

CHEMISORPTION ISOTHERMS FOR ISING-ANDERSON HAMILTONIAN

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The adsorption isotherms for Ising-Anderson type model Hamiltonian describing the chemisorbed system was calculated. The submonolayer coverage of the substrate surface was considered on the equal footing together with the electronic characteristics of the chemisorbed adatoms in a self-consistent manner. The resulting adsorption isotherms depend in explicit way on the electronic parameters describing the chemisorbed adatoms and substrate metal.

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1. Introduction

The chemisorption of hydrogen (or hydrogen-like) atoms on surfaces of transition metals at low or submonolayer coverages has received considerable attention in fundamental and applicable researches (see, e.g. [1, 2]). In this context, great theoretical efforts have been made to understand the mechanism of the single adatom chemisorption process, as well as the chemisorption at finite coverages (see, e.g. [3, 4]).

Usually, in investigations concerning the chemisorption at finite coverages the coverage rate was assumed as a given quantity and the electronic characteristics, such as the adatom charge or adatom local density of states were calculated on the basis of the assumed model Hamiltonian [4] or using *ab initio* methods [5]. Especially, the method of model Hamiltonians is well suited for better understanding and not only for reproducing the experimentally observed features. The reason that in papers using the model Hamiltonians the electronic properties were calculated for a given coverage was a consequence of model Hamiltonians used in these calculations. Namely, the Anderson-type Hamiltonians were used constructed on the basis of electron annihilation and creation operators, only [3]. In order to calculate the coverage rate one has to calculate the correlation function $\langle N_\alpha \rangle$, where N_α is the adion number operator equal to $C_\alpha^+ C_\alpha$, C_α^+ (C_α) corresponds to the annihilation (creation) operator of the adion at the adsorption

center α and the brackets $\langle \dots \rangle$ denote the statistical average within the grand canonical ensemble. It means that in order to calculate on the same level the electronic (e.g. $\langle n_{\alpha\sigma} \rangle$, where $n_{\alpha\sigma} = a_{\alpha\sigma}^{\dagger} a_{\alpha\sigma}$ denotes the adatom electron occupation number and $a_{\alpha\sigma}$ ($a_{\alpha\sigma}^{\dagger}$) is the adatom electron annihilation (creation) operator) and ionic (e.g. the coverage rate $\langle N_{\alpha} \rangle$) characteristics of the chemisorption system we should have a proper model Hamiltonian consisting of adion and electron operators. Such Ising–Anderson type Hamiltonian intended to describe the hydrogen (hydrogen-like) adatoms on metal surfaces was recently introduced in Ref. [6]. (see also [7]). The complex adsorbate–adsorbent system was represented by the sum of electron subsystem (the substrate band electrons plus the 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. Now, the required correlation function $\langle C_{\alpha}^{\dagger} C_{\alpha} \rangle$ and electron correlation functions can be simultaneously calculated in the self-consistent manner. They can be obtained from the knowledge of appropriate double-time, retarded Green’s functions (GF) calculated, for example, within the equation of motion method. Such idea of simultaneous calculations of the coverage rate and the electronic properties of the chemisorbed overlayer was given by Gavrilenko [6]. Here we follow this idea and present the explicit evaluations of the adsorption isotherms for system described by a relatively simple Hamiltonian, describing however, the most characteristic features of the chemisorption phenomena.

We want to emphasize that the adsorption isotherm calculations for Ising-type models are treated in the literature for a long time [8]. However, only in the formalism presented here it is a possibility to consider the electron and adion subsystems on the same level in a self-consistent way. The calculated coverage is a result of the equilibrium between the gas phase and adsorbed adlayer as well as depends on the adatom electron charge calculated simultaneously with it in a self-consistent manner.

The organization of the present paper is as follows: In Sec. 2 the Hamiltonian describing the chemisorption system is formulated in which the adion and electron components are taken into account. An approximate method of adsorption isotherms calculations is developed in Sec. 3. The numerical results, discussion and concluding remarks are present in the final section.

2. Hamiltonian

In general, the Hamiltonian describing the adatoms chemisorbed on the metal surface can be written in the following form [9]:

$$\begin{aligned}
 H = A_0 + \sum_{\alpha} N_{\alpha} A_{\alpha} + \sum_{\substack{\alpha \neq \beta \\ \alpha \beta}} N_{\alpha} N_{\beta} A_{\alpha\beta} \\
 + \sum_{\substack{\alpha \neq \beta \neq \gamma \\ \alpha \beta \gamma}} N_{\alpha} N_{\beta} N_{\gamma} A_{\alpha\beta\gamma} + \sum_{\substack{\alpha \neq \beta \neq \gamma \neq \sigma \\ \alpha \beta \gamma \sigma}} N_{\alpha} N_{\beta} N_{\gamma} N_{\sigma} A_{\alpha\beta\gamma\sigma}. \quad (1)
 \end{aligned}$$

We assume the adsorption centers form a given configuration on the metal surface and the summation is performed over all adsorption centers which may either be occupied by adion or be empty. The second sum runs over all pairs once, the third sum runs over all triangles once and the fourth sum runs over all "quatro" terms once.

The coefficients A consist of the electron annihilation and creation operators and various matrix elements involving bare potentials of the layer-substrate surface system [6, 7, 9]. Note that the Hamiltonian (1) has very interesting structure. With respect to the adion number operators N_α , it has the form of the Ising model with coefficients, which consist of the electron annihilation and creation operators. On the other hand, with respect to the electron operators, it represents the generalized Anderson-Newns model. Just because of the fact that this Hamiltonian contains in its structure the adion as well as the electron operators, we have possibility to calculate the coverage rate on the same level with the electronic characteristics.

For calculation of the coverage rate (adsorption isotherms) we shall use very simple model Hamiltonian for which most of calculations can be done without any approximations. At the same time, this Hamiltonian contains most important terms describing the adsorbed adatoms on the metal surface. Such Hamiltonian can be written as follows:

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

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, $a_{k \sigma}$, $a_{\alpha \sigma}$ ($a_{k \sigma}^{\dagger}$, $a_{\alpha \sigma}^{\dagger}$) are the substrate and adatom electron annihilation (creation) operators, respectively. The parameters ε , $\varepsilon_{\alpha \beta}$, ε_k , ε_{α} and U denote effective on-site adion binding energy, pairwise interaction energy between adions located at adsorption α and β sites, energy of the one-electron states of the substrate metal, 1-s adatom's electron orbital energy 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 , respectively, and ν is the energy of the electron localized at the empty (vacancy) adsorption center. Such term must be included if one wants to use the standard equation of motion formalism for appropriate GFs (see [6] for details). At the end of the calculations one puts $\nu = \infty$ in order to exclude contributions from such non-physical 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.

The first two terms in (2) can be identified with common used lattice gas model and the next three terms represent the simplest version of the Anderson-Newns Hamiltonian generalized to nonzero coverages [6]. We do not consider here the terms corresponding to the mixing of adatom and substrate electrons. These terms can be, in principle, treated in some approximate manner, but it would be awfully complicated to solve the resulting equation for isotherms. As we do not

perform calculations for well defined adsorption system and our goal is merely to check the general possibility of the adsorption isotherm's calculation together with the electronic characteristics, we hope that our choice of the model Hamiltonian can be justified. In addition, one should remember that the parameter ε_α is an effective one and the information about mixing of substrate and adatom electrons is, to some extent, contained in it. The parameter ε_α is as follows [6, 7]:

$$\varepsilon_\alpha = V_{\alpha\alpha}(\alpha) + A^{-2} \sum_{\beta,\gamma} S_{\alpha\beta}^* S_{\alpha\gamma} D_{\beta\gamma}, \quad (3)$$

where

$$D_{\alpha\beta} = \langle \alpha | \beta \rangle \epsilon - W_{\alpha\beta}(\beta) - \sum_k \langle \alpha | k \rangle \varepsilon_k | \beta \rangle,$$

$$W_{\alpha\beta}(\beta) = \int dx \phi_\alpha^*(x) \phi_\beta(x) V(R_\beta - x), \quad V(x) = e^2/|x|.$$

Here, $|k\rangle$ and $\phi_\alpha(x) \equiv |\alpha\rangle$ are the substrate's electron wave function and the adatom's valence orbital, respectively, and ϵ is the isolated adatom's electron ionization level. The coefficient A and matrix S are introduced to take into account the nonorthogonality between adatom valence orbitals localized on different adsorption centers and between adatom's valence orbital and substrate electron wave functions [6, 7]. As one can see, the parameter ε_α , which is usually interpreted as the effective $1s$ -level or ionization potential of the adatom, has very complicated structure and depends also on the substrate electron system. Thus, although the adatom-substrate interaction term is absent in explicit form in this Hamiltonian, this does not mean that this interaction is missing in our model. It enters, to some extent, through the parameter ε_α .

3. Adsorption isotherms

Many properties of the considered system can be calculated from the knowledge of appropriate retarded, double-time Green's functions. In our case, in order to obtain the adsorption isotherm, i.e. the dependence of the coverage rate on pressure of the gaseous adsorbate phase, we need to calculate the correlation function $\langle C_\alpha^+ C_\alpha \rangle$. This function can be expressed in terms of GF $\langle\langle C_\alpha(t) | C_\alpha^+(t') \rangle\rangle$ defined as follows [10]:

$$\langle\langle C_\alpha(t) | C_\alpha^+(t') \rangle\rangle = -\theta(t - t') \{ \{ C_\alpha(t), C_\alpha(t')^+ \} \} \quad (4)$$

within usually used notation. The formalism we used here to calculate GF (4) is the equation of motion method. As usually, equation of motion for a given GF will produce higher order GFs. For these new GFs we may again construct equation of motion and continuing further this procedure, we obtain an open chain of coupled equation for GFs of increasing order. In our case, for the Fourier transforms of the appropriate GFs we obtain

$$(E + \tilde{\mu}_I) \langle\langle c_\alpha | c_\alpha^+ \rangle\rangle = \varepsilon_\alpha^e \sum_\sigma \langle\langle n_{\alpha\sigma} c_\alpha | c_\alpha^+ \rangle\rangle + \frac{1}{2} U \sum_\sigma \langle\langle n_{\alpha\sigma} n_{\alpha-\sigma} c_\alpha | c_\alpha^+ \rangle\rangle + \sum_\beta \varepsilon_{\alpha\beta} \langle\langle N_{\alpha\beta} c_\alpha | c_\alpha^+ \rangle\rangle, \quad (5)$$

$$(E + \tilde{\mu}_I - \varepsilon_\alpha^e) \langle\langle n_{\alpha\sigma} c_\alpha | c_\alpha^+ \rangle\rangle = \langle n_{\alpha\sigma} \rangle + (\varepsilon_\alpha^e + U) \langle\langle n_{\alpha\sigma} n_{\alpha-\sigma} c_\alpha | c_\alpha^+ \rangle\rangle + \sum_\beta \varepsilon_{\alpha\beta} \langle\langle N_\beta n_{\alpha\sigma} c_\alpha | c_\alpha^+ \rangle\rangle, \quad (6)$$

$$(E + \tilde{\mu}_I - 2\varepsilon_\alpha^e - U) \langle\langle n_{\alpha\sigma} n_{\alpha-\sigma} c_\alpha | c_\alpha^+ \rangle\rangle = \langle n_{\alpha\sigma} n_{\alpha-\sigma} \rangle + \sum_\beta \varepsilon_{\alpha\beta} \langle\langle N_\beta n_{\alpha\sigma} n_{\alpha-\sigma} c_\alpha | c_\alpha^+ \rangle\rangle, \quad (7)$$

where $\varepsilon_\alpha^e = \varepsilon_\alpha - \mu_e - \nu$ and $\tilde{\mu}_I = \mu_I - \varepsilon$. We are not going to continue this process writing down the next equations for higher-order GFs, but instead we introduce the following decoupling approximations (for $\beta \neq \alpha$):

$$\begin{aligned} \langle\langle N_\beta c_\alpha | c_\alpha^+ \rangle\rangle &\approx \langle N_\beta \rangle \langle\langle c_\alpha | c_\alpha^+ \rangle\rangle, \\ \langle\langle N_\beta n_{\alpha\sigma} c_\alpha | c_\alpha^+ \rangle\rangle &\approx \langle N_\beta \rangle \langle\langle n_{\alpha\sigma} c_\alpha | c_\alpha^+ \rangle\rangle, \\ \langle\langle N_\beta n_{\alpha-\sigma} n_{\alpha\sigma} c_\alpha | c_\alpha^+ \rangle\rangle &\approx \langle N_\beta \rangle \langle\langle n_{\alpha\sigma} n_{\alpha-\sigma} c_\alpha | c_\alpha^+ \rangle\rangle. \end{aligned} \quad (8)$$

This kind of the decoupling approximations means that we have neglected the possible correlated distribution of the adatoms on the substrate surface. As we are interested in the possibilities of the method presented here and we have neglected some details of real systems, then these decouplings should not introduce additional significant changes in the final result. Thus, from Eqs. (5)–(7) one obtains the adion GF in the form

$$\begin{aligned} \langle\langle c_\alpha | c_\alpha^+ \rangle\rangle &= \frac{1 - \sum_\sigma \langle n_{\alpha\sigma} \rangle + \langle n_{\alpha\uparrow} n_{\alpha\downarrow} \rangle}{E + \tilde{\mu}_I - J\theta} + \frac{\langle n_{\alpha\uparrow} n_{\alpha\downarrow} \rangle}{E + \tilde{\mu}_I - \varepsilon_\alpha^e - J\theta} \\ &+ \langle n_{\alpha\uparrow} n_{\alpha\downarrow} \rangle \left(\frac{1}{E + \tilde{\mu}_I - 2\varepsilon_\alpha^e - U - J\theta} - \frac{2}{E + \tilde{\mu}_I - \varepsilon_\alpha^e - J\theta} \right), \end{aligned} \quad (9)$$

where $J = \sum_{\beta}^{\alpha \neq \beta} \varepsilon_{\alpha\beta}$.

In the following we can calculate the electron correlation functions $\langle n_{\alpha\sigma} \rangle$ and $\langle n_{\alpha\sigma} n_{\alpha-\sigma} \rangle$ (needed in Eq. (9)) from the knowledge of GFs $\langle\langle a_{\alpha\sigma} | a_{\alpha\sigma}^+ \rangle\rangle$ and $\langle\langle n_{\alpha-\sigma} a_{\alpha\sigma} | a_{\alpha\sigma}^+ \rangle\rangle$, respectively. Again, writing down the equations of motion for these GFs, using Green's function spectral representation and taking the limit $\nu \rightarrow \infty$ we get the needed electron correlation functions in the form (cp. [6]) (these correlation functions are calculated exactly, as the corresponding set of equations for GFs is closed):

$$\begin{aligned} \langle n_{\alpha\sigma} \rangle &= \frac{\langle N_\alpha (1 - n_{\alpha-\sigma}) \rangle}{\exp[(\varepsilon_\alpha - \mu_e)/kT] + 1} + \frac{\langle N_\alpha n_{\alpha-\sigma} \rangle}{\exp[(\varepsilon_\alpha + U - \mu_e)/kT] + 1}, \\ \langle n_{\alpha\sigma} n_{\alpha-\sigma} \rangle &= \frac{\langle N_\alpha n_{\alpha-\sigma} \rangle}{\exp[(\varepsilon_\alpha + U - \mu_e)/kT] + 1}. \end{aligned} \quad (10)$$

Finally, using Eqs. (9) and (10) and Green's function spectral representation formula one can obtain the coverage $\theta \equiv \langle N_\alpha \rangle$ in the form

$$\theta = [1 + \exp(-\mu_I/kT) \exp[(\varepsilon + J\theta)/kT] L(\varepsilon_\alpha, U, \mu_e, T)]^{-1}, \quad (11)$$

where $L = \{1 + 2 \exp[(\mu_e - \varepsilon_\alpha)/kT] + \exp[2(\mu_e - \varepsilon_\alpha)/kT - U/kT]\}^{-1}$.

Equation (11) 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 the adsorption centers form a two-dimensional quadratic lattice on the substrate surface and $\varepsilon_{\alpha\beta} \neq 0 = \varepsilon_1$ for nearest neighbors only, then the adsorption isotherm takes the form

$$\theta/(1 - \theta) = \exp[(\mu_I + |\varepsilon|)/kT] \exp[\pm 4|\varepsilon_1|\theta/kT] L^{-1}, \quad (12)$$

where $\varepsilon < 0$ and $+/-$ corresponds to attractive/repulsive interactions between nearest neighbor adions. Note that if we neglect the electron contribution terms in the Hamiltonian (2) (the effective coefficients of (2) should be changed, of course), then the expression (12) takes the form of known Bragg-Williams adsorption isotherm.

4. Results and conclusions

In this section we give numerical results for the adsorption isotherms calculated according to Eq. (12). We are going to perform a thorough analysis of the influence of the electronic characteristics on the adsorption isotherms — it is described by the function L contained in Eq. (11). Note that the adsorption isotherms for phenomenological lattice gas model are given in terms of effective parameters describing the adsorbed adatoms on the metal surface. In this way such electronic parameters as for example the adatom ionization level or the hybridization matrix elements between metal and adatom electron states are “hidden” in effective parameters modeling that system. In lattice gas models a value of the nearest-neighbor adatom-adatom interaction (it can be positive as well as negative) is a result of many complicated processes. In our case, as we consider the adions and electrons separately, the corresponding parameters describing these interactions, i.e. $\varepsilon_{\alpha\beta}$, should be in principle positive. In this context a difficult problem of estimation of these parameters appears, as they should be different in comparison with those used in lattice gas models. On the other hand, as the Hamiltonian (2) does not contain all terms given in Eq. (1), then it should be considered as a model Hamiltonian and our parameters cannot be calculated according to their definitions [6, 9]. These parameters should be also considered as effective ones. However, our description is more exact in comparison with the lattice gas model, as it includes in explicit form the electron subsystem with its intrinsic parameters. For reasons mentioned above we have done the calculations for attractive, $\varepsilon_{\alpha\beta} < 0$, as well as for repulsive, $\varepsilon_{\alpha\beta} > 0$, interactions between nearest-neighbor adions. The trivial dependence of the isotherms on the binding energy ε has been eliminated taking the plots θ vs. $(\mu_I + |\varepsilon|)/kT$ rather than μ_I/kT . Note that for any values of parameters entering into the function L the resulting adsorption isotherms are shifted towards the smaller values of $(\mu_I + |\varepsilon|)/kT$. It means that for given temperature and pressure of the gaseous adsorbate introduction of the term L into adsorption isotherm formula leads to the increase in the

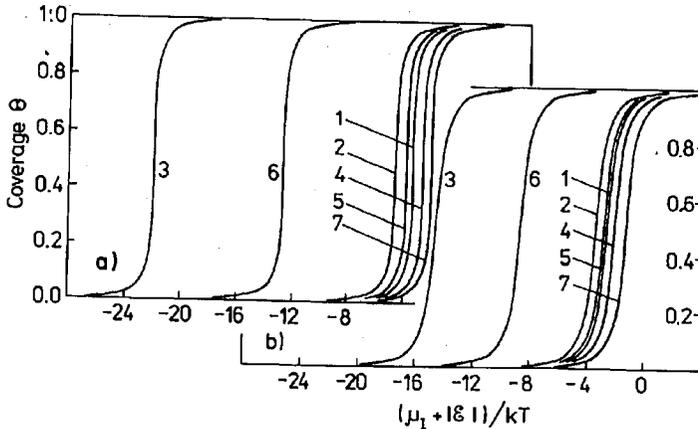


Fig. 1. The adsorption isotherms for $\varepsilon_1 < 0$. The curves no. 1, 2, 3, 4, 5, 6 and 7 correspond to η equal to (0, 0), (0, 1), (0, 10), (0, -1), (2, 1), (20, 10) and (0, -10), respectively. The lattice gas isotherm coincides with curve no. 7. The upper (lower) panel corresponds to $kT/|\varepsilon_1| = 1$ (1.5).

coverage. The value of this shift Δ — on $(\theta, (\mu_I + |\varepsilon|)/kT)$ plane — defined as follows:

$$\Delta = \ln\{1 + 2 \exp[(E_F - \varepsilon_\alpha)/kT] + \exp[2(E_F - \varepsilon_\alpha)/kT - U/kT]\}, \quad (13)$$

changes within limits $0 \leq \Delta \leq \infty$.

Let us consider the case of $U = 0$. For $E_F - \varepsilon_\alpha > 0$ (the effective adatom's ionization level is moving down) the shift Δ strongly increases — the isotherms are shifted to the left. For $E_F - \varepsilon_\alpha = |\varepsilon_1|$ and the temperature, say, $T = 480$ K, this shift equals to 2.6, but for $E_F - \varepsilon_\alpha = 10|\varepsilon_1|$ it increases to 20. Thus, for $\varepsilon_\alpha < E_F$ the localization of the isotherms on $(\theta, (\mu_I + |\varepsilon|)/kT)$ plane is very sensitive on the localization of the effective adatom's ionization level relative to the Fermi energy. In contrary, if ε_α moves up ($\varepsilon_\alpha \geq E_F$), then Δ equals to $\ln 4$ for $\varepsilon_\alpha = E_F$ and vanishes for $\varepsilon_\alpha - E_F = \infty$. In this latter case the isotherm coincides with that obtained within lattice gas models. The above statements are illustrated in Fig. 1. It corresponds to the case of the attractive effective adion-adion nearest-neighbor interactions for the temperature $kT = |\varepsilon_1|$ — the left panel, and for $kT = 1.5|\varepsilon_1|$ — the right panel. The curves numbered 1, 2, 3, 4 and 7 correspond to $U = 0$ and $(E_F - \varepsilon_\alpha)/|\varepsilon_1| \equiv \xi = 0, 1, 10, -1$ and -10 , respectively. The curves 5 and 6 are calculated for symmetric model, $2(E_F - \varepsilon_\alpha) = U$, for $\xi = 1$ and 10, respectively. We can observe a fast increasing shift of isotherms towards the lower values of pressure with increasing values of the difference between E_F and ε_α ($\varepsilon_\alpha < E_F$) and this shift is greater for lower than for higher temperatures. Let us consider, for example, the isotherms no. 1 and no. 3. The first curve is calculated for $E_F = \varepsilon_\alpha$ and the next one for $E_F - \varepsilon_\alpha = 10|\varepsilon_1|$, respectively. The value of the gaseous adsorbate pressure needed for monolayer coverage of the substrate surface is much smaller for the second case than for the first one. On the other hand, the localization of ε_α above the Fermi level has a very small influence on the

isotherms. Already for $\varepsilon_\alpha - E_F = 10|\varepsilon_1|$ the isotherms achieve their asymptotic forms and coincide with the lattice gas adsorption isotherm — curve no. 7. In order to observe the influence of nonvanishing U , let us compare the isotherm no. 2 with no. 5 and isotherm no. 3 with no. 6, respectively. The isotherms no. 2 and 3 are calculated for $U = 0$ and $\xi = 1$ and 10, respectively. The isotherm no. 5 is obtained for $U = 2|\varepsilon_1|$, $\xi = 1$ and isotherm no. 6 for $U = 20|\varepsilon_1|$ and $\xi = 10$. Generally, the nonvanishing electron–electron interaction causes a shift of the adsorption isotherms towards higher pressures.

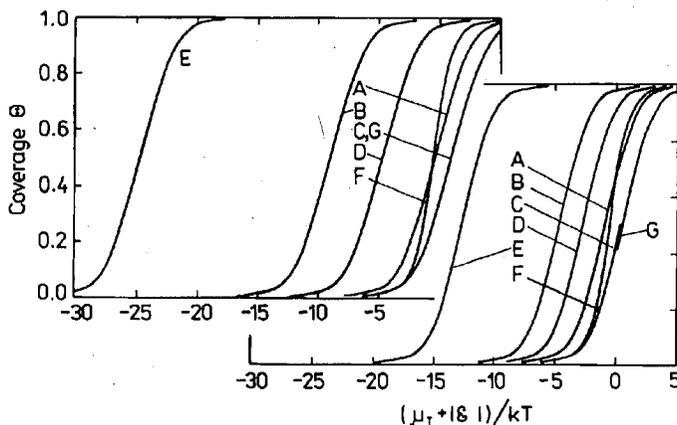


Fig. 2. The adsorption isotherms for $\varepsilon_1 > 0$. The curves A, B, C, D and E correspond to η equal to (0, 0), (0, 10), (0, -10), (20, 10) and (100, 50), respectively; F denotes the lattice gas isotherm. The upper (lower) panel corresponds to $kT/|\varepsilon_1| = 2$ (4). The curve G denotes the lattice gas isotherm for $\varepsilon < 0$ and $kT/|\varepsilon_1| = 4$.

In Fig. 2 we present the isotherms calculated for repulsive adion–adion interaction for $kT = 2|\varepsilon_1|$ — the upper panel and for $kT = 4|\varepsilon_1|$ — the lower panel. For comparison, the isotherm denoted by F was obtained for attractive adion–adion interaction for $kT = 4|\varepsilon_1|$. We observe similar distribution of isotherms along the $(\mu_I + |\varepsilon|)/kT$ axis, although their slope is greater now in comparison with attractive adion–adion case.

Figure 3 illustrates more detailed comparison of isotherms calculated for different nonzero values of U and for attractive adion–adion interaction. The curves denoted by letters A, B and C correspond to the isotherms calculated for $kT = 1$, 1.25 and 1.5 (in units of $|\varepsilon_1|$), respectively. The panel a shows isotherms calculated for $(U/|\varepsilon_1|, (E_F - \varepsilon_\alpha)/|\varepsilon_1|) \equiv \eta$ equal to (0, 10), the panel b for $\eta = (20, 10)$ and panel c for $\eta = (2, 1)$, respectively.

Figure 4 contains the isotherms calculated for $\varepsilon_1 > 0$ and the parameter η for panels a, b and c is the same as in Fig. 3. The curves A, B, C, D and E correspond to the temperature $kT/|\varepsilon_1|$ equal to 0.5, 0.75, 1.0, 1.25 and 1.5, respectively. It is clear, for example, from panels a and b that the nonvanishing values of U cause shifts of the isotherms to higher values of pressure and these

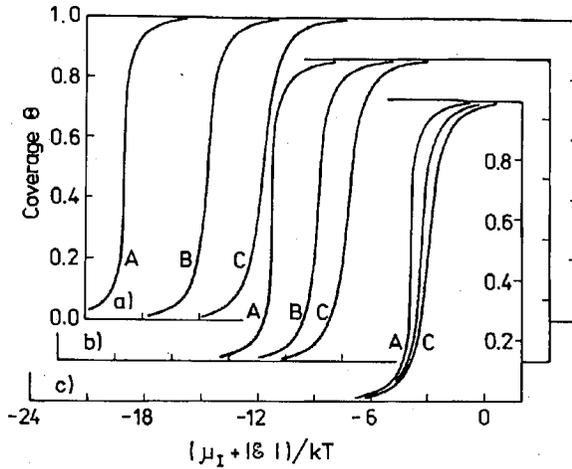


Fig. 3. The adsorption isotherms for $\epsilon_1 > 0$. The curves A, B and C correspond to $kT/|\epsilon_1| = 1, 1.25$ and 1.5 , respectively. The panels a, b and c correspond to η equal to $(0, 10)$, $(20, 10)$ and $(2, 1)$ respectively.

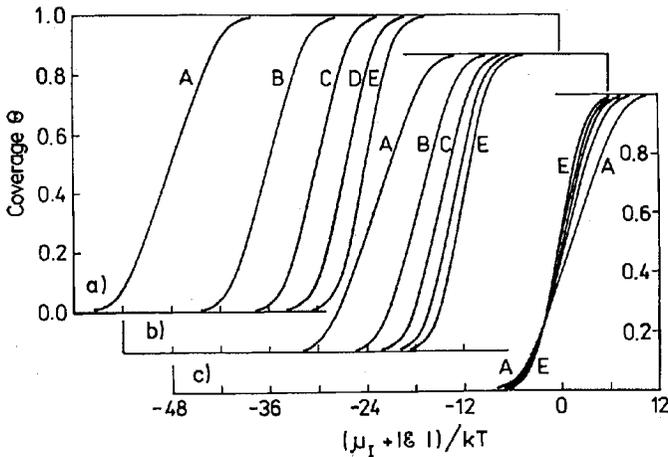


Fig. 4. The adsorption isotherms for $\epsilon_1 > 0$. The curves A, B, C, D and E correspond to $kT/|\epsilon_1| = 0.5, 0.75, 1, 1.25$ and 1.5 , respectively. The panels a, b and c correspond to η equal to $(0, 10)$, $(20, 10)$ and $(2, 1)$, respectively.

shifts decrease with increasing temperature. In the panel c we show the case when the isotherms calculated for different temperatures intersect themselves in one point. Below this point, for a given value of pressure, the coverage increases with decreasing temperature, and above this point the sequence of isotherms with decreasing temperature is changed. Now, for a given pressure the coverage increases with increasing temperature. To analyze this effect in some details we present the isotherms for different temperatures and values of $E_F - \epsilon_\alpha$ in Fig. 5 (for repulsive

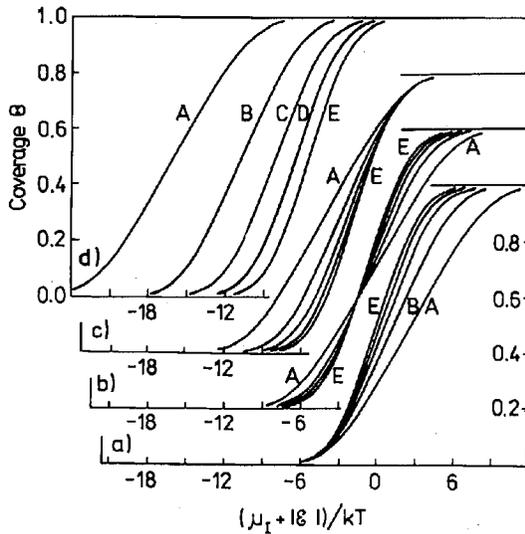


Fig. 5. The adsorption isotherms for $\varepsilon_1 > 0$ and $U = 0$. The panels *a*, *b*, *c* and *d* correspond to ξ equal to 0, 1, 2 and 5, respectively. The curves *A*, *B*, *C*, *D* and *E* are calculated for different temperatures as in Fig. 4.

adion–adion interaction and $U = 0$). In top panel, for low lying adsorbate's effective ionization level, $E_F - \varepsilon_\alpha = 5|\varepsilon_\alpha|$, the sequence of isotherms agrees with the lattice gas model predictions, i.e. for a given pressure the coverage rate increases with decreasing temperature. The panel *c*, *b* and *a* represent the same isotherms for decreasing values of $(E_F - \varepsilon_\alpha)/|\varepsilon_1|$ equal to 2, 1 and 0, respectively. In the case when the Fermi energy equals to the adatom's effective ionization level, we obtain a different picture of the chemisorption process in comparison with the lattice gas model predictions. We conclude that the degree of inverse arrangement of the isotherms on $(\theta, (\mu_I + |\varepsilon|)/kT)$ plane increases with decreasing displacement of the effective adatom's ionization level from the Fermi level.

Analyzing the results of the numerical calculations for isotherms and trying to compare them with real systems one has to remember the relatively simply model we have used here. Therefore, it is probably too early to make any comparison with experiment. Here we want to emphasize only that there is a possibility of simultaneous calculations of the electronic properties, e.g. $\langle n_{\alpha\sigma} \rangle$, and ionic properties, e.g. $\langle N_\alpha \rangle \equiv \theta$, in a self-consistent approach. The used model is characterized by the parameters describing the electronic structure of the adatom as well as of the substrate metal. In this way the isotherm's equation contains more information about the described system in comparison with the standard lattice gas model.

In conclusion, we have obtained the adsorption isotherm in the model which includes the electron subsystem in explicit way. The coverage rate was calculated on the same level as the adatom's electronic characteristics in a self-consistent way. The adsorption isotherms were obtained for different positions of the adsorbate's ionization level as well as for different values of the intra-adatom's electron–electron

Coulomb interaction. All these isotherms were investigated for different temperatures. We find that isotherms strongly depend on the position of the effective adsorbate's ionization level relative to the Fermi level. In some circumstances it leads to results different from those obtained within standard lattice gas model. It seems, however, that before any comparisons with real definite systems one has to include in explicit way the hybridization term describing the hops of electrons between adatoms and substrate surface (and vice versa). Such improvement of the present theory is now under investigation.

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References

- [1] T. Einstein, D. Hertz, J. Schrieffer, in: *Theory of Chemisorption*, Ed. J.R. Smith, Springer, Berlin 1980.
- [2] K. Christman, *Surf. Sci. Rep.* **9**, 1 (1980).
- [3] D.M. Newns, *Phys. Rev.* **178**, 1123 (1969); W. Brenig, K. Schönhammer, *Z. Phys. B* **267**, 201 (1974); G. Doyen, G. Ertl, *Surf. Sci.* **65**, 641 (1977); J. Rubio, M.C. Refalio, M.P. Lopez Sancho, J.H. Lopez Sancho, *Phys. Rev. B* **38**, 3142 (1988).
- [4] J. Kudrnovsky, B. Velicky, *Czech. J. Phys. B* **35**, 1017, 1179 (1985); G.M. Gavrilenko, R. Cardenas, V.K. Fedyanin, *Surf. Sci.* **217**, 468 (1988); R. Taranko, R. Cardenas, E. Taranko, V.K. Fedyanin, *Surf. Sci.* **238**, 293 (1990).
- [5] H. Ishida, K. Terakura, *Phys. Rev. B* **36**, 4510 (1987); H. Ishida, *Phys. Rev. B* **38**, 8006 (1988); *Phys. Rev. B* **39**, 5492 (1989).
- [6] G.M. Gavrilenko, *Physica A* **150**, 137 (1988).
- [7] G.M. Gavrilenko, R. Taranko, E. Taranko, V.K. Fedyanin, *Surf. Sci.* **203**, 212 (1988).
- [8] Y.K. Tovbin, V.K. Fedyanin, *Kinetika Kataliz* **19**, 989 (1978) (in Russian); K. Binder, D.P. Landau, *Surf. Sci.* **108**, 503 (1981); S. Sircar, A.L. Myers, *Surf. Sci.* **205**, 353 (1988); H.J. Kreuzer, Jun Zhang, *Appl. Phys. A* **51**, 183 (1990); K. Kitani, H. Kobayashi, A. Yoshimori, *Surf. Sci.* **253**, 405 (1991); G. Wiatrowski, J.C. Le Bossé, J. Lopez, J. Rousseau, I. Zasada, *Acta Phys. Pol. A* **83**, 587 (1993); M.A. Zaluska-Kotur, *Surf. Sci.* **165**, 196 (1992).
- [9] E. Taranko, R. Taranko, *Int. J. Mod. Phys. B* **8**, 1893 (1994).
- [10] D.N. Zubarev, *Usp. Fiz. Nauk* **71**, 71 (1960) (in Russian).