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## Magnetic states in the surface dimer model for adsorption

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For the electrons of surface dimer formed by adsorbed particle and substrate atom effects of the intra- and interatomic Coulomb interactions are taken into account. Two cases are considered: adsorption of magnetic particle on nonmagnetic substrate and adsorption of nonmagnetic particle on magnetic substrate. Analytical expressions for the surface dimer magnetization are obtained for the regimes of weak and strong dimer — substrate coupling.

**Keywords:** adsorbate, substrate, occupation number, magnetization

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The solid-state approach to model description of adsorption reduces to the problem of interaction between the local state of an adsorbed atom and the continuum of substrate states [1,2]. We refer to this approach as the standard adsorption model (SAM). A more detailed description, the model of a surface dimer (MSD), was proposed in [3,4]. The adsorption system is presented in this model as a „sum“ of a surface molecule, which is formed by the adsorbed particle and the nearest surface atom, and the rest of the substrate. The cluster approach to adsorption is actually not a new one (see, e.g., [5–7]) and is limited to numerical calculations, while SAM and MSD provide an opportunity to obtain analytical expressions. The roughness of the obtained results is offset by the possibility to demonstrate fairly easily the mechanism of the studied phenomenon by identifying the parameters that govern certain characteristics of it. This is the goal set in the present study, which is aimed at determining the magnetization of a surface dimer upon adsorption of a magnetic atom on a nonmagnetic substrate (case A) and a nonmagnetic atom on a magnetic substrate (case B).

Let us consider a free dimer consisting of a magnetized particle and a surface nonmagnetic atom of the substrate (case A) that are characterized by single-electron levels with energies  $\varepsilon_a$  and  $\varepsilon_s$ . The Hamiltonian of a free dimer in the mean-field approximation takes the form

$$H_{dim}^0 = \sum_{\sigma} H_{dim}^{0\sigma},$$

$$H_{dim}^{0\sigma} = w_s \hat{n}_{s\sigma} + w_{a\sigma} \hat{n}_{a\sigma} - t(s_{\sigma}^{\dagger} a_{\sigma} + a_{\sigma}^{\dagger} s_{\sigma}) - U_a n_{a\uparrow} n_{a\downarrow} - G n_s n_a. \quad (1)$$

Here,  $U_a$  is the intraatomic Coulomb repulsion of electrons with opposite spins at the particle;  $G$  is the Coulomb repulsion of electrons of the particle and the substrate atom;  $t$  is the amplitude (energy) of electron transition between the particle and the surface atom;  $w_s = \varepsilon_s + G n_a$ ,

$w_{a\sigma} = \varepsilon_a + U_a n_{a-\sigma} + G n_s$ ;  $\hat{n}_{s\sigma} = s_{\sigma}^{\dagger} s_{\sigma}$  and  $\hat{n}_{a\sigma} = a_{\sigma}^{\dagger} a_{\sigma}$  are the occupation number operators for the atom and the particle;  $\sigma = (\uparrow, \downarrow)$  is the spin projection;  $s_{\sigma}^{\dagger}(s_{\sigma})$ ,  $a_{\sigma}^{\dagger}(a_{\sigma})$  are the creation (annihilation) operators;  $\hat{n}_{a(s)\sigma} = \sum_{\sigma} \hat{n}_{a(s)\sigma}$ ,  $n_{s(a)\sigma} = \langle \hat{n}_{s(a)\sigma} \rangle$ ,  $n_{s(a)} = \langle \hat{n}_{s(a)} \rangle$ ;  $\langle \dots \rangle$  is averaging over the ground state. The following Green's functions correspond to Hamiltonian  $H_{dim}^{0\sigma}$ :

$$G_{a(s)}^{0\sigma}(\omega) = g_{a(s)\sigma} [1 - g_{a\sigma}(\omega) g_s(\omega) t^2]^{-1}, \quad (2)$$

where

$$g_s^{-1}(\omega) = \omega - w_s + i0^+, \quad g_{a\sigma}^{-1}(\omega) = \omega - w_{a\sigma} + i0^+,$$

$\omega$  is the energy variable. Dimer levels defined by the poles of Green's functions (2) are  $\omega_{\sigma}^{\pm} = \bar{w}_{\sigma} \pm R_{\sigma}$ ,  $R_{\sigma} = \sqrt{\Delta_{\sigma}^2 + t^2}$ , where  $\bar{w}_{\sigma} = (w_{a\sigma} + w_s)/2$  and  $\Delta_{\sigma} = (w_{a\sigma} - w_s)/2$ .

Let us now take the substrate into account. It is easy to demonstrate, following [3,4], that the densities of states of an epitaxial dimer (epidimer)  $\rho_{\sigma}^{dim}(\omega)$  and of its components  $\rho_{a(s)\sigma}(\omega)$  in the limit of weak dimer–substrate coupling ( $\Gamma(\omega) \ll t$ ) may be presented as

$$\rho_{a(s)\sigma}(\omega) = D_{\sigma}^{\pm} \rho_{\sigma}^{\pm}(\omega) + D_{\sigma}^{\mp} \rho_{\sigma}^{\mp}(\omega),$$

$$\rho_{\sigma}^{dim}(\omega) = \rho_{\sigma}^{+}(\omega) + \rho_{\sigma}^{-}(\omega),$$

$$D_{\sigma}^{\pm} = (1 \pm \Delta_{\sigma}/R_{\sigma})/2,$$

$$\rho_{\sigma}^{\pm}(\omega) = \frac{1}{\pi} \frac{\Gamma(\omega)}{(\omega - \omega_{\sigma}^{\pm} - \Lambda(\omega))^2 + \Gamma^2(\omega)}. \quad (3)$$

Here,  $\Gamma(\omega) = \pi V^2 \rho_s(\omega)$  is the function of broadening of local dimer levels  $\omega_{\sigma}^{\pm}$ , while function  $\Lambda(\omega) = V^2 P \int_{-\infty}^{\infty} \rho_s(\omega') (\omega - \omega')^{-1} d\omega'$  defines the shift of these levels ( $\rho_s(\omega)$  is the density of states of the substrate,  $V$  is the matrix element of interaction of levels  $\omega_{\sigma}^{\pm}$  with the continuum of substrate states, and  $P$  denotes the principal

value). For further analysis, we need to specify the substrate by setting function  $\rho_s(\omega)$ .

Let us consider adsorption on an  $sp$  metal. Setting  $\rho_s(\omega) = \rho_m = \text{const}$  (Anderson model [1,2]), we find  $\Gamma(\omega) = \Gamma_m = \pi V^2 \rho_m$  and  $\Lambda(\omega) = \Lambda_m = 0$ . The densities of states of epidimer components  $\rho_{a(s)\sigma}^m(\omega)$  are then the sum of two Lorentzian profiles  $\rho_{m\sigma}^\pm(\omega) = \Gamma_m / \pi [(\omega - \omega_\sigma^\pm)^2 + \Gamma_m^2]$  with weight factors  $D_{m\sigma}^\pm$  [3,4]. At zero temperature, occupation numbers  $n_{m\sigma}^\pm = \int_{-\infty}^{\varepsilon_F} \rho_{m\sigma}^\pm(\omega) d\omega$  ( $\varepsilon_F$  is the Fermi level of the system). Thus,  $n_{m\sigma}^\pm = (1/\pi) \text{arccot}[(\omega_\sigma^\pm - \varepsilon_F)/\Gamma_m]$  [3,4]. Let us introduce epidimer occupation numbers  $n_{m\sigma}^{dim} = n_{m\sigma}^+ + n_{m\sigma}^-$ ,  $n_{m\sigma}^{dim} = \sum_{\sigma} n_{m\sigma}^{dim}$  and epidimer magnetization  $m_m^{dim} = n_{m\uparrow}^{dim} - n_{m\downarrow}^{dim}$  and determine the conditions under which  $m_m^{dim} \neq 0$ . Setting  $\varepsilon_s + \varepsilon_a + 2G + U_a/2 = 0$ ,  $n_a = n_{a\uparrow} + n_{a\downarrow}$ ,  $m_a = n_{a\uparrow} - n_{a\downarrow}$  and  $U_a^\pm = U_a(n_a - 1 \pm m_a)/2$ , we obtain

$$2\bar{w}_{\uparrow,\downarrow} = G(n_a + n_s - 2) + U_a^\mp,$$

$$2\Delta_{\uparrow,\downarrow} = \varepsilon_a - \varepsilon_s + G(n_s - n_a) + U_a^\mp.$$

If  $\varepsilon_F = 0$ , charge transfer between the epidimer and the substrate is lacking. Therefore,  $n_a + n_s = 2 = n_m^{dim}$ . Then  $2\bar{w}_{\uparrow,\downarrow} = U_a^\mp$  and  $2\Delta_{\uparrow,\downarrow} = \varepsilon_a - \varepsilon_s - 2G(n_a - 1) + U_a^\mp$ .

Let us consider the case when  $\omega_\sigma^- < 0$ ,  $\omega_\sigma^+ > 0$ , and  $|\omega_\sigma^\pm|/\Gamma_m \gg 1$ . Assuming that  $1 \gg |m_a| \neq 0$ , we then find the following as a first approximation in small parameter  $\Gamma_m/|\omega_\sigma^\pm|$ :

$$m_m^{dim}/m_a \approx \frac{U_a \Gamma_m}{\pi(t^2 + \Delta_{0a}^2 - \bar{w}_{0a}^2)} \left( 1 - \frac{2\Delta_{0a} \bar{w}_{0a}}{t^2 + \Delta_{0a}^2 - \bar{w}_{0a}^2} \right), \quad (4)$$

where  $\bar{w}_{0a}$  and  $\Delta_{0a}$  are equal to  $\bar{w}_{a\sigma}$  and  $\Delta_{a\sigma}$  at  $m_a = 0$ . At  $t^2 \gg \Delta_{0a}^2 - \bar{w}_{0a}^2$ , we have  $m_m^{dim}/m_a \approx U_a \Gamma_m / \pi t^2$ . Since  $U_a \sim t$  (see, e.g., [8,9]), we obtain  $m_m^{dim}/m_a \ll 1$ . The value of  $m_a$  is determined as

$$m_a = (1/\pi) [\text{arctg}(w_{a\downarrow}/\Gamma_m) - \text{arctg}(w_{a\uparrow}/\Gamma_m)], \quad (5)$$

where  $w_{a\uparrow,\downarrow} = U_a(n_a - 1 \mp m_a)/2 - G n_a - \varepsilon_s$ . Let us assume that  $|m_a| \ll 1$ . At  $|w_{a\sigma}|/\Gamma_m \gg 1$  and  $w_{a\uparrow} w_{a\downarrow} > 0$ , we find

$$m_a \approx (1/\pi) \text{arctg}(m_a \Gamma_m U_a / w_{0a}^2),$$

which suggests that the fulfillment of inequality  $\Gamma_m U_a / \pi w_{0a}^2 < 1$  is the condition of existence of a nonzero spin moment  $m_a$ . At  $|w_{a\sigma}|/\Gamma_m \ll 1$ , we find inequality  $\pi \Gamma_m / U_a < 1$ . The latter inequality matches the solution of the problem of a localized magnetic moment in a nonmagnetic metal (see, e.g., Fig. 4 in [10] or Fig. 18.3 in [11] at  $x = 0.5$ ); in other words, it agrees with the SAM results.

Let us pass on to the limit of strong coupling between a dimer and a metal  $sp$  substrate ( $\Gamma_m \gg t$ ). Generalizing the results of [4], we obtain the following in the zeroth approximation in  $t^2/\Gamma_m^2$  at  $\varepsilon_F = 0$ :

$$n_{a(s)\sigma} \approx (1/\pi) \text{arccot}(w_{a(s)\sigma}/\Gamma_m), \quad (6)$$

which corresponds to adsorption of a particle and a surface atom that do not interact with each other. Thus, we obtain  $m_m^{dim} \approx m_a$ , where  $m_a$  is determined using Eq. (5). Therefore, the dipole moment of a dimer ( $|m_m^{dim}|$ ) decreases from  $|m_m^{dim}/m_a| \sim 1$  to  $|m_m^{dim}/m_a| \ll 1$  as we switch from the regime of strong coupling to the regime of weak coupling between a dimer and a metallic substrate.

It has been known since the early studies of Friedel and Anderson [11,12], which formed the basis for SAM [1,2], that an  $sp$  metal suppresses the spin moment of an impurity atom. The obtained estimates suggest that this is also true in MSD. However, in contrast to SAM, MSD provides an opportunity to determine the induced magnetization of a surface substrate atom without any additional calculations. Unfortunately, these data on induced magnetization are lacking in studies into the adsorption of individual magnetic atoms [13–15] and monolayers [16] on a nonmagnetic substrate. Note that adsorbed trimers of magnetic atoms may act as nanomagnets [17].

Let us now consider case *B*: adsorption of a nonmagnetic particle on a magnetic transition metal (MTM). Expressions (1) and (2) for a free dimer remain valid in this case if we swap lower indices  $a$  and  $s$  of all parameters. We use the Friedel model for density of states  $\rho_{d\sigma}(\omega)$  of the  $d$  MTM band:  $\rho_{d\sigma}(\omega) = 5/W_d$  at  $|\omega - \omega_{d\sigma}| \leq W_d/2$  and 0 at  $|\omega - \omega_{d\sigma}| > W_d/2$ , where  $W_d$  is the width of the  $d$  band and  $\omega_{d\sigma}$  is the center of the subband for spin projection  $\sigma$ . Setting  $\Gamma_d = 5\pi V^2/W_d$ , one may demonstrate easily [18] that the shift function of levels  $\omega_\sigma^\pm$  is  $\Lambda_{d\sigma} = (\Gamma_d/\pi) \ln |f_+/f_-|$ , where  $f_\pm = \omega - \omega_{d\sigma} \pm W_d/2$ . Performing derivations similar to those made above, we find the following instead of occupation numbers  $n_{m\sigma}^\pm$  in the regime of weak coupling between a dimer and an MTM substrate ( $\Gamma_d \ll t$ ):

$$n_{d\sigma}^\pm = (1/\pi) \text{arccot}[(\tilde{\omega}_\sigma^\pm - \varepsilon_F)/\Gamma_d],$$

where  $\tilde{\omega}_\sigma^\pm = \omega_\sigma^\pm + \Lambda_{d\sigma}(\omega_\sigma^\pm)$ . The final result is expression (4) with ratio  $m_m^{dim}/m_s$  at the left-hand side and  $\Gamma_m$ ,  $U_a$ ,  $\bar{w}_{0a}$ , and  $\Delta_{0a}$  substituted with  $\Gamma_d$ ,  $U_s$ ,  $\bar{w}_{0s}$ , and  $\Delta_{0s}$ , respectively, at the right-hand side. Likewise, expression (6) with the same parameter substitutions is obtained in the regime of strong coupling ( $\Gamma_d \gg t$ ).

The effect of adsorption of hydrogen and oxygen on the magnetic properties of an iron monolayer on Ir(001) was studied in [19], and it was demonstrated that this effect is significant. Unfortunately, the issue of magnetization of H and O atoms induced by the substrate has not been discussed. Thus, just as in [13–17] (case A), the issue of induced magnetization was left out. This precludes one from comparing the results of such studies directly to the MSD results.

Thus, in the present study we took into account both the interatomic Coulomb repulsion, which facilitates interatomic charge transfer [4], and the intraatomic repulsion, which induces spin polarization of a surface dimer. The obtained results for metals may be generalized both to the case of

bulk semiconductor (dielectric) substrates [2] and to the case of two-dimensional graphene-like structures [3,4]. Of note in this connection is the growing interest in studies into the adsorption of magnetic atoms on graphene [20–22].

### Conflict of interest

The authors declare that they have no conflict of interest.

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