

On the Theory of the Adsorption of Atoms onto a Metal Surface in the Presence of an External Quantizing Magnetic Field

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Abstract—The Anderson–Newns model for the adsorption of atoms onto metals is generalized to the case of the presence of an external transverse quantizing magnetic field. Analytical expressions for the density of metal states in the external magnetic field are obtained. Analytical expressions for the density of adatom states are obtained in the approximation taking only the change in the density of substrate states into account. The charge exchange between the adatom and the metal is studied. The dependences of the density of adatom and transition-charge states on the magnetic field are studied for different values of the interaction constant. An analytical expression for the density of substrate states perturbed by adsorption is obtained.

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INTRODUCTION

The study of the adsorption of atoms and molecules onto the surface of different metal and semiconductor structures is the most important problem of condensed matter physics and, in particular, surface physics [1]. Such interest is due to several reasons. One of them is the fact that adsorption can cardinaly change the energy spectrum of the adsorbent (open the energy gap; change the work function, the surface conductivity, and the magnetic properties; affect the spectrum of surface plasmons; etc.) [2–4]. Thus, it becomes possible to obtain the desired characteristics of different structures using adsorbed atoms and molecules. The adsorption of atoms and molecules affects especially significantly the properties of low-dimensional structures [5–12], because the surface effects dominate over bulk ones.

The degree of influence of the adsorbate on the characteristics of the adsorbent depends strongly on the concentration of adsorbed particles (the degree of coverage) [3]. However, variation in the degree of adsorbate coverage is not the most convenient way of affecting the substrate in a controllable manner. This is related to technical inconvenience. It is more convenient to use an external field (electric or magnetic one) for this purpose. Moreover, in the case of an applied field, it is possible to vary the properties of both the adsorbate and the adsorbent. Such considerations make the study of adsorption in the presence of external fields important. In this report, we make an

effort to solve such a problem using an approach based on the model Anderson Hamiltonian.

ANDERSON–NEWNS MODEL FOR ADSORPTION ONTO A METAL

One of the widespread analytical models of adsorption onto a metal is the Anderson–Newns model [4–19]. This model is based on the following Hamiltonian:

$$H = \sum_{\mathbf{p}, \sigma} \varepsilon(\mathbf{p}) c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma} + E_a \sum_{\sigma} a_{i\sigma}^{\dagger} a_{i\sigma} + \mathcal{V} a_{i\uparrow}^{\dagger} a_{i\uparrow} a_{i\downarrow}^{\dagger} a_{i\downarrow} + \frac{V}{\sqrt{N}} \sum_{\mathbf{p}, \sigma} (c_{\mathbf{p}\sigma}^{\dagger} a_{i\sigma} + \text{h.c.}), \quad (1)$$

where E_a is the energy of an atom electron in the state $|a\sigma\rangle$; $\mathcal{V}$ is the intra-atomic Coulomb repulsion of electrons with opposite spins, $c_{\mathbf{k}\sigma}^{\dagger}$ ($c_{\mathbf{k}\sigma}$) is the operator of creation (annihilation) of substrate electrons in the state $|\mathbf{p}\sigma\rangle$; $\mathbf{p}$ is the quasimomentum of the substrate electron, $a_{i\sigma}^{\dagger}$ ($a_{i\sigma}$) is the operator of creation (annihilation) of an adatom electron, V is the hybridization potential (in this paper, we follow an approximation in which this quantity is independent of $|\mathbf{p}\sigma\rangle$); N is the number of substrate adatoms, and σ is the spin number. Next, we restrict ourselves to one spin state. Using

Hamiltonian (1), we obtain the expression for Green's function (GF) of the adatom:

$$G_i^0 = (\omega - \varepsilon_a - \Lambda(\omega) - i\Gamma_c(\omega))^{-1}, \quad (2)$$

where $\varepsilon_a = E_a + \mathfrak{g}\langle a_\sigma^+ a_\sigma \rangle$,

$$\Gamma_c(\omega) = \pi|V|^2 \rho(\omega), \quad (3)$$

$$\Lambda(\omega) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \Gamma_c(\omega') d\omega' / (\omega - \omega') \quad (4)$$

is the half-width and the function of the quasilevel shift, respectively, and $\rho(\omega)$ is the density of the substrate states (DoS). The sign of P means integration in the sense of the principal value. In the Anderson–Newns model, the density of metal states is approximated as follows:

$$\rho(\omega) = \rho_0 = \text{const.} \quad (5)$$

In the general case, the energy-independent density of states corresponds to a two-dimensional electron gas with a quadratic spectrum. Indeed, for the element of the phase volume of such a gas, we have

$$dV = \frac{4\pi S p dp}{(2\pi\hbar)^2} = \frac{4\pi m S \sqrt{E} dE}{(2\pi\hbar)^2} = \frac{4\pi m S dE}{(2\pi\hbar)^2}, \quad (6)$$

whence we obtain the expression for the density of states

$$\rho_0 = \frac{mS}{\pi\hbar^2}, \quad (7)$$

where S is the area of the considered region of the two-dimensional gas and m is the effective electron mass.

In the adopted approximation, we have

$$\Lambda(\omega) = 0, \quad \Gamma_c(\omega) = \Gamma_c = \pi|V|^2 \rho_0. \quad (8)$$

GENERALIZATION OF THE ANDERSON–NEWNS MODEL TO THE CASE OF THE PRESENCE OF AN EXTERNAL MAGNETIC FIELD

If an external magnetic field that is perpendicular to the substrate surface is applied, then the characteristics of the substrate and the adatom and the processes of exchange between the substrate and adatom are changed. The main changes in the adatom–substrate system can be formulated as follows: (i) the density of substrate states changes under the action of this field, (ii) the energy quasilevel of paramagnetic adatoms (alkali, transition, and rare-earth metals) is split (the Zeeman effect), and (iii) the removal of spin degeneracy leads to a change in the Coulomb repulsion between electrons with opposite spins (the third term in Hamiltonian (1)).

The problem in the second item can be omitted under well-known stipulations. That is, it can be assumed that the Zeeman splitting is small in the case under consideration. The third item contains a very important effect, which requires separate consideration within the framework of macroscopic theory. The presence of the magnetic field leads to the fact that the expression for the quasilevel contains the exchange interaction. The latter is related to the fact that additional repulsion between electrons appears, because the directions of their spins are the same as the result of the effect of magnetic field. In this paper, we take only the first point into account.

As was mentioned above, the metal substrate is represented in the form of a two-dimensional gas with a quadratic spectrum in the Anderson–Newns model. In the presence of an external quantizing magnetic field, the energy spectrum of electrons is quantized and has the form

$$E_{n,v} = v\hbar\omega_c (n + 1/2), \quad (9)$$

where $\omega_c = eH/m_c c$ is the cyclotron frequency, m_c is the cyclotron mass, H is the strength of the magnetic field, c is the velocity of light in free space, and v is the band subscript: $v = +1$ corresponds to the conduction band, and $v = -1$, to the valence band. In our model, it is assumed that the valence and conduction bands are equivalent to each other completely. To determine the density of states, it is necessary to know the spectral function, which in this case is defined as follows:

$$A_n(\omega) = \frac{s}{(\omega - E_{n,v})^2 + s^2} = \pi\delta(\omega - E_{n,v}), \quad (10)$$

where $s = 0^+$. The density of states is

$$\rho(\omega) = \frac{1}{\pi} \sum_{n=0, v=\pm 1}^{\infty} \frac{s}{(\omega - E_{n,v})^2 + s^2}. \quad (11)$$

In actual practice, summation must be performed up to a certain level n_0 corresponding to the boundary of the band of allowed energies. The energy corresponding to n_0 in metals is usually much higher than the Fermi energy, therefore we can pay no attention to the numerical value of n_0 , because the last is absolutely not important for the considered problem. The main thing is that n_0 must be much higher than the Fermi level. The δ -like spectral function corresponds to the lack of damping in the system ($s = 0^+$), i.e., to the case of free particles. However, there is always quasiparticle damping in a real system. Moreover, the adsorbed layer of atoms is an additional source of quasiparticle scattering, which also leads to their damping. Therefore, we set $s = \Gamma \neq 0$. In addition, each Landau level is characterized by the degeneracy factor defined as the ratio of the area of the considered sample (S) (perpendicular to the magnetic field) to that of the region in which there is quantization ((πl_H^2) , where $l_H = (\hbar c / eH)^{1/2}$ is the

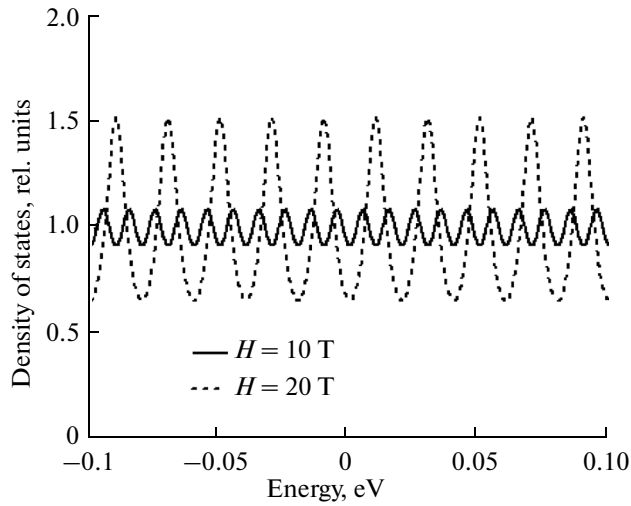


Fig. 1. Density of states of electrons of the metal surface layer in an external magnetic field. The solid line corresponds to $H = 10$ T, and the dashed curve, to $H = 20$ T. The density of states is given in ρ_0 .

magnetic length). Thus, the degeneracy factor for each Landau level is

$$\mu = SeH/\pi c\hbar = Sm\omega_c/\pi\hbar = \rho_0\hbar\omega_c.$$

Finally, we have the expression for the density of states

$$\rho(\omega) = \frac{\rho_0\hbar\omega_c}{\pi} \sum_{n=0, \nu=\pm 1}^{\infty} \frac{\Gamma}{(\omega - E_{n,\nu})^2 + \Gamma^2}. \quad (12)$$

Here and hereafter, we set $m_c = m_e$ and $\Gamma = 0.001$ eV, where m_e is the free electron mass. For such parameters, we have $\hbar\omega_c \approx 10^{-3}H$ eV; in this case, the magnetic field in this expression is given in tesla. Figure 1 shows the density of states (12) for different strengths of the magnetic field. It can be seen that the density of states is Lorentz contours, whose width is obviously determined by Γ . For the shift function, we have

$$\Lambda(\omega) = \rho_0\hbar\omega_c|V|^2 \sum_{n=0, \nu=\pm 1}^{\infty} \frac{(\omega - E_{n,\nu})}{(\omega - E_{n,\nu})^2 + \Gamma^2}. \quad (13)$$

Figure 2 shows the dependence of the reduced shift function $\Lambda(\omega)/\rho_0|V|^2$ on the energy variable. It can be seen from this figure that the shift function is strongly oscillating. The last is related to the presence of the magnetic field and also to the fact that the distance between levels is very small in ordinary metals. As $H \rightarrow 0$, we have $\rho(\omega) \rightarrow \rho_0$ and $\Lambda(\omega) \rightarrow 0$; i.e., we arrive at the model of an infinitely wide band (formula (8)).

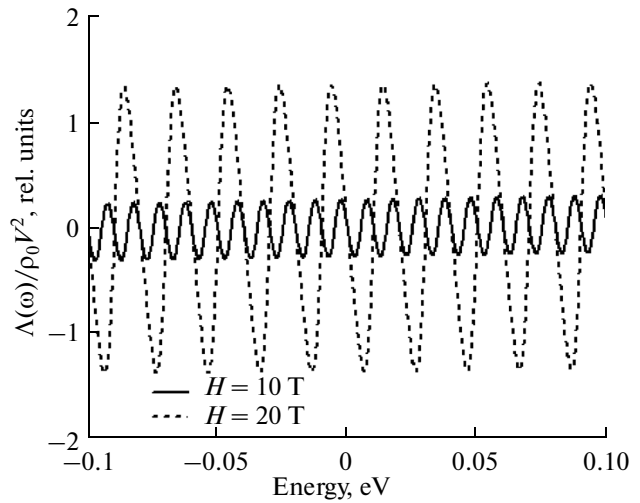


Fig. 2. Shift function of the adatom quasilevel in an external magnetic field.

It is also possible to take the spins of substrate electrons into account. In this case, the energy spectrum of the substrate must be written in the form

$$E_{n,\nu} = \nu\hbar\omega_c(n + 1/2) \pm \frac{\hbar\omega_c}{2}.$$

The last expression can be rewritten as

$$E_{n,\nu} = \nu\hbar\omega_cn,$$

in this case, each value with $n \neq 0$ occurs twice, and that with $n = 0$, once. In other words, the density of states with $n \neq 0$ is given by the same formula (12), and it is two times smaller for $n = 0$.

The model used here can also be generalized to the case of adsorption onto semiconductors [20] and alloys [21, 22] in the general case.

DENSITY OF ADATOM STATES AND THE TRANSITION CHARGE

The density of adatom states is determined by the imaginary part of Green's function (2)

$$\rho_a(\omega) = \frac{1}{\pi} \text{Im} G_a(\omega) = \frac{1}{\pi} \frac{\Gamma_c}{(\omega - \varepsilon_a - \Lambda(\omega))^2 + \Gamma_c^2}. \quad (14)$$

Using (12), (13), and (14), we obtain the density of adatom states with a positive quasilevel energy for different values of the magnetic-field strength and for different values of the hybridization potential (Fig. 3). Figure 4 shows the analogous dependences for an adatom with a negative quasilevel energy. The density of adatom states differs from zero most significantly for energies close to ε_a . The last is obvious, because the atom under consideration contains one electron with the energy ε_a . If there is no interaction with the sub-

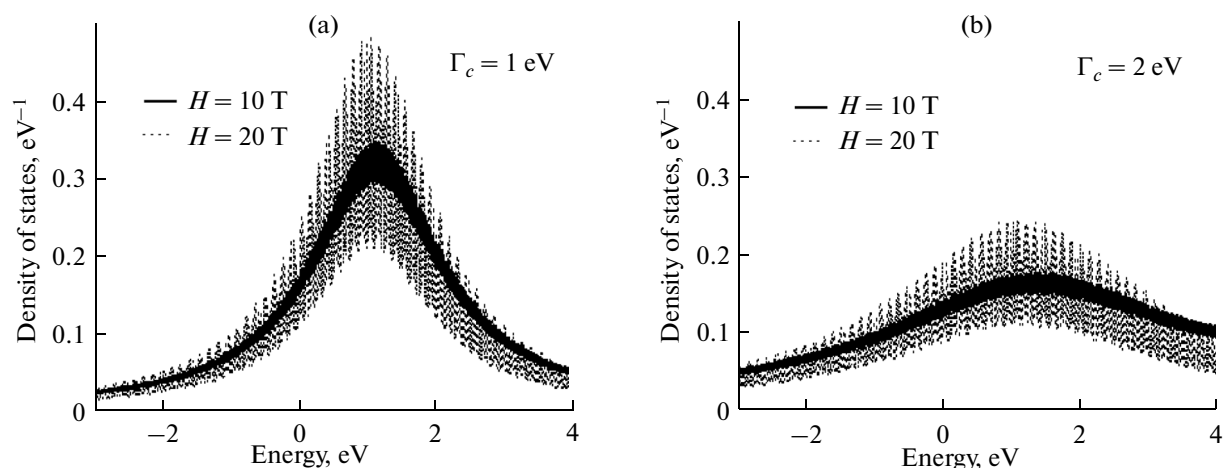


Fig. 3. Density of adatom states with a positive quasilevel energy $\varepsilon_a = 1$ eV for different values of magnetic-field strengths and hybridization potential.

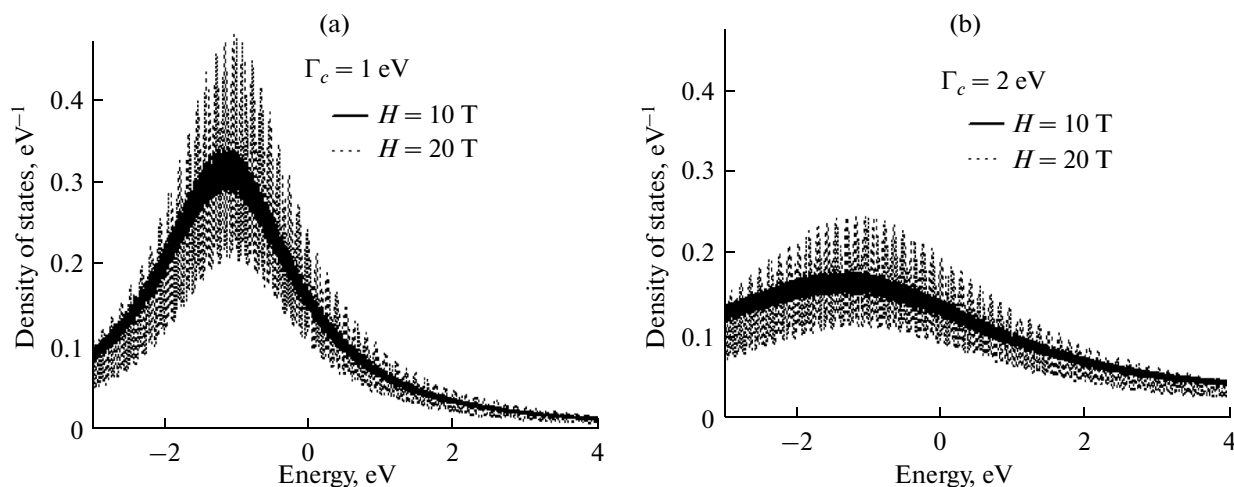


Fig. 4. Density of adatom states with a positive quasilevel energy $\varepsilon_a = -1$ eV for different values of the magnetic-field strengths and hybridization potential.

strate, the density of states is, naturally, the δ function with the argument $\omega - \varepsilon_a$. The most interesting conclusion that can be made from Figs. 3 and 4 is the following. As the magnetic field decreases, the quasilevel broadening decreases and the peak height increases for ε_a . This demonstrates that an increase in the magnetic field leads to a decrease in the interaction between the adatom and the substrate. The last can be easily understood from the following consideration. As the magnetic field increases, the distance between neighboring Landau levels increases. Naturally, this leads to a decrease in the number of Landau levels under the Fermi level. A decrease in the levels means a decrease in the number of electrons participating in the adatom–substrate coupling.

The adatom occupation number is defined in the standard way [2]:

$$n_a = \int_{-\xi}^{E_F} \rho_a(\omega) d\omega, \quad (15)$$

where E_F is the Fermi energy and ξ is the width of the allowed energies of the valence band. Here we consider the general laws of adatom charge variation if quantities, such as the hybridization potential and the adatom quasilevel energy, are varied. The most important quantity determining the nature of adsorption is the transition charge, which is equal to the induced adatom charge and defined, obviously, as $\Delta q =$

$(1 - n_a)e$, where e is the electron charge. Figure 5 shows the dependence of the transition charge on the adatom quasilevel energy.

When plotting the curves in Fig. 5, we set $\xi = 5$ eV and $E_F = 1$ eV. It can be concluded from Fig. 5 that the transition charge is small for $\varepsilon_a < E_F$ and approaches unity for $\varepsilon_a \geq E_F$. This can be explained by the fact that all levels below the Fermi level are occupied by electrons, and, as a result, the electron belonging to the adatom cannot make the transition to these levels. The opposite case occurs for energies $\varepsilon_a \geq E_F$. It can be seen from Fig. 5 that the dependence of the transition charge from the magnetic field is rather weak. This can be explained by the fact that, in ordinary metals, the distance between the Landau levels is very small and electrons with energies on the order of 1 eV barely “perceive” it. It is also interesting to note that, for large interaction constants (Fig. 5c), the transition charge depends almost linearly on the adatom quasilevel energy.

ADSORPTION-INDUCED VARIATION IN THE DENSITY OF METAL STATES

Obviously, the electronic structure of the metal changes in the case of the adsorption of atoms onto this metal. Here we consider the problem of adsorption-induced variation in the density of substrate states. For Green's function of the perturbed substrate onto which the atomic layer with the concentration η is adsorbed, using the Dyson equation, in the first approximation, we obtain

$$\tilde{G}_{nn'} = G_{nn'}\delta_{nn'} + \frac{1}{N_a} G_n \sum_{i,j} V_{ni} G_{ij} V_{jn} G_{nn'}, \quad (16)$$

where the summation is taken over all adatoms, N_a is the total number of sites in the adatom lattice ($N_a = N$ in the case of the T type of adsorption where the adatom is located just above the substrate atom), and G_{ij} is Green's function of a single adatom. Note that we neglect possible interactions between adatoms (direct and indirect electron exchanges, dipole interaction, and so on). The last are, generally, responsible for very important phenomena in both the adsorbate and adsorbent [4, 18, 19]. We assume below that one substrate atom corresponds to one adatom. Taking into account that the function $G_{ij} = G_a$ is independent of the adatom location in the adatom lattice and that $V_{ni} = V$, we obtain

$$\tilde{G}_n = G_n + \eta V^2 G_n G_a G_n. \quad (17)$$

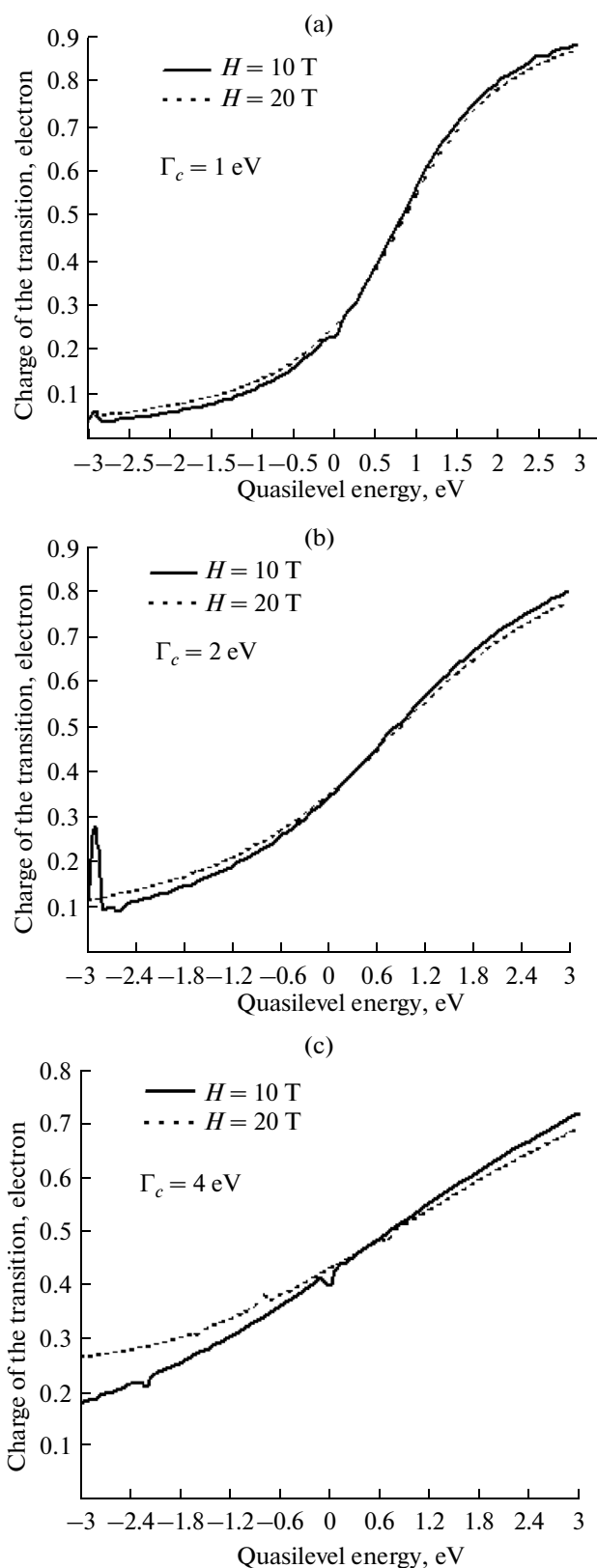


Fig. 5. Dependence of the transition charge on the adatom quasilevel energy for different values of interaction constants and magnetic-field strength.

Before we perform summation over the wave vector, we note that

$$(G_n)^2 = \frac{1}{(\omega - E_{n,v} - is)^2} \\ = -\frac{\partial}{\partial \omega} \left(\frac{1}{\omega - E_{n,v} - is} \right) = -\frac{\partial G_n}{\partial \omega}.$$

Then

$$\tilde{G}(\omega) = \sum_{n,v=\pm 1} \tilde{G}_n(\omega) = G(\omega) - \eta V^2 \frac{\partial G(\omega)}{\partial \omega} G_a(\omega). \quad (18)$$

Finally, for the density of states, we have

$$\tilde{\rho}(\omega) = \pi^{-1} \text{Im} \tilde{G}(\omega) \\ = \rho(\omega) - \eta V^2 \text{Im} \left(\frac{\partial}{\partial \omega} (\pi^{-1} \text{Re} G(\omega) + i\rho(\omega)) \right) \\ \times (\text{Re} G_a(\omega) + i\pi\rho_a(\omega)), \quad (19)$$

where

$$\text{Re} G_a(\omega) = \frac{\pi(\omega - \varepsilon_a - \Lambda(\omega))\rho_a(\omega)}{\Gamma(\omega)},$$

$$\text{Re} G^0(\omega) = \Lambda(\omega)/V^2.$$

Finally, for the density of states, we have

$$\tilde{\rho}(\omega) = \rho(\omega) - \eta V^2 \rho_a(\omega) \\ \times \left(\frac{\partial}{\partial \omega} \text{Re} G(\omega) + \frac{\pi(\omega - \varepsilon_a - \Lambda(\omega))}{\Gamma(\omega)} \frac{\partial}{\partial \omega} \rho(\omega) \right). \quad (20)$$

DISCUSSION AND CONCLUSIONS

To calculate the atom charge, two characteristics of the adatom must be known: the quasilevel energy and the hybridization potential, which depends on the type of adatom and adsorption. In analogy with [8, 9], we determine the quasilevel energy using the relation [3]

$$\varepsilon_a = \Phi - I + e^2/4\lambda, \quad (21)$$

where Φ is the substrate work function, I is the adatom ionization potential, λ is the average distance between the adatom and substrate surface, and $e^2/4\lambda$ is the intra-atomic Coulomb repulsion. We found the ionization potentials of various atoms in [23]. The quantity λ is usually found using various approximations of the substrate surface structure or from experimental data. The hybridization potential can be found in the same way as in [8, 9] using the Harrison bond-orbital method [24, 25]. For example, for the adsorption of alkali metal atoms onto s and p substrates, the s and p orbitals play the main role, and, consequently, the following formula can be used:

$$V = V_{ij\alpha} = \eta_{ij\alpha} \frac{\hbar^2}{m_0(r_a + r_c)^2}, \quad (22)$$

where the subscripts i and j mean the respective states of the adatom and the substrate atom, which participate in the hybridization ($i, j = s, p$), $\alpha = \pi, \sigma$ is the type of bond (the σ or π bond) between the adatom and graphene, $\eta_{ij\alpha}$ is the characteristic interaction constant, and m_0 is the free electron mass. If these parameters are used, it is possible to quantitatively calculate the adsorption characteristics of particular atoms. However, we here are interested in qualitative effects, which are studied above rather thoroughly. And the calculations for particular atoms are interesting if there are experimental data on the problem under study. Unfortunately, the last are unknown to the authors, and, consequently, the quantitative calculations at this stage will be useless in some sense.

The phenomena considered here are also interesting for another reason. The authors of [26–28] proposed an analytical model of epitaxial graphene, in accordance with which it is represented in the form of adsorbed C atoms forming a hexagonal structure. This model was then developed in [30–38]. All the results of our work can be applied to the case of epitaxial graphene formed on a metal surface.

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