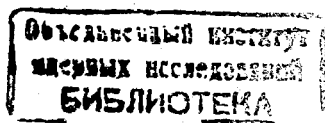
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In recent years, there has been an increasing interest in chemisorption phenomena. Great theoretical efforts have been made to understand the mechanism of the chemisorption at finite coverages. But up to now, in most cases the electronic properties of the chemisorbed systems at a given coverage rate were not investigated (see, e.g. [1,2]). It is obvious, that in the next step, we should deal with the coverage rate not as a given parameter but as a quantity which should be calculated in a self-consistent way together with electronic characteristics of the system. In other words, we have to take into consideration an adsorbent-adsorbate-gas system in the thermodynamic equilibrium at a temperature T and pressure p of the gaseous adsorbate. The idea of simultaneous calculations of the coverage rate and the electronic properties of the chemisorbed overlayer was given in ref. [3]. In this letter we develop this idea and present the explicit evaluation of the adsorption isotherms for the system described by a relatively simple Hamiltonian of the Anderson-Ising type postponing calculations for more realistic model in future work.

It is obvious, that in order to understand the chemisorption process on a microscopic level and, in particular, to predict the possible coverage as a function of pressure, one needs a proper model. Here we use the model Hamiltonian intended to describe the system of the hydrogen-like adatoms chemisorbed on a metal surface which recently has been derived [3,4]. The complex adsorbate-plus-adsorbent system was represented by the electron subsystem (the substrate band electrons and adatom valence electrons) and the ion subsystem (adions plus ions forming the substrate metal).



Performing the generalized second quantization procedure the Hamiltonian constructed on the basis of the adion number operators and electron annihilation and creation operators was obtained. Just because of the fact, that this Hamiltonian consists of the adion number operators $N_\alpha = C_\alpha^\dagger C_\alpha$, where C_α (C_α^\dagger) corresponds to the annihilation (creation) operator of the adion at the adsorption centre α , and simultaneously contains the electron operators, there is the possibility of the coverage rate $\theta = \langle N_\alpha \rangle$ calculations on the same level with the electron characteristics. Here, $\langle \dots \rangle$ means the statistical average within the grand canonical ensemble.

Thus, the model Hamiltonian consisting of most important for our purpose terms reads:

$$H = \sum_{\alpha} \epsilon N_{\alpha} + \frac{1}{2} \sum_{\alpha \neq \beta} \epsilon_{\alpha\beta} N_{\alpha} N_{\beta} + \sum_{k\sigma} \epsilon_k n_{k\sigma} + \sum_{\alpha\sigma} N_{\alpha} \epsilon_{\alpha} n_{\alpha\sigma} + \frac{U}{2} \sum_{\alpha\sigma} N_{\alpha} n_{\alpha\sigma} n_{\alpha-\sigma} + \nu \sum_{\alpha\sigma} (1 - N_{\alpha}) n_{\alpha\sigma} - \mu_e N_e - \mu_I N_I, \quad (1)$$

where $N_I = \sum_{\alpha} N_{\alpha}$, $N_e = \sum_{k\sigma} n_{k\sigma} + \sum_{\alpha\sigma} N_{\alpha} n_{\alpha\sigma}$.

Here, as usually, $n_{k\sigma} = a_{k\sigma}^\dagger a_{k\sigma}$ ($n_{\alpha\sigma} = a_{\alpha\sigma}^\dagger a_{\alpha\sigma}$) denotes the substrate (adatom) electron occupation number operator and $a_{k\sigma}$, $a_{\alpha\sigma}$ ($a_{k\sigma}^\dagger$, $a_{\alpha\sigma}^\dagger$) are the substrate and adatom electron annihilation (creation) operators, respectively. The parameters ϵ , $\epsilon_{\alpha\beta}$, ϵ_k , ϵ_{α} and U denote effective on-site adion binding energy, pairwise interaction energy between adions located at adsorption sites α and β , energy of the one-electron states of the substrate metal, 1-s electron orbital

energy of the adion and on-adatom effective electron-electron Coulomb interaction, respectively. The chemical potential of the electron and adion subsystems are denoted by μ_e and μ_I and ν is the energy of the electron located at the empty (vacancy) adsorption centre. Such term must be included if one wants to use the standard equation of motion formalism for appropriate Green's Functions (GF) (see [3] for details). At the end of calculations one puts $\nu = \infty$ in order to exclude contributions from such unphysical states (electrons cannot be localized at the empty adsorption sites). Finally, N_e and N_I are the total numbers of the electrons and adions, respectively. Note, that electron subsystem does depend on the adion subsystem directly via occupation numbers N_{α} which enter into electron part of the Hamiltonian (1). In (1) we have neglected the number of terms, the most important being those describing direct hops of electrons from adion to substrate and vice versa. One should emphasize, however, that the effective adatom's ionization level ϵ_{α} contains some information about the substrate metal [3]. For that reason the absence of electron hopping terms does not denote the existence of two (adsorbate and adsorbent) fully independent electron systems.

In most of the works describing the thermodynamic phenomena the coverage rate θ has been assumed to be independent of the electron subsystem. The electronic properties of the chemisorbed system have been introduced in this type of calculations only through the values of the coefficients of the Ising-type Hamiltonians (lattice gas models) usually used in this type of calculations. In view of the structure of the Hamiltonian (1) it is great oversimplification. In

order to obtain the adsorption isotherm, i.e. the dependence of the coverage rate on the pressure of the gaseous adsorbate phase, we need to calculate the correlation function $\langle C_{\alpha}^{\dagger} C_{\alpha} \rangle$. This function can in turn be expressed in terms of the double-time adionic GF

$\langle C_{\alpha}(t) | C_{\alpha}^{\dagger}(t') \rangle$ defined as follows [5]:

$$\langle C_{\alpha}(t) | C_{\alpha}^{\dagger} \rangle = -i\theta(t) \langle \{ C_{\alpha}(t), C_{\alpha}^{\dagger} \} \rangle, \quad (2)$$

which can be obtained only through the knowledge of the electron GFs. Here, $\theta(t)$ denotes the Heaviside function, $\langle \dots \rangle$ and $\{ , \}$ stand for averaging over Gibb's grand canonical ensemble and anticommutator respectively, and the operators are written in the Heisenberg representation. To find the GF (2) we use the equations of motion method [6] obtaining in result many of higher order GFs. Without going into details, here we only show symbolically what kind of the higher order GFs (or rather their Fourier transforms) and correlation functions appear during the calculations of GF (2):

$$\langle C_{\alpha} | C_{\alpha}^{\dagger} \rangle \Rightarrow \langle n_{\alpha\sigma} C_{\alpha} | C_{\alpha}^{\dagger} \rangle, \langle n_{\alpha-\sigma} n_{\alpha\sigma} C_{\alpha} | C_{\alpha}^{\dagger} \rangle, \langle N_{\beta} C_{\alpha} | C_{\alpha}^{\dagger} \rangle;$$

$$\langle n_{\alpha\sigma} C_{\alpha} | C_{\alpha}^{\dagger} \rangle \Rightarrow \langle n_{\alpha\sigma} \rangle, \langle n_{\alpha\sigma} n_{\alpha-\sigma} C_{\alpha} | C_{\alpha}^{\dagger} \rangle, \langle N_{\beta} n_{\alpha\sigma} C_{\alpha} | C_{\alpha}^{\dagger} \rangle; \quad (3)$$

$$\langle n_{\alpha\sigma} n_{\alpha-\sigma} C_{\alpha} | C_{\alpha}^{\dagger} \rangle \Rightarrow \langle n_{\alpha\sigma} n_{\alpha-\sigma} \rangle, \langle N_{\beta} n_{\alpha\sigma} n_{\alpha-\sigma} C_{\alpha} | C_{\alpha}^{\dagger} \rangle.$$

Using decouplings ($\alpha \neq \beta$): $\langle N_{\beta} n_{\alpha\sigma} n_{\alpha-\sigma} C_{\alpha} | C_{\alpha}^{\dagger} \rangle \approx \langle N_{\beta} \rangle \langle n_{\alpha\sigma} n_{\alpha-\sigma} C_{\alpha} | C_{\alpha}^{\dagger} \rangle$,

$\langle N_{\beta} C_{\alpha} | C_{\alpha}^{\dagger} \rangle \approx \langle N_{\beta} \rangle \langle C_{\alpha} | C_{\alpha}^{\dagger} \rangle$ and $\langle N_{\beta} n_{\alpha\sigma} C_{\alpha} | C_{\alpha}^{\dagger} \rangle \approx \langle N_{\beta} \rangle \langle n_{\alpha\sigma} C_{\alpha} | C_{\alpha}^{\dagger} \rangle$,

one can obtain for $\langle C_{\alpha} | C_{\alpha}^{\dagger} \rangle$ the expression :

$$\langle C_{\alpha} | C_{\alpha}^{\dagger} \rangle = \frac{1 - \langle n_{\alpha\downarrow} \rangle - \langle n_{\alpha\uparrow} \rangle + \langle n_{\alpha\downarrow} n_{\alpha\uparrow} \rangle}{E + \bar{\mu}_I - J \langle N_{\alpha} \rangle} + \frac{\langle n_{\alpha\downarrow} \rangle + \langle n_{\alpha\uparrow} \rangle}{E + \bar{\mu}_I - \epsilon_{\alpha}^{\circ} - J \langle N_{\alpha} \rangle} + \langle n_{\alpha\downarrow} n_{\alpha\uparrow} \rangle \left[(E + \bar{\mu}_I - 2\epsilon_{\alpha}^{\circ} - U - J \langle N_{\alpha} \rangle)^{-1} - 2(E + \bar{\mu}_I - \epsilon_{\alpha}^{\circ} - J \langle N_{\alpha} \rangle)^{-1} \right], \quad (4)$$

where

$$\epsilon_{\alpha}^{\circ} = \epsilon_{\alpha} - \mu_e - \nu, \quad \bar{\mu}_I = \mu_I - \epsilon, \quad J = \sum_{\beta}^{\beta \neq \alpha} \epsilon_{\alpha\beta}.$$

The decouplings introduced above denote, that we have neglected the possible correlated distribution of the adatoms on the metal surface. The correlation functions $\langle n_{\alpha\sigma} \rangle$ and $\langle n_{\alpha\sigma} n_{\alpha-\sigma} \rangle$ can be obtained from the knowledge of GFs $\langle a_{\alpha\sigma} | a_{\alpha\sigma}^{\dagger} \rangle$ and $\langle n_{\alpha-\sigma} a_{\alpha\sigma} | a_{\alpha\sigma}^{\dagger} \rangle$, respectively. These correlation functions can be expressed in terms of $\langle N_{\alpha} n_{\alpha\sigma} \rangle$ in our model exactly. Finally, using the Green's Function spectral representation and taking $\nu = \infty$, one gets for the coverage θ

$$\theta = \left[1 + \exp[-\mu_I/kT] \exp[(\epsilon_{\alpha} + J\theta)/kT] L(\epsilon_{\alpha}, U, \mu_e, T) \right]^{-1},$$

where

$$L(\epsilon_{\alpha}, U, \mu_e, T) = \left(1 + 2 \exp[(\mu_e - \epsilon_{\alpha})/kT] + \exp[2(\mu_e - \epsilon_{\alpha})/kT - U/kT] \right)^{-1}. \quad (5)$$

The equation (5) represents the adsorption isotherm. As usually, the coupling to the gas phase can be achieved by its chemical potential μ_{gas} equal to μ_I and the chemical potential of the electron subsystem is identified as a Fermi energy E_F . If we confine ourselves to the case when only the attractive interactions between the nearest neighbour adatoms are present ($\epsilon_{\alpha\beta} = -|\epsilon_1|$) and the

adsorption centers form a two-dimensional quadratic lattice on the substrate surface, then the adsorption isotherm is as follows:

$$\frac{\theta}{1-\theta} = \exp [(\mu_1 + |\epsilon|)/kT] \exp (4|\epsilon_1| \theta /kT) L^{-1}, \quad (6)$$

Note, that if we neglect the electron contribution terms in the Hamiltonian (1), then the expression (6) takes the known Bragg-Williams adsorption isotherm form.

In the Figure we show some examples of adsorption isotherms. We plot θ vs. $(\mu_1 + |\epsilon|)/kT$ rather μ_1/kT in order to eliminate the dependence of the isotherms on the binding energy ϵ . All curves are plotted for $kT/|\epsilon_1| = 1$. The curve no.1 corresponds to $E_f = \epsilon_\alpha$ (the effective adatom's ionization level coincides with the Fermi level) and curves numbered 2,3,4 and 5 correspond to $(E_f - \epsilon_\alpha)/|\epsilon_1| = 1, 10, -1$ and -10 , respectively. All these curves are calculated for $U=0$. The curves 6 and 7 are calculated for parameters corresponding to the so-called symmetric Anderson model, $2(E_f - \epsilon_\alpha) = U$, for $(E_f - \epsilon_\alpha)/|\epsilon_1|$ equal to 1 and 10, respectively. The Bragg-Williams isotherm (for the same parameters) coincides with the curve no.5. We can observe very distinct influence of the electron subsystem characteristics on the adsorption isotherms. Let us consider the case of $U=0$ (curves 1,2,3,4 and 5). For the adatom's ionization level moving down relative to the Fermi level the adsorption isotherms are shifted to smaller values of $(\mu_1 + |\epsilon|)/kT$ corresponding to smaller values of the gaseous adsorbate pressure - curves 2 and 3. On the other hand, if ϵ_α moves up, the corresponding isotherms are shifted to greater values of the gaseous adsorbate pressure. This shift is, however, much smaller and for increasing values of $(E_f - \epsilon_\alpha)$ the corresponding

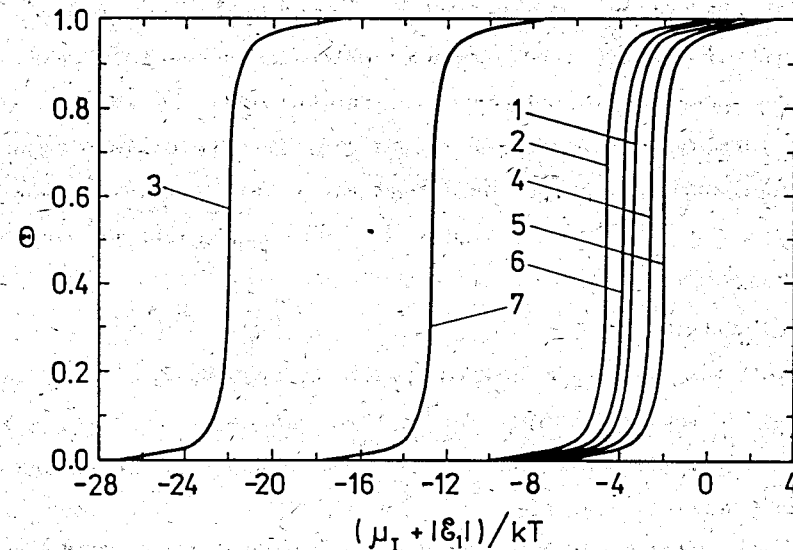


Figure. Adsorption isotherms for $kT/|\epsilon_1| = 1$ and attractive nearest neighbour interactions. The curves 1,2,3,4 and 5 correspond to $U = 0$, $(E_f - \epsilon_\alpha)/|\epsilon_1| = 0, 1, 10, -1$ and -10 , respectively. The curves 6 and 7 correspond to $(E_f - \epsilon_\alpha)/|\epsilon_1| = U/2|\epsilon_1| = 1$ and 10 , respectively. The Bragg-Williams isotherm coincides with the curve no.5

curves tend towards the Bragg-Williams isotherm - curve no. 5. In the case of nonvanishing value of the intra-adatom Coulomb interaction U , the general behaviour of the adsorption isotherms is similar - curves 6 and 7. With increasing value of the distance of ϵ_α from the Fermi level the corresponding isotherms are shifted to smaller values of the gaseous adsorbate pressure. This shift is, however, much smaller in comparison with the case of nonvanishing U - compare curve 2 with 6 and 3 with 7, respectively.

In conclusion, we have used the recently derived Anderson-Ising type Hamiltonian to study the adsorption isotherms in dependence on ϵ_α , the position of adatom's ionization level in respect to the Fermi level E_F and on U , the value of intra-site Coulomb repulsion. Our approach treats the ionic and electronic subsystems on equal footing, thus providing a method for further detailed studies of the chemisorption process.

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Теория хемисорбции на металлах при конечных покрытиях.
Изотерма адсорбции

Предложен метод самосогласованного описания электронных и термодинамических характеристик при хемисорбции металлами. Для исследования поведения равновесных характеристик открытой системы газ-адсорбат использован формализм функций Грина и гамильтониан типа Изинга — Андерсона. На равных основаниях учитываются и электронная подсистема и адионная. Предложенная схема расщепления гриновских функций приводит к изотерме Брэгга — Вильямса, существенно модифицируемой характеристиками электронной подсистемы.

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Theory of Chemisorption on Metals at Finite Coverages:
Adsorption Isotherms

A self-consistent description of the electronic and thermodynamic characteristics of the chemisorbed adatoms on the substrate metal surfaces is given. The thermodynamic equilibrium in the adsorbate-gas system is investigated within the generalized Anderson — Ising type Hamiltonian and the equation of motion formalism for Green functions. The electronic and adionic properties of the chemisorbed system are treated on equal footing. The decoupling scheme has been proposed which leads to Bragg — Williams adsorption isotherms with significant modifications due to the electron subsystem.

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

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