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Generalized Lattice Gas Model
in Adsorbed Surface Layer Investigations

Uogólniony model gazu sieciowego w badaniach zaadsorbowanych warstw
powierzchniowych

1. INTRODUCTION

The adsorption of hydrogen or hydrogen-like atoms on surfaces of transition metals at low (submonolayer) coverages has been subject of many studies (see, e.g. [1]). Many numerical calculations have been done using, for example, the density functional formalism [2] or cluster methods [3]. Although these approaches seem to be successful in describing the individual cases, model calculations are still useful. Usually, to describe the chemisorption phenomenon the model Anderson hamiltonian has been used. This model introduced for description of the local moment formation on magnetic impurities in a bulk nonmagnetic host [4] was adopted by N e w n s [5] in the chemisorption theory. On the other hand, for modelling of chemisorbed or physisorbed monolayers on substrate surfaces, in order to overcome the difficulties of the analytical treatments of many-body problems and give a more deeper interpretation of the adsorption isotherms or phase diagrams, the lattice gas model or appropriately transformed Ising model are widely used. These two classes of model hamiltonians differ considerably between themselves. The Anderson-Newns model is constructed on the basis of the substrate and adatom electron annihilation and creation operators with the

coefficients having appropriate meaning, for example, the substrate electron energy band dispersion, the adatom ionization level or the hybrydization matrix elements between the valence adatom orbitals and electron wave functions of a pure substrate metal. On the other hand, the lattice gas models are used to describe the behaviour of the adatoms on the substrate surface. Usually, they are constructed from the adatom number operators with coefficients describing the effective interaction of these adatoms with the substrate surface or between themselves.

So, these two classes of model hamiltonians, the Anderson-type and Ising-type, describe the physics of the surface phenomena in terms of different operators. Therefore, if we calculate the adsorption isotherms using the lattice gas model, as it is usually done, then the resulting isotherms, irrespective of the approximations used, are expressed in terms of the parameters inherent in this model. In other words, the resulting isotherms depend on the effective interactions between adatoms and substrate surface and effective parameters describing the interaction between two, three or more adatoms (so-called lattice-gas models with non-additive lateral interactions). In this way, such electronic parameters, as for example, the adatom ionization level or other are "hidden" in the effective parameters of the lattice gas model.

In this paper we make an attempt to obtain the adsorption isotherm in the form in which the parameters describing the electron subsystem enter in an explicit way. To this end, we use the model hamiltonian, recently introduced in [6]. This hamiltonian has an unusual structure. With respect to adatom (adion) number operators it has the form of the Ising model with the operator coefficients consisting of the electron creation, annihilation and number operators. With respect to electron operators it has the structure of the Anderson model but with coefficients being the adatom (adion) number operators. In general, similar in structure hamiltonians are widely used in the solid state theory. We remark only the model hamiltonians describing the spin-phonon or electron-phonon interactions (see, e.g. [7, 8]).

The model hamiltonian we shall use in adsorption isotherm calculations is very well suited for such kind of calculations. It is constructed from the electron and adion operators. The adsorption isotherm θ (or the coverage) can be calculated as the correlation function $\langle N_\alpha \rangle$, where brackets denote the appropriate averaging. It is obvious now, that the adsorption isotherm calculated in this way will contain the parameters of the electron subsystem.

We want to emphasize that the adsorption isotherm calculations for Ising-type models are treated in the literature for a long time. However, only in the formalism presented in this paper it is possible to consider the

electron and adion subsystems on the same level. The calculated coverage is a result of the equilibrium between the gas phase and adsorbed layer, as well as, it depends on the adatom electron charge calculated simultaneously in a selfconsisting way.

The remainder of this paper is organized as follows. In Sec. 2 we define the model hamiltonian describing the adsorption on metal surfaces. In Sec. 3 we present the calculations of the appropriate Green's Functions needed to analyze the coverage dependence on the parameters of the model. The last section contains a brief discussion and resume of this work.

2. THE MODEL HAMILTONIAN

Recently, a very general model Hamiltonian intended to describe the system of adatoms localized on a metal surface was obtained [6]. 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 the 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. The quantization procedure takes into consideration this physical fact that the electrons cannot be localized at the empty (without adion) adsorption centre. In other words, the electrons may occupy the adsorption centre α only, if this centre is already occupied by the adatom ion. Therefore, for example, for the electron field creation operator the following form was accepted [6]:

$$\widehat{\psi}^+(X) = \sum_{\vec{k}\sigma} a^+_{\vec{k}\sigma} \varphi^\star_{\vec{k}\sigma}(X) + \sum_{\alpha\sigma} N_\alpha a^+_{\alpha\sigma} \Phi^\star_{\alpha\sigma}(X). \qquad (1)$$

Here $a^+_{\vec{k}\sigma}$, $a^+_{\alpha\sigma}$ denote the substrate and adatom electron creation operators for electrons in one-electron substrate state $(\vec{k}, \sigma)$ described by the function $\varphi_{\vec{k}\sigma}(X)$ and in the adatom electron state (α, σ) described by $\Phi_{\alpha\sigma}(X)$. Here, as usually, $X = \{\vec{r}, \kappa\}$, where κ is the spin variable. N_α is the adion number operator for the adsorption centre α and the summation over α is carried out over all (empty and filled) adsorption centers (for details see [6]). We consider only the case when there is no more than one adatom in each adsorption center and all effects connected with its migration and other degrees of freedom are neglected. Using such kind of the electron field operators one can obtain very general second quantization representation of

the initial model. In the resulting hamiltonian, among many terms there are terms corresponding to the Anderson-Newns model, although generalized to nonzero coverages [9].

In our recent work we have calculated the chemisorption isotherm for the model described by the hamiltonian [10]:

$$
\begin{aligned}
H &= \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} n_{\vec{k}\sigma} + \sum_{\alpha} \epsilon N_{\alpha} + \frac{1}{2} \sum_{\alpha\beta} \epsilon_{\alpha\beta} N_{\alpha} N_{\beta} + \sum_{\alpha\sigma} E_{\alpha} N_{\alpha} n_{\alpha\sigma} + \\
&+ \frac{U}{2} \sum_{\alpha\sigma} N_{\alpha} n_{\alpha\sigma} n_{\alpha-\sigma} - \\
&- \mu_e N_e - \mu_I N_I + \nu \sum_{\alpha\sigma} (1 - N_{\alpha}) n_{\alpha\sigma} \, .
\end{aligned}
\tag{2}
$$

Here $\epsilon, \epsilon_{\alpha\beta}$ are the parameters describing the binding of the adions with the surface and interaction between adions, respectively. The parameters concerning electron subsystem are as follows: $\epsilon_{\vec{k}}$ — the substrate electron energy band, ϵ_{α} — the adatom ionization level and U — the Coulomb interaction between two electrons localized on the adatom. The number operators $n_{\vec{k}\sigma}$ and $n_{\alpha\sigma}$ corresponds to the substrate and adatom electrons, respectively.

The chemical potentials for the electron and adion subsystem are denoted as μ_e and μ_I, respectively. In addition, the last term corresponds to the electron localized at the empty adsorption centre α. To exclude such un-physical state contributions one has put parameter ν equal to infinity in the final expressions for calculated correlation functions [6]. As one can see, we did not include into this hamiltonian the terms corresponding to the mixing of adatom an substrate electron. We have argued, that, to some extent, the coupling between adatom and substrate electron subsystems was introduced through the effective parameter E_{α} (it depends also on the substrate elec-tronic characteristics [6]). In addition, the chemical potential μ_e was kept as a constant, so the substrate electron subsystem was considered as some sort of the electron bath.

In this paper we are going to consider rather physisorbed than chemi-sorbed adlayer on the substrate surface. For that reason we do not keep the chemical potential μ_e as a constant — it has to be calculated in a selfcon-sisting way with an increasing coverage. The model hamiltonian taken for further considerations reads:

$$H = \sum_{\alpha} \epsilon N_{\alpha} + \sum_{\alpha\beta} \epsilon_{\alpha\beta} N_{\alpha} N_{\beta} + \sum_{\alpha\sigma} E_{\alpha} N_{\alpha} n_{\alpha\sigma} + \frac{U}{2} \sum_{\alpha\sigma} N_{\alpha} n_{\alpha\sigma} n_{\alpha-\sigma} +$$

$$+ \frac{1}{2} \sum_{\alpha\beta\sigma\tau} \omega_{\alpha\beta} N_{\alpha} N_{\beta} n_{\alpha\sigma} n_{\alpha\tau} + \sum_{\alpha\beta\sigma} \Omega_{\alpha\beta} N_{\alpha} N_{\beta} n_{\alpha\sigma} + \tag{3}$$

$$+ \nu \sum_{\alpha\sigma} (1 - N_{\alpha}) n_{\alpha\sigma} - \mu_e \sum_{\alpha\sigma} N_{\alpha} n_{\alpha\sigma} - \mu_I \sum_{\alpha} N_{\alpha} \, .$$

The fifth and sixth terms correspond to the electron-electron interaction (electrons are localized on adions at neighbouring adsorption sites) and to the electron (at site α) — adion (at the neighbouring site β) interaction.

The first two terms can be identified with commonly used lattice gas model and the next terms represent the Anderson-Newns hamiltonian generalized to nonzero coverages supplemented with terms usually not considered in simple treatments of the adsorption phenomena. This form of the hamiltonian can be extracted from the general one obtainted within generalized second quantization procedure given in [6]. We believe that for the description of the adsorbed adlayer the terms given in (3) are most important and other contributions could be taken into consideration through the appropriate parametrization of this model.

3. THE ADSORPTION ISOTHERM CALCULATIONS

The adsorption isotherm can be obtained from the knowledge of the $\langle N_{\alpha} \rangle \equiv \langle C_{\alpha}^{+} C_{\alpha} \rangle$ correlation function. This correlation function can be given in terms of the retarded, double-time Green's Function (GF) $\ll C_{\alpha}(t) | C_{\alpha}^{+}(t') \gg$ defined as follows:

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

within usually used notation. Here $C_{\alpha}(C_{\alpha}^{+})$ represents the annihilation (creation) operator for the adion in the adsorption centre α. For calculations of $\langle N_{\alpha} \rangle$ we will follow along the equation of motion method. As usually, the equation of motion for a given GF will produce higher-order GFs. This approach gives the open chain of coupled equations for GFs of increasing order and some decoupling procedures will be needed. Here we do not give the explicit form of the corresponding equation of motion for all GFs present in our calculations, we rather give only the information about higher order

GFs which enter into equation for a given GF. Next, we present decoupling procedure we have used to simplify the calculations.

The equation for time Fourier transform of GF (4) $\ll C_\alpha | C_\alpha^+ \gg$ introduces the following higher order GF:

$$\ll C_\alpha | C_\alpha^+ \gg \Longrightarrow \ll n_{\alpha\sigma} C_\alpha | C_\alpha^+ \gg, \ll n_{\alpha\sigma} n_{\alpha-\sigma} C_\alpha | C_\alpha^+ \gg,$$

$$\ll N_\beta C_\alpha | C_\alpha^+ \gg, \ll N_\beta n_{\beta\sigma} n_{\alpha\sigma} C_\alpha | C_\alpha^+ \gg . \tag{5}$$

Similarly, for new GFs we have

$$\ll n_{\alpha\sigma} C_\alpha | C_\alpha^+ \gg \Longrightarrow \ll n_{\alpha\sigma} n_{\alpha-\sigma} C_\alpha | C_\alpha^+ \gg,$$

$$\ll N_\beta n_{\alpha\sigma} C_\alpha | C_\alpha^+ \gg, \tag{6}$$
$$\ll N_\beta n_{\beta\sigma} n_{\alpha\sigma} C_\alpha | C_\alpha^+ \gg,$$
$$\ll N_\beta n_{\beta\sigma} n_{\alpha\sigma} n_{\alpha-\sigma} C_\alpha | C_\alpha^+ \gg .$$

$$\ll n_{\alpha\sigma} n_{\alpha-\sigma} C_\alpha | C_\alpha^+ \gg \Longrightarrow \ll N_\beta n_{\beta\sigma} n_{\alpha\sigma} n_{\alpha-\sigma} C_\alpha | C_\alpha^+ \gg . \tag{7}$$

In Eqs. (5–7) the indices α, β represent the nearest-neighbour adsorption sites.

In the following we have used the decoupling approximations:

$$\ll N_\beta C_\alpha | C_\alpha^+ \gg \simeq \langle N_\beta \rangle \ll C_\alpha | C_\alpha^+ \gg,$$

$$\ll N_\beta n_{\beta\sigma} n_{\alpha\sigma} C_{\alpha\sigma} | C_\alpha^+ \gg \to \frac{\langle N_\beta n_{\beta\sigma} \rangle}{\theta} \ll n_{\alpha\sigma} C_\alpha | C_\alpha^+ \gg,$$

$$\tag{8}$$

$$\ll N_\beta n_{\beta\sigma} n_{\alpha\sigma} n_{\alpha-\sigma}, C_\alpha | C_\alpha^+ \gg \to \frac{\langle N_\beta n_{\beta\sigma} \rangle}{\theta} \ll n_{\alpha\sigma} n_{\alpha-\sigma} C_\alpha | C_\alpha^+ \gg .$$

As the indices α and β do not coincide then such decoupling should work relatively good. Note, that more drastic decoupling $\ll N_\alpha n_{\alpha-\sigma} a_{\alpha\sigma} | a_{\alpha\sigma}^+ \gg \simeq$

$\frac{\langle N_\alpha n_{\alpha-\sigma}\rangle}{\theta} \ll N_\alpha a_{\alpha\sigma}|N_\alpha a_{\alpha\sigma}^+ \gg$ leads to sufficiently good Hartree-Fock result [11]. Solving Eqs. (5)–(7) and using Eq. (8) we can obtain $\ll C_\alpha|C_\alpha^+ \gg$ in the form:

$$
\begin{aligned}
\ll C_\alpha|C_\alpha^+ \gg \;=\; & (1-\langle n_{\alpha\uparrow}+n_{\alpha\downarrow}-n_{\alpha\uparrow}n_{\alpha\downarrow}\rangle)(E+\tilde{\mu}_I-J\theta-\tilde{\Omega})^{-1}+ \\
& +\;\langle n_{\alpha\uparrow}+n_{\alpha\downarrow}\rangle\Big[(E+\tilde{\mu}_I-\epsilon_\alpha^e-J\theta-D-\Omega\theta-\tilde{\Omega})^{-1}+ \\
& +\;\langle n_{\alpha\downarrow}n_{\alpha\uparrow}\rangle(E+\tilde{\mu}_I-2\epsilon_\alpha^e-U-J\theta-2D-2\Omega\theta-\tilde{\Omega})^{-1}- \\
& -\;2\langle n_{\alpha\downarrow}n_{\alpha\uparrow}\rangle(E+\tilde{\mu}_I-\epsilon_\alpha^e-J\theta-D-\Omega\theta-\tilde{\Omega})^{-1}\Big]\,,
\end{aligned}
\tag{9}
$$

where: $\bar{\mu}_J = \mu_J - \epsilon$, $\epsilon_\alpha^e = \epsilon_\alpha - \nu$, $\tilde{\Omega} = \Omega\langle n_{\alpha\uparrow}+n_{\alpha\downarrow}\rangle/\theta$, $D = d\langle n_{\alpha\uparrow}+n_{\alpha\downarrow}\rangle/\theta$, $\Omega = \sum_\alpha \Omega_{\alpha\beta}$, $d = \sum_\alpha \omega_{\alpha\beta}$, and the summation in Ω and d is performed over nearest neighbours of the adsorption site β.

Using the Green's Function spectral representation and taking the constant ν equal to infinity we obtain the correlation function $\langle N_\alpha\rangle \equiv \theta$ in the form:

$$
\begin{aligned}
\theta \;=\; & (1-\langle n_{\alpha\uparrow}+n_{\alpha\downarrow}-n_{\alpha\uparrow}n_{\alpha\downarrow}\rangle)\Big[1+\exp[\beta(-\bar{\mu}_I+J\theta+\tilde{\Omega})]\Big]^{-1}+ \\
& +\;\langle n_{\alpha\uparrow}+n_{\alpha\downarrow}-n_{\alpha\uparrow}n_{\alpha\downarrow}\rangle\,, \quad \text{where} \quad \beta = 1/kT\,.
\end{aligned}
\tag{10}
$$

In the following we should calculate the electron correlation functions $\langle n_{\alpha\sigma}\rangle$ and $\langle n_{\alpha\sigma}n_{\alpha-\sigma}\rangle$. These functions can be obtained from the knowledge of the GFs $\ll a_{\alpha\sigma}|a_{\alpha\sigma}^+ \gg$ and $\ll n_{\alpha-\sigma}a_{\alpha\sigma}|a_{\alpha\sigma}^+ \gg$, respectively. Again, the equation of motion for these GFs introduces new GFs $\ll N_\alpha a_{\alpha\sigma}|a_{\alpha\sigma}^+ \gg$, $\ll N_\beta n_{\beta\tau} N_\alpha a_{\alpha\sigma}|a_{\alpha\sigma}^+ \gg$ and $\ll N_\alpha n_{\alpha-\sigma}a_{\alpha\sigma}|a_{\alpha\sigma}^+ \gg$. Writing down the equation of motion for these higher order GFs one can close the chain of equations making the following decouplings (similar to these in Eq. (8):

$$
\ll N_\beta n_{\beta\tau} N_\alpha a_{\alpha\sigma}|a_{\alpha\sigma}^+ \gg \simeq \frac{\langle N_\beta n_{\beta\tau}\rangle}{\theta}\ll N_\alpha a_{\alpha\sigma}|a_{\alpha\sigma}^+ \gg,
$$

$$
\ll N_\beta n_{\beta\tau} N_\alpha n_{\alpha-\sigma}a_{\alpha\sigma}|a_{\alpha\sigma}^+ \gg \simeq \frac{\langle N_\beta n_{\beta\tau}\rangle}{\theta}\ll N_\alpha n_{\alpha-\sigma}a_{\alpha\sigma}|a_{\alpha\sigma}^+ \gg.
\tag{11}
$$

To this end, we have

$$
\langle n_{\alpha\sigma}\rangle = \frac{\theta - \langle N_\alpha n_{\alpha-\sigma}\rangle}{1 + \exp[\beta(\epsilon_\alpha - \mu_e + D + \theta\Omega)]} +
$$
$$
+ \frac{\langle N_\alpha n_{\alpha-\sigma}\rangle}{1 + \exp[\beta(\epsilon_\alpha - \mu_e + U + D + \Omega\theta)]}, \tag{12}
$$

$$
\langle n_{\alpha\uparrow} n_{\alpha\downarrow}\rangle = \frac{\langle N_\alpha n_{\alpha\downarrow}\rangle}{1 + \exp[\beta(\epsilon_\alpha - \mu_e + U + D + \Omega\theta)]}. \tag{13}
$$

Finally, the adsorption isotherm can be written in the form

$$
\theta = [1 + \exp[-\beta\tilde{\mu}_I] \exp[\beta(J\theta + \tilde{\Omega})]\mathcal{L}]^{-1}, \tag{14}
$$

where $\mathcal{L} = 1 - \langle n_\uparrow + n_\downarrow - n_\uparrow n_\downarrow\rangle/\theta$, $\langle N_\alpha n_{\alpha\sigma}\rangle = \langle n_{\alpha\sigma}\rangle = \langle n_{\alpha-\sigma}\rangle$ and we assume that $\langle n_{\alpha\sigma}\rangle$ does not depend on the adsorption center α.

The Eqs. (12), (13) and (14) represent the closed set of equations for the adsorption isotherm and should be solved in a selfconsistent manner together with the condition for the chemical potential μ_e:

$$
\sum_\alpha (\langle n_{\alpha\uparrow}\rangle + \langle n_{\alpha\downarrow}\rangle) = N_A = \theta \cdot N. \tag{15}
$$

Here, N_A and N denote the number of the adsorbed atoms and total number of the adsorption centers.

This condition simply says that the number of electrons in the adsorbed layer is equal to the number of adatoms, as each adsorbed atom introduces to layer one electron (we consider adsorption of the hydrogen or hydrogen-like atoms). Eq. (15) gives us:

$$
\mu_e = E_\alpha + \frac{U}{2} + d + \Omega. \tag{16}
$$

This result is similar to this one obtained in the case of the Hubbard model in atomic limit at half filling [12].

Solving Eqs. (12, 13, 15) and taking into account Eq. (16) we obtain for the adsorption isotherm

$$
\tilde{\mu}_I\beta = \ln\left(\frac{\theta}{1-\theta}\right) + \beta J\theta + \beta\Omega - \ln 2[1 + \exp(\beta U/2)]. \tag{17}
$$

As usually, the coupling to the gas phase can be achieved by its chemical potential μ_{Gas} equal to μ_I. As one can see, the first two terms corresponds to the Langmuir isotherm, and the first three terms to Bragg-Williams isotherm, respectively. We should note, that here the parameter J is not the same as in lattice gas models because now it corresponds to effective adion-adion rather than adatom-adatom interaction.

4. DISCUSSION AND CONCLUDING REMARKS

We have presented a simple method for evaluation of the adsorption isotherms. This method allows us to express the adsorption isotherm in terms of the parameters describing the electron subsystem. 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 too early to make any comparison with experiment. Here we want to emphasize only, that there is a possibility in adsorption isotherm calculations to take into account more information about adsorbing atoms than it is possible using the standard lattice gas model. However, a difficult problem of estimation of parameters entering in the final formula appears. As the hamiltonian (8) should be considered as effective one then its parameters cannot be calculated according to their definitions [6, 10] and should be taken as effective one, too. However, regardless of these difficulties and regardless of the parameter values taken for calculations we observe that the isotherms are always shifted towards lower values of $(\mu_I\beta)$ with comparison with the Bragg-Williams curves. Thus, for a given value of μ_I/kT and temperature T, the coverage θ increases with increasing value of the Coulomb interaction U and Ω.

In conclusion, we have presented calculations of the adsorption isotherms for generalized Anderson-Newns model in which the electron subsystem was taken into consideration in an explicit manner. It was possible because the model hamiltonian was constructed on the basis of the electron and adion operators. Then, the adion correlation function, e.g. the coverage $\theta = \langle N_\alpha \rangle$, as well as the electron correlation functions, e.g. $\langle n_{\alpha\sigma} \rangle$, were calculated simultaneously in the same selfconsisting manner. With increasing values of the Coulomb electron-electron (on the same adatom) interaction U and electron-adion interaction Ω (at neighbouring adsorption sites) the resulting adsorption isotherms are always, regardless of the parameters used, shifted towards lower values of μ_I/kT in comparison with Langmuir or Bragg-Wiliams isotherms.

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STRESZCZENIE

W ramach uogólnionego modelowego hamiltonianu Andersona-Isinga rozważono w niniejszym artykule adsorpcję atomów wodoropodobnych na substratach metalicznych. Przy wyprowadzeniu wyrażenia na izotermę adsorpcji wykorzystano podstawowe wielkości charakteryzujące podukład elektronowy. Stopień pokrycia i elektronowe funkcje korelacyjne zostały obliczone w sposób samouzgodniony. Otrzymano przesunięcie izoterm w kierunku mniejszych wartości potencjału chemicznego adsorbatu ze wzrostem wartości niektórych parametrów elektronowych układu.