Surface Dimer Model in the Theory of Adsorption on Graphene

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Article history	Abstract
	Model of the surface dimer formed by coupling adsorbing atom and surface substrate atom by covalent bond is proposed. This model is used for the calculations of the charge transfers between dimer's atoms and between dimer and graphene substrate. Effects of Coulomb and electron-phonon interaction on charge transfers are thoroughly studied. Role of inter-adatoms dipole-dipole repulsion and exchange interactions are examined. Adsorption on epitaxial graphene is briefly discussed.

1. INTRODUCTION

Since the seminal publication [1] demonstrated that graphene can detect a single gas molecule, a great interest in the performance of graphene-based gas sensors [2–4] and biosensors [4–10] arose. To understand the mechanism of these sensors operation, corresponding theory is needed (see, for example, Refs. [11–14] and references therein). Most of the theoretical works in the field are first-principal numerical calculations, based on the different versions of the density functional theory (DFT). Here we concentrate on the model description of adsorption [15], based on the Anderson magnetic impurity Hamiltonian [16] and pioneering works [17–19]. As far as we know, the first model for the adsorption on single-layer free-standing graphene was put forward in Ref. [20]. The same approach to the adsorption on epitaxial graphene (epigraphene) is described in Ref. [21]. All these papers, which have been done in the scope of the standard adsorption model (SAM), ignore the geometry of adsorption complex. On the other hand, the alternative cluster models ignore band structures of substrates. The model that takes into account combination of both approaches, or surface dimer model (SDM), was originally proposed in Ref. [22]. It is the model that will be used below. The general aim of this paper is not to consider some specific cases of adsorption on graphene but to demonstrate (in the scape of SDM) how one can obtain analytical estimations of charge transfer due to the covalent intra-dimer covalent bond and Coulomb inter-action and electron-phonon coupling between dimer and substrate. Adsorption on an epitaxial graphene is also discussed.

2. MODEL OF SURFACE DIMER

In the work [22] all the space of the adsorbate–substrate system is divided into surface dimer (SD), consisting of an adsorbed particle (a) and the substrate surface atom (s) that is bound to it by a covalent bond, and the rest of the space. The corresponding Hamiltonian for the isolated (not connected with substrate) SD is

$$\bar{H}_{SD} = \varepsilon_a \hat{n}_a + \varepsilon_s \hat{n}_s - t(a^+ s + s^+ a). \qquad (1)$$

Here ε_a and ε_s are the energies of atoms a and s orbitals (each initially contains one electron) forming adsorption bond, $\hat{n}_a = a^+ a$ and $\hat{n}_s = s^+ s$ are the operators of occupation numbers for the substrate atom in the $|a\rangle$ state and adatom in the $|s\rangle$ state; $s^+(s)$ and $a^+(a)$ are the corresponding creation (annihilation) operators, t is the hopping energy between a and s atoms. The Green functions for the atoms a and s of the isolated SD has the form

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$$\overline{G}_{a,s}(\omega) = \frac{g_{a,s}(\omega)}{1 - g_a(\omega)g_s(\omega)t^2}, \tag{2}$$

where $g_{a,s}^{-1}(\omega) = \omega - \varepsilon_{a,s} + i0^+$ and ω is the energy variable. It was shown in Ref. [22] that the density of states (DOS) $\overline{\rho}_{a,s}(\omega)$ and occupation numbers $\overline{n}_{a,s}$ for isolated SD, corresponding to Green function (2), is

$$\overline{\rho}_{a,s}(\omega) = \overline{D}_{\pm}\delta(\omega - \omega_+) + \overline{D}_{\mp}\delta(\omega - \omega_-),$$

$$\overline{n}_{a,s} = 2[\overline{D}_{\pm}\theta(\omega - \omega_+) + \overline{D}_{\mp}\theta(\omega - \omega_-)]. \tag{3}$$

Here $\overline{D}_{\pm} = (1 \pm \overline{\Delta}/\overline{R})/2$, $\omega_{\pm} = \overline{\varepsilon} \pm \overline{R}$, $\overline{R} = \sqrt{\overline{\Delta}^2 + t^2}$, $\overline{\varepsilon} = (\varepsilon_a + \varepsilon_s)/2$, $\overline{\Delta} = (\varepsilon_a - \varepsilon_s)/2$, $\delta(...)$ is the Dirac delta function, $\theta(...)$ is the Heaviside function, ω_- (ω_+) is the energy of bonding (antibonding) state of the isolated SD. The resulting DOS of SD, interacting with substrate, can be written as

$$\rho_{a,s}(\omega) = \overline{D}_{\pm}\rho_+(\omega) + \overline{D}_{\mp}\rho_-(\omega), \quad \rho_{SD}(\omega) = \rho_+(\omega) + \rho_-(\omega),$$

$$\rho_{\pm}(\omega) = \frac{1}{\pi}\frac{\Gamma_{sub}(\omega)}{(\omega - \omega_{\pm} - \Lambda_{sub}(\omega))^2 + \Gamma_{sub}^2(\omega)}, \tag{4}$$

where $\Gamma_{sub}(\omega)$ and $\Lambda_{sub}(\omega)$ are half-width and shift of SD states, respectively, induced by substrate [22]. Since $\Gamma_{sub}(\omega) = \pi V^2 \rho_{sub}(\omega)$ ($\rho_{sub}(\omega)$ is the substrate DOS, V is the adsorbate–substrate coupling) and $\Lambda_{sub}(\omega)$ is the Hilbert transform of $\Gamma_{sub}(\omega)$, one has to define function $\rho_{sub}(\omega)$.

Now we turn to the adsorption on a free-standing single layer graphene (SLG) [23]. In low-energy approximation of SLG its DOS is

$$\rho_{Gr}(\Omega) = 2|\Omega_{Gr}|/\xi^2, \quad |\Omega_{Gr}| \le \xi, \tag{5}$$

where $\Omega_{Gr} = \omega - \varepsilon_D$, ε_D is the Dirac point ($\varepsilon_D = \varepsilon_s$), $\xi = t_{Gr}\sqrt{2\pi\sqrt{3}}$ is the cut-off energy [24]. SD DOS gives the following shift function [23]:

$$\Lambda_{Gr}(\Omega_{Gr}) = \frac{2V^2\Omega_{Gr}}{\xi^2}\ln\frac{\Omega_{Gr}^2}{|\xi^2 - \Omega_{Gr}^2|}. \tag{6}$$

Inserting Eq. (6) into (4) for a weak coupling regime $2\pi V^2/\xi^2 \ll 1$ we get approximately

$$\rho_{\pm}(\omega) \approx \frac{1}{\pi}\frac{\Gamma_{\pm}}{(\omega - \tilde{\omega}_{\pm})^2 + \Gamma_{\pm}^2}, \tag{7}$$

where $\tilde{\omega}_{\pm} = \omega_{\pm}L_{\pm}$, $L_{\pm} = 1 + (2V^2/\xi^2)\ln(\omega_{\pm}^2/|\xi^2 - \omega_{\pm}^2|)$, $\Gamma_{\pm} = 2\pi V^2|\omega_{\pm}|/\xi^2$. Then at zero temperature for the occupation numbers $n_{a,s} = 2\int_{-\xi}^{\varepsilon_F}\rho_{a,s}(\omega)d\omega$ and $n_{\pm} = 2\int_{-\xi}^{\varepsilon_F}\rho_{\pm}(\omega)d\omega$ we obtain

$$n_{SD} = n_a + n_s = n_+ + n_-, \quad n_{\pm} \approx \frac{2}{\pi}\text{arccot}\frac{\tilde{\omega}_{\pm} - \varepsilon_F}{\Gamma_{\pm}}, \tag{8}$$

where ε_F is the Fermi level and we put $\arctan[(\xi + \varepsilon_F)/\Gamma_{\pm}] = \pi/2$. Now we can estimate charge transfer effects. We may characterize the charge transfer between adatom and substrate as in SAM, by the value of the charge of adatom $Z_a = 1 - n_a$ or $Z_a = Z_+ + Z_-$, where $Z_{\pm} = 1 - \overline{D}_{\pm}n_{\pm}$. If $Z_a > 0$, adatom acts as a donor; if $Z_a < 0$, adatom acts as an acceptor. The specific SDM charge transfer characteristics are: the SD-substrate charge transfer $Z_{SD} = 2 - n_{SD}$ and the intra-SD charge transfer $\delta n_{dim} = n_a - n_s = (\overline{\Delta}/\overline{R})\delta n_{\pm}$, where $\delta n_{\pm} = n_+ - n_-$.

For the undoped SLG, when $\varepsilon_F = \varepsilon_D = 0$, we obtain

$$n_{SD} \approx 2 - Z_{SD}, \quad Z_{SD} \approx (4V^2/\xi^2)(L_-^{-1} - L_+^{-1}),$$

$$\delta n_{dim} \approx (\overline{\Delta}/\overline{R})[2 - (4V^2/\xi^2)(L_-^{-1} + L_+^{-1})], \tag{9}$$

where it was taken into account that $n_+ \approx 4V^2/\xi^2 L_+$ and $n_- \approx 2 - 4V^2/\xi^2 L_-$. Since $dL_{\pm}/d\overline{\Delta} = 4V^2\overline{\Delta}/\omega_{\pm}\overline{R}(\xi^2 - \omega_{\pm}^2)$, we find $\partial n_{SD}/\partial\overline{\Delta} = -\partial Z_{SD}/\partial\overline{\Delta} \sim V^4/\xi^4 \sim 0$ for $\omega_{\pm}^2 \ll \xi^2$ and $\partial\delta n_{dim}/\partial\overline{\Delta} \sim 2t^2/\overline{R}^3$. Further, since $dL_{\pm}/dt = 4V^2t/\omega_{\pm}\overline{R}(\xi^2 - \omega_{\pm}^2)$, we find $\partial n_{SD}/\partial\overline{\Delta} = -\partial Z_{SD}/\partial\overline{\Delta} \sim V^4/\xi^4 \sim 0$ for $\omega_{\pm}^2 \ll \xi^2$ and $\partial\delta n_{dim}/\partial\overline{\Delta} \sim 2t^2/\overline{R}^3$. Thus, only intra-SD charge transfer significantly depends on $\overline{\Delta}$. As to the dependences of charge transfer characteristics on V, they are clear from Eq. (9).

For the doped SLG, when $0 < |\varepsilon_F| \ll |\omega_{\pm}|$, we get $\delta n_{\pm} \approx -(4V^2/|\omega_{\pm}|\xi^2 L_{\pm}^2)\delta\varepsilon_F$. Rough numerical estimates for the parameters are: $t_{Gr} \sim 3$ eV and $\xi \sim 10$ eV; t is of the order or less than t_{Gr}; for a weak-coupling regime V has to be much less than 4 eV.

Above considerations have been fulfilled for a weak SD-substrate interaction. In the strong coupling regime $2\pi V^2/\xi^2 \gg 1$ it is easy to show that (for the zero order in $\xi^2/2\pi V^2$) the considered problem is reduced to the SAM result for two non-interacting adatoms a and s [16,17], characterized by the following DOS:

$$\rho_{a,s}^{SAM}(\omega) \approx \frac{1}{\pi}\frac{\Gamma_G(\omega)}{\Omega_{a,s}^2 + \Gamma_G^2(\omega)}, \tag{10}$$

where $\Omega_{a,s} = \omega - \varepsilon_{a,s} - \Lambda_G(\omega)$. Note that in general case SDM leads to higher occupation numbers than in the SAM [22].

The A-type (atop) of adsorption, where an adatom interacts with one substrate surface atom being directly above that atom, was considered here. It is not difficult, however, to generalize the obtained results to the B-type

(bridge) of adsorption, when the adatom interacts with two adjacent surface atoms that are closest to it, and the C-type (center) of adsorption, when the adatom is at the center of the surface unit cell [18].

3. EFFECT OF COULOMB INTERACTIONS ON CHARGE TRANSFER

Interest in elucidating the role of Coulomb interaction in the problem of adsorption arose simultaneously with the appearance of original Newns' model [16]. Here we consider Coulomb repulsion G between electrons of the adsorbed particle a and substrate atom s and determine how the account of this interaction influences charge transfer effects.

Consider a free SD [25], described by Hamiltonian

$$\bar{H}_{SD}^C = \varepsilon_a \hat{n}_a + \varepsilon_s \hat{n}_s - t(a^+ s + s^+ a) + G\hat{n}_a \hat{n}_s. \tag{11}$$

In the framework of the Hartree–Fock theory, Hamiltonian (11) can be expressed as follows:

$$\bar{H}_{SD}^C = w_a \hat{n}_a + w_s \hat{n}_s - t(a^+ s + s^+ a) - Gn_a n_s, \tag{12}$$

where $w_{a,s} = \varepsilon_{a,s} + Gn_{s,a}^C$, $n_{a,s}^C = \langle \hat{n}_{a,s} \rangle$ and $\langle ... \rangle$ denotes averaging over the ground state of Hamiltonian (11). Then instead of Eq. (2) we obtain

$$\bar{G}_{a,s}^C(\omega) = \frac{g_{a,s}^C(\omega)}{1 - g_a^C(\omega)g_s^C(\omega)t^2}, \tag{13}$$

where $g_{a,s}^C(\omega) = (\omega - w_{a,s} + i0^+)^{-1}$. Energy levels of the free SD defined by the $\bar{w} = (w_a + w_s)/2$, $\Delta_C = (w_a - w_s)/2$. Now DOS $\bar{\rho}_{a,s}^C(\omega)$ of the isolated SD is given by Eq. (2), where one has to put $\bar{w}$, R_C, $D_{\pm}^C$ instead of $\bar{\varepsilon}$, $\bar{R}$, $\bar{D}_{\pm}$; DOS $\rho_{a,s}^C(\omega)$ and $\rho_{\pm}^C(\omega)$ are defined by Eq. (3) for $\omega_{\pm}^C$ instead of $\omega_{\pm}$. Eqs. (7)–(9) are also valid with the replacement of $\omega_{\pm}$, $L_{\pm}$, $\Gamma_{\pm}$ on $\omega_{\pm}^C$, $L_{\pm}^C$, $\Gamma_{\pm}^C$. Note, that for $G \neq 0$ the occupation numbers $n_{a,s}^C$ and $n_{\pm}^C$ are self-consistent: $n_{a,s}^C = f(n_{s,a}^C)$ and $n_{\pm}^C = f'(n_{\mp}^C)$.

It is easy to obtain now that $\partial n_{SD}^C / \partial \Delta_C = -\partial Z_{SD}^C / \partial \Delta_C \sim V^4 / \xi^4 \sim 0$ for $(\omega_{\pm}^C)^2 << \xi^2$, $\partial \delta n_{dim}^C / \partial \Delta_C \sim 2t^2 / R_C^3$. Thus, as in Section 2, only intra-SD charge transfer significantly depends on G. It is easy to demonstrate, that the account of intra-SD adsorption system $\langle \bar{H}_{SD}^C \rangle \propto G(n_a^C + n_s^C) + Gn_a^C n_s^C$ for $n_a^C + n_s^C \approx 2$ decreases for $n_{a,s}^C << n_{s,a}^C$ compared with $n_{a,s}^C \sim n_{s,a}^C$. In accordance with Ref. [26], for the nearest carbon atoms in graphene $G \approx 8.5$ eV without screening or 5.5 eV with the account of screening. Since the interatomic distance in SD is of the

order or larger than 1.42 Å, G has to be of the order or smaller than these values.

In the strong coupling regime $2\pi V^2 / \xi^2 >> 1$ instead of Eq. (10) we have $\rho_{a,s}^C(\omega) \approx \Gamma_G(\omega) / \pi[(\Omega_{a,s}^C)^2 + \Gamma_G^2(\omega)]$, where $\Omega_{a,s}^C = \omega - w_{a,s} - \Lambda_G(\omega)$.

We can also take into account intra-atomic Coulomb repulsions U_a and U_s for electrons with opposite spins (see Ref. [16]). In a non-magnetic case and Hartree-Fock approximation this leads to the orbital energies $w_{a,s} = \varepsilon_{a,s} + Gn_{s,a}^C + U_{a,s}n_{a,s}^C / 2$. It can be shown that the account of intra-atomic Coulomb repulsion prevents intra-SD charge transfer. For graphene $U_s = 17.0$ eV (without screening) and 9.3 eV (with account of screening) [26]; values of U_a for other atoms can be taken from Ref. [27].

4. EFFECT OF ELECTRON-PHONON INTERACTION ON CHARGE TRANSFER

Influence of the electron-phonon coupling (EPC) on adsorption on graphene within the scope of SAM has been originally considered in Ref. [28], where results of previous works [29,30] have been used. In these papers it was shown that, under certain conditions, the EPC can "prepare" two stable states of an adatom, each characterized by its occupation number and the corresponding equilibrium position (adsorption bond length). In this case, under the action of external fields or the interaction of adatoms, electron transitions leading to reconstruction of the adsorbed layer (in particular, doubling of its lattice constant) can take place.

Here we consider how the vibrations of SD act on the electronic states of adsorption system. While it is more correct to speak about the vibronic–electron interaction we will further use term EPC. In accordance with Ref. [28], we have Hamiltonian as a following sum:

$$H_{SD}^{vib} = \bar{H}_{SD} + H_{vib} + H_{int}, \tag{14}$$

where the first term is given by Eq. (1); the second term representing vibrations of free SD in classical representation is

$$H_{vib} = \frac{1}{2}M\dot{l}^2 + \frac{1}{2}k(l - l_0)^2, \tag{15}$$

where M, $k = M\Omega^2$, Ω and l (l_0) are the reduced mass, force constant, frequency and length (equilibrium length) of SD, respectively. The third term describes EPC in the form

$$H_{int} = \nu(\hat{n}_a + \hat{n}_s)(l - l_0), \tag{16}$$

where ν is the deformation potential of SD. Using the relation $\partial \langle H_{SD}^{vib} \rangle / \partial l = \langle \partial H_{SD}^{vib} / \partial l \rangle$, we obtain $l - l_0 = -\nu(n_a + n_s)/k$. Then H_{SD}^{vib} becomes

$$H_{\dim} = \tilde{\varepsilon}_a \hat{n}_a + \tilde{\varepsilon}_s \hat{n}_s - t(s^+ a + a^+ s) + H', \qquad (17)$$

where renormalized atomic energies $\tilde{\varepsilon}_{a(s)} = \varepsilon_{a(s)} - \lambda n_{a(s)}$, EPC constant $\lambda = v^2 / k$ and H' represents term which does not contain operators. Using Ref. [31], we get $v = (\partial \tilde{R} / \partial l)_{l=l_0} = 2t$, $k = 4\alpha_c t(1 - 2\alpha_p^2) / l_0^2$, where $\alpha_c = t / \tilde{R}$ and $\alpha_p = |\Delta| / \tilde{R}$ are the covalency and polarity of the interatomic bond in SD [32] and $\tilde{R} = \sqrt{\tilde{\Delta}^2 + t^2}$, $\tilde{\Delta} = (\tilde{\varepsilon}_a - \tilde{\varepsilon}_s) / 2$. Now we can use all the results of Section 2 with the exchange of $\overline{\varepsilon}$, $\overline{\Delta}$, $\overline{R}$, $\overline{D}_\pm$ on $\tilde{\varepsilon}$, $\tilde{\Delta}$, $\tilde{R}$, $\tilde{D}_\pm$. In particular, we obtain $\partial \delta \tilde{n}_{\dim} / \partial \lambda \sim -(2t^2 / \tilde{R}^3) \delta \tilde{n}_{\dim}$. Thus, account of EPC decreases intra-SD charge transfer. Other charge transfers are vanishingly small.

In the strong coupling regime $2\pi V^2 / \xi^2 \gg 1$ we have $\tilde{\rho}_{a,s}(\omega) \approx \Gamma_G(\omega) / \pi[(\tilde{\Omega}_{a,s}^2 + \Gamma_G^2(\omega)]$ instead of Eq. (10), where $\tilde{\Omega}_{a,s} = \omega - \tilde{\varepsilon}_{a,s} - \Lambda_G(\omega)$. It is easy to account simultaneously both Coulomb and electron-phonon interactions induced energies $\tilde{w}_{a,s} = \varepsilon_{a,s} + G n_{s,a}^* - \lambda n_{a,s}^*$ instead of $w_{a,s} = \varepsilon_{a,s} + G n_{s,a}^C$.

5. INTERACTION OF ADATOMS IN SUBMONOLAYERS ON GRAPHENE

5.1. Dipole–dipole repulsion

Let us consider the adsorption problem for a nonzero concentration of adatoms N_a characterized by the coverage $\Theta = N_a / N_{ML}$, where N_{ML} is the adatoms concentration in the monolayer. There are three main channels of adatom interaction: (i) dipole–dipole repulsion of charged adatoms, (ii) indirect interaction (exchange) of adatoms via the substrate electrons, and (iii) direct interaction (exchange), when orbitals of neighboring adatoms overlap [33]. If adatom has a charge $Z_a(\Theta) = 1 - n_a(\Theta)$, this charge and the corresponding image charge form surface dipole. It was shown [34,35] that, in the presence of dipole–dipole repulsion, the energy ε_a transforms to $\varepsilon_a(\Theta) = \varepsilon_a - \zeta \Theta^{3/2} Z_a(\Theta)$, where $\zeta = 2e^2 d^2 N_{ML}^{3/2} A$ is the dipole repulsion energy (e is the elementary charge, $2d$ is width of a double-electric layer of adatoms and images charges, $A \sim 10$ is a coefficient weakly depending only on the geometry of the adsorbed layer). Underline here, that all the adatoms are supposed to take an equivalent position on the substrate.

This scheme, initially developed in SAM, is completely applicable to SDM. According to Section 2, we arrive at the self-consistent equation

$$Z_a(\Theta) = \frac{2}{\pi}\left[\overline{D}_+(\Theta) \arctan \frac{\omega_+(\Theta) - \varepsilon_F}{\Gamma_+(\omega_+(\Theta))} + \overline{D}_-(\Theta) \arctan \frac{\omega_-(\Theta) - \varepsilon_F}{\Gamma_-(\omega_-(\Theta))} \right], \qquad (18)$$

where $\overline{D}_\pm(\Theta) = [1 \pm \overline{\Delta}(\Theta) / \overline{R}(\Theta)] / 2$, $\omega_\pm(\Theta) = \overline{\varepsilon}(\Theta) \pm \overline{R}(\Theta)$, $\overline{R}(\Theta) = \sqrt{\overline{\Delta}^2(\Theta) + t^2}$, $\overline{\varepsilon}(\Theta) = [\varepsilon_a(\Theta) + \varepsilon_s] / 2$, $\overline{\Delta}(\Theta) = [\varepsilon_a(\Theta) - \varepsilon_s] / 2$. At low coverage $\Theta \ll 1$ we can put $\varepsilon_a(\Theta) \approx \varepsilon_a - \zeta \Theta^{3/2} Z_a$, where $Z_a = Z_a(0)$. Then for a weak coupling regime $2\pi V^2 / \xi^2 \ll 1$ at $\varepsilon_F = \varepsilon_D = 0$ we find from Eq. (9) that the intra-SD charge transfer $n_{\dim} \approx 2\overline{\Delta}(\Theta) / \overline{R}(\Theta)$ and $\partial \delta n_{\dim}(\Theta) / \partial \Theta \sim -3\zeta t^2 \sqrt{\Theta} / 2\overline{R}^3$. For other charge transfers effect of dipole-dipole repulsion is vanishingly small. At high coverage limit, when $\Theta \sim 1$, we can find $Z_{ML} = Z_a(1)$ self-consistently, using $\varepsilon_{ML} = \varepsilon_a(1)$, $\omega_{ML}^\pm = \overline{\varepsilon}(1) \pm \overline{R}(1)$, $\overline{R}(1) = \sqrt{\overline{\Delta}^2(1) + t^2}$, $\overline{\varepsilon}(1) = (\varepsilon_{ML} + \varepsilon_s) / 2$ and $\overline{\Delta}(1) = (\varepsilon_{ML} - \varepsilon_s) / 2$.

5.2. Exchange interactions

It was demonstrated [33,36], that the exchange interactions in adsorbed layers can be modeled by the interaction of only two adatoms. The origin of this possibility is that both the indirect and direct interactions give rise to the same change in the adatom DOS, namely, the one hump DOS function $\rho_a(\omega) = \Gamma_a(\omega) / \pi[(\omega - \varepsilon_a)^2 + \Gamma_a^2(\omega)]$ spreads out in the presence of exchange interaction into a double-humped band of the form of Eq. (7), with this spread out increasing (the humps move apart) with increasing Θ. Indirect exchange for two species was originally considered for impurities in metals [37], adatoms on metals [38] and adatoms on graphene [39]. Direct exchange of adatoms was discussed in Ref. [39].

To use the results of Refs. [39,40] obtained in the SAM, we have to consider two SD coupled by exchange matrix element t_{ex}. Using Eq. (3), we find Green function for two interacting SD in the form

$$\overline{G}_a^{ex}(\omega) = \frac{\overline{G}_a(\omega)}{1 - \overline{G}_a^2(\omega) t_{ex}^2}. \qquad (19)$$

From the poles of Eq. (19) we get equation

$$(\omega - \omega_+)^2 (\omega - \omega_-)^2 - (\omega - \varepsilon_a)^4 t_{ex}^2 / (\omega - \varepsilon_s)^2 = 0. \qquad (20)$$

Underline, that for the direct exchange $t_{ex} = \text{const}$, while for the indirect exchange $t_{ex} = t_{ex}(\omega_\pm^\pm)$ [37,39].

Supposing for low coverage that $t_{ex} / t \ll 1$ and putting $\omega - \omega_\pm = \upsilon_\pm$, $|\upsilon_\pm| \ll |\omega_\pm|$, we have

$$\upsilon_\pm \approx \pm \frac{(\omega_\pm - \varepsilon_a)^2}{|\omega_\pm - \varepsilon_s|} \frac{t_{ex}^2}{4\overline{R}^2}. \tag{21}$$

Thus, in the SDM we have four SD levels $\omega_\pm^\pm$, where upper indices refer to the signs of $\upsilon_\pm$. Energies ω_+^- and ω_-^+ may be compared with LUMO (lowest unoccupied molecular orbital) and HOMO (highest occupied molecular orbital). Considering for simplicity level ω_+^+ as completely empty and level ω_-^- as completely filled we reduce four-level problem to two-level problem of Section 2. Thus, all the results of Section 2 are valid.

For the case $t_{ex}/t \gg 1$, realized at high coverage $\Theta \sim 1$, Eq. (20) transforms to $(\omega - \overline{\varepsilon} + \overline{\Delta})^4 - (\omega - \overline{\varepsilon} - \overline{\Delta})^2 t_{ex}^2 \approx 0$. For $|\overline{\Delta}| \ll t_{ex}$ we obtain four SD levels $\omega_{1,2} \sim \overline{\varepsilon}$ and $\omega_{3,4} \sim \overline{\varepsilon} \pm t_{ex}$. Again, reducing the problem to two degenerated levels $\omega_{1,2}$, we can use results of Section 2.

6. CONCLUDING REMARKS

Firstly, let us discuss two additional factors that affect charge transfer in adsorption system. We begin with the role of temperature T which was considered in Ref. [40] in the scope of SAM. For the SLG, the considerable effect of temperature on the charge transfer is observed when the adatom level ε_a is near the Dirac point ε_D. It was shown that the DOS of adatom has a characteristic central peak at energies close to the Dirac point. The height of this peak increases, and the width decreases as ε_a approaches ε_D. At $\varepsilon_a = \varepsilon_D$ this peak transforms into the delta function. The SDM scheme permits to avoid this singularity, because $\omega_\pm = \overline{\varepsilon} \pm \sqrt{\Delta^2 + t^2} \neq \varepsilon_D = 0$. Thus, using DOS (4), it is easy to find occupation numbers $n_i(T) = 2\int_{-\xi}^{\xi} \rho_i(\omega) f_{FD}(\omega, T) d\omega$, where $f_{FD}(\omega, T)$ is the Fermi-Dirac distribution function and index $i = a, s$, plus and minus.

Now let us briefly discuss adsorption on epitaxial graphene (epigraphene). Influence of metallic and semiconductor (dielectric) substrates on the SLG electronic spectrum has been thoroughly studied in Refs. [33,41] with the use of simple models of substrate DOS $\rho_{sub}(\omega)$. With the $\rho_{sub}(\omega)$ in hand we immediately have the substrate-induced half-width function $\Gamma_{sub}(\omega) = \pi V_{Gr/sub}^2 \rho_{sub}(\omega)$ and shift function $\Lambda_{sub}(\omega) = \pi^{-1} P \int_{-\infty}^{\infty} \Gamma_{sub}(\omega')(\omega - \omega')^{-1} d\omega'$, where matrix element $V_{Gr/sub}$ describes substrate – graphene interaction and P is the symbol of the principal value. The simplest DOS model for the metallic substrate is $\rho_{met}(\omega) = \text{const}$ [16,37], which gives $\Gamma_{met}(\omega) = \text{const}$ and $\Lambda_{met}(\omega) = 0$. For the semiconductor the Haldane-

Anderson model [42] is the simplest: $\rho_{sc}(\Omega) = \text{const}$ for $|\Omega| > E_g/2$ and $\rho_{sc}(\Omega) = 0$ for $|\Omega| \leq E_g/2$, where $\Omega = \omega - \omega_0$, ω_0 and E_g are the center and width of an energy band gap. This DOS gives $\Gamma_{sc}(\Omega) = \gamma_{sc} = \text{const}$ for $|\Omega| > E_g/2$, $\Gamma_{sc}(\Omega) = 0$ for $|\Omega| \leq E_g/2$ and $\Lambda_{sc}(\Omega) = (\gamma_{sc}/\pi) \ln |(\Omega - E_g/2)/(\Omega + E_g/2)|$ [43].

To obtain the electronic spectrum of epigraphene we use the scheme thoroughly described in Ref. [44]. In this scheme one begins with the single adsorbed carbon atom and then build the 2D hexagonal lattice of adatoms. The resulting epigraphene Green function is $G_{EpGr}(\omega, \mathbf{k}) = (\omega - \varepsilon(\mathbf{k}) - \Lambda_{sub}(\omega) + i\Gamma_{sub}(\omega))^{-1}$, where $\varepsilon(\mathbf{k})$ is the electronic spectrum of SLG. Then one has to determine corresponding DOS $\rho_{EpGr}(\omega)$. Some specific substrate effects on the SLG properties in the scope of SAM were considered in Refs. [45–48]. In the SLG–substrate weak-coupling limit $V_{Gr/sub}^2/\xi^2 \ll 1$ for the rough estimations we can represent the epigraphene's DOS as given by Eq. (5) for SLG, but with $\Omega_{EpGr} = \omega - \varepsilon_D - \Lambda_{sc}(\varepsilon_D)$ (for $|\varepsilon_D - \varepsilon_0| \ll E_g/2$) instead of $\Omega_{Gr} = \omega - \varepsilon_D$. Note, that only weak-coupling regime conserves unique SLG properties, since strong-coupling regime leads to the almost noninteracting carbon adatoms.

The Green function for atom adsorbed on epigraphene in SAM is

$$G_a^{-1}(\omega) = \omega - \varepsilon_a - \Lambda_{EpGr}(\omega) + i\Gamma_{EpGr}(\omega), \tag{22}$$

where $\Gamma_{EpGr}(\omega) = \pi V_{a/EpGr}^2 \rho_{RpGr}(\omega)$, $\Lambda_{EpGr}(\omega) = \pi^{-1} P \times \int_{-\infty}^{\infty} \Gamma_{EpGr}(\omega')(\omega - \omega')^{-1} d\omega'$ and $V_{a/EpGr}$ is the matrix element of the adatom–epigraphene interaction (see details in Ref. [43]). Account of the Coulomb and electron-phonon interactions in the problem on epigraphene is fulfilled in Ref. [49,50]. Adaptation of these interactions for SDM is the same as described in Sections 2–5.

In this paper we outlined only theoretical schemes, based on the simple models, which permit to obtain analytical results. Results of the numerical calculations for a wide range of parameters can be found in our papers cited here. As it was mentioned in Introduction, it is now generally accepted that the DFT is the state of the art in condensed matter physics. We think, however, that the model Hamiltonian approaches are still useful for the description of the whole complex of objects and clarifying the corresponding tendencies. Thus, it is relevant to repeat Anderson's words from his Nobel lecture [51]: "Very often such a simplified model throws more light on the real workings of nature than any number of *ab initio* calculations of individual situations, which even where correct often contain so much details as to conceal rather than reveal reality".

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REFERENCES

[1] F. Schedin, A.K. Geim, S.V. Morozov, E.W. Hill, P. Blake, M.I. Katsnelson, K.S. Novoselov, *Detection of individual gas molecules adsorbed on graphene*, Nat. Mater., 2007, vol. 6, pp. 652–655.

[2] D.J. Buckley, N.C.G. Black, E.G. Castanon, C. Melios, M. Hardman, O. Kazakova, *Frontiers of graphene and 2D material-based gas sensors for environmental monitoring*, 2D Mater., 2020, vol. 7, no. 3, art. no. 032002.

[3] S.Z.N. Demon, A.I. Kamisan, N. Abdullah, S.A.M. Noor, O.K. Khim, N.A.M. Kasim, M.Z.A. Yahya, N.A.A. Manaf, A.F.M. Azmi, N.A. Halim, *Graphene-based materials in gas sensor applications: A review*, Sens. Mater., 2020, vol. 32, no. 2(3), pp. 759–777.

[4] C.I. Justino, A.R. Gomes, A.C. Freitas, A.C. Duarte, T.A. Rocha-Santos, *Graphene based sensors and biosensors*, TrAC Trends Anal. Chem., 2017, vol. 91, pp. 53–66.

[5] T. Terse-Thakoor, S. Badhulika, A. Mulchandani, *Graphene based biosensors for healthcare*, J. Mater. Res., 2017, vol. 32, no. 15, pp. 2905– 2929.

[6] S. Szunerits, R. Boukherroub, *Graphene-based biosensors*, Interface Focus, 2018, vol. 8, no. 3, art. no. 20160132.

[7] J. Peña-Bahamonde, H.N. Nguyen, S.K. Fanourakis, D.F. Rodrigues, *Recent advances in graphene-based biosensor technology with applications in life sciences*, J. Nanobiotechnol., 2018, vol. 16, no. 1, art. no. 75.

[8] T.J.M. Fraga, M.N. Carvalho, M.G. Ghislandi, M.A. da Motta Sobrinho, *Functionalized graphene-based materials as innovated adsorbents of organic pollutants: A consise overview*, Braz. J. Chem. Eng., 2019, vol. 36, no. 1, pp. 1–31.

[9] Y. Bai, T. Xu, X. Zhang, *Graphene-based biosensors for detection of biomarkers*, Micromachines, 2020, vol. 11, no. 1, art. no. 60.

[10] A.A. Lebedev, S.Yu. Davydov, I.A. Eliseyev, A.D. Roenkov, O. Avdeev, S.P. Lebedev, Yu. Makarov, M. Puzyk, S. Klotchenko, A.S. Usikov, *Graphene on SiC substrate as biosensor: Theoretical background, preparation, and characterization*, Materials, 2021, vol. 14, no. 3, art. no. 590.

[11] L. Kong, A. Enders, T.S. Rahman, P.A. Dowben, *Molecular adsorption on graphene*, J. Phys. Condens. Matter, 2014, vol. 26, no. 44, art. no. 443001.

[12] Y. You, J. Deng, X. Tan, N. Gorjizadeh, M. Yoshimura, S.C. Smith, V. Sahajwalla, R. Joshi, *On the mechanism of gas adsorption for pristine, defective and functionalized graphene*, Phys. Chem. Chem. Phys., 2017, vol. 19, no. 8, pp. 6051–6056.

[13] S. Kumar, Meenakshi, H. Sharma, *Effect of gas adsorption on graphene nanoribbons: A density functional theory*, Mater. Today Proc., 2017, vol. 4, no. 9, pp. 10441–10445.

[14] U. Patil, N.M. Caffrey, *Adsorption of common solvent molecules on graphene and MoS_2 from first-principles*, J. Chem. Phys., 2018, vol. 149, no. 9, art no. 094702.

[15] S.G. Davison, K.W. Sulston, *Green-function theory of chemisorption*, Springer, Dordrecht, The Netherlands, 2016.

[16] P.W. Anderson, *Localized magnetic states in metals*, Phys. Rev., 1961, vol. 124, no. 1, pp. 41–53.

[17] D.M. Newns, *Self-consistent model of hydrogen chemisorption*, Phys. Rev., 1969, vol. 178, no. 3, pp. 1123–1135.

[18] J.W. Gadzuk, J.K. Hartman, T.N. Rhodin, *Approach to alkali-metal chemisorption within the Anderson model*, Phys. Rev. B, 1971, vol. 4, no. 2, pp. 241–255.

[19] J.R. Schrieffer, *Theory of chemisorption*, J. Vac. Sci. Technol., 1972, vol. 9, no. 2, pp. 561–568.

[20] S.Yu. Davydov, G.I. Sabirova, *Model of adsorption on graphene*, Phys. Solid State, 2011, vol. 53, no. 3, pp. 654–664.

[21] S.Yu. Davydov, *On the theory of adsorption on graphene-like compounds*, Semiconductors, 2017, vol. 51, no. 2, pp. 217–224.

[22] S.Yu. Davydov, A.V. Zubov, A.A. Lebedev, *A model of a surface dimer in the problem of adsorption*, Tech. Phys. Lett., 2019, vol. 45, no. 5, pp. 461–463.

[23] S.Yu. Davydov, O.V. Posrednik, *Low-energy approximation in the theory of adsorption on graphene*, Phys. Solid State, 2015, vol. 57, no. 8, pp. 1695–1698.

[24] N.M.R. Peres, F. Guinea, A.H. Castro Neto, *Electronic properties of disordered two-dimensional carbon*, Phys. Rev. B, 2006, vol. 73, no. 12, art. no. 125411.

[25] S.Yu. Davydov, A.V. Zubov, A.A. Lebedev, *Coulomb electron interaction between an adsorbate and substrate: A model of a surface dimer*, Tech. Phys. Lett., 2019, vol. 45, no. 9, pp. 924–926.

[26] T.O. Wehling, E. Sasioglu, C. Friedrich, A.I. Lichtenstein, M.I. Katsnelson, S. Blügel, *Strength of effective Coulomb interactions in graphene and graphite*, Phys. Rev. Lett., 2011, vol. 106, no. 23, art. no. 236805.

[27] W.A. Harrison, *Coulomb interaction in semiconductors and insulators*, Phys. Rev. B, 1985, vol. 31, no. 4, pp. 2121–2132.

[28] S.Yu. Davydov, *Evaluation of constants of electron–phonon coupling between gas molecules and graphene*, Tech. Phys. Lett., 2018, vol. 44, no. 2, pp. 105–107.

[29] F.D.M. Haldane, *Hartree-Fock study of the Anderson model coupled to a boson field; mixed valence states*, Phys. Rev. B, 1977, vol. 15, no. 1, pp. 281–289.

[30] V.E. Kravtsov, A.G. Mal'shukov, *Structural and electronic alterations in an adsorbed layer*, Sov. Phys. JETP, 1978, vol. 48, no. 2, pp. 348–355.

[31] S.Yu. Davydov, O.V. Posrednik, *On the theory of elastic properties of two-dimensional hexagonal structures*, Phys. Solid State, 2015, vol. 57, no. 4, pp. 837–843.

[32] W.A. Harrison, *Theory of the two-center bond*, Phys. Rev. B, 1983, vol. 27, no. 6, pp. 3592–3604.

[33] S.Yu. Davydov, S.V. Troshin, *Adsorption on metals and semiconductors: Anderson-Newns and Haldane-Anderson models*, Phys. Solid State, 2007, vol. 49, no. 8, pp. 1583–1588.

[34] J.P. Muscat, D.M. Newns, *The interpretation of work-function variation in alkali chemisorption from the atomic viewpoint*, J. Phys. C: Solid State Phys., 1974, vol. 7, no. 15, pp. 2636–2644.

[35] S.Yu. Davydov, *The interaction of atoms in layers adsorbed on graphene*, Tech. Phys. Lett., 2014, vol. 40, no. 7, pp. 565–567.

[36] O.M. Braun, V.K. Medvedev, *Interaction between particles adsorbed on metal surfaces*, Sov. Phys. Usp., 1989, vol. 32, no. 4, pp. 328–348.

[37] S. Alexander, P.W. Anderson, *Interaction between localized states in metals*, Phys. Rev., 1964, vol. 133, no. 6A, pp. A1594–A1603.

[38] T.L. Einstein, J.R. Schrieffer, *Indirect interaction between adatoms on a tight-binding solid*, Phys. Rev. B, 1973, vol. 7, no. 8, pp. 3629–3648.

[39] S.Yu. Davydov, *The Alexander–Anderson problem for two atoms adsorbed on graphene*, Phys. Solid State, 2012, vol. 54, no. 8, pp. 1728–1731.

[40] S.Yu. Davydov, *On the role of temperature in the problem of adsorption on graphene*, Tech. Phys., 2016, vol. 61, no. 7, pp. 1106–1108.

[41] S.Yu. Davydov, *On the specific features of the density of states of epitaxial graphene formed on metal and semiconductor substrates*, Semiconductors, 2013, vol. 47, no. 1, pp. 95–104.

[42] F.D.M. Haldane, P.W. Anderson, *Simple model of multiple charge states of transition-metal impurities in semiconductors*, Phys. Rev. B, 1976, vol. 13, no. 6, pp. 2553–2559.

[43] S.Yu. Davydov, A.A. Lebedev, *On the electronic state of an atom asorbed on epitaxial graphene formed on metallic and semiconductor substrates*, Phys. Solid State, 2015, vol. 57, no. 1, pp. 213–218.

[44] S.Yu. Davydov, *Graphene-like $A_N B_{8-N}$ compounds on metals and semiconductors*, in: *Handbook of Graphene, Volume 2: Physics, Chemistry, and Biology*, ed. by T. Stauber, Scrivener Publishing LLC, New York, 2019, Ch. 17, pp. 549–591.

[45] Z.Z. Alisultanov, *On renormalization of the Fermi velocity in epitaxial graphene*, Tech. Phys. Lett., 2013, vol. 39, no. 7, pp. 597–600.

[46] Z.Z. Alisultanov, I.K. Kamilov, *Transport properties of epitaxial graphene formed on the surface of a metal*, Phys. Solid State, 2013, vol. 56, no. 4, pp. 854–858.

[47] Z.Z. Alisultanov, I.K. Kamilov, *Transport properties of epitaxial graphene on the surface of a superconductor*, Semiconductors, 2014, vol. 48, no. 7, pp. 924–934.

[48] Z.Z. Alisultanov, *The Berry phase and Landau levels of epitaxial graphene in crossed magnetic and electric fields*, Tech. Phys. Lett., 2015, vol. 41, no. 10, pp. 998–1001.

[49] S.Yu. Davydov, *On the extended Holstein–Hubbard model for epitaxial graphene on metal*, Semiconductors, 2018, vol. 52, no. 2, pp. 226–230.

[50] S.Yu. Davydov, *Electron–electron and electron–phonon interactions in graphene on a semiconductor substrate: Simple estimations*, Semiconductors, 2018, vol. 52, no. 3, pp. 335–340.

[51] P.W. Anderson, *Local moments and localized states*, Rev. Mod. Phys., 1978, vol. 50, no. 2, pp. 191–202.

Модель поверхностного димера в теории адсорбции на графене

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Аннотация. Предложена модель поверхностного димера, образованного путем ковалентного взаимодействия адсорбированного атома и поверхностного атома подложки. Эта модель используется для расчетов переноса заряда между атомами димера и между димером и графеновой подложкой. Тщательно изучены влияния кулоновского и электрон-фононного взаимодействия на перенос заряда. Рассмотрена роль межадатомного диполь-дипольного отталкивания и обменных взаимодействий. Кратко обсуждается адсорбция на эпитаксиальном графене.

Ключевые слова: перенос заряда; кулоновское взаимодействие; электрон-фононное взаимодействие; дипольное отталкивание и обменное взаимодействие адатомов; эпитаксиальный графен