Atomic Hydrogen Adsorption on the Single-Layer Grapheme

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Abstracts: Atomic hydrogen adsorption for the zero (single adatom) and nonzero (submonolayer) coverages is considered. It is shown that all main channels of the adatom interactions (dipole-dipole repulsion, direct and indirect exchange interactions) lead to depolarization of hydrogen adatoms. Numerical estimations for all the cases considered give quite reasonable results.

Key words: Hydrogen, adsorption, adatom

INTRODUCTION

The unique electronic properties of the Single-Layer Grapheme (SLG) makes it very perspective for a great number of device applications [1-6]. Due to high electron mobility one of the significant graphene application is the resistivity sensors [7-10].

Since the Drude-Lorentz conductivity \( \sigma = e n \mu \), where \( e \) is the positron charge, \( n \) is the electron concentration, \( \mu \) is the electron mobility, it is clear that adsorption induced surface conductivity variation \( \Delta \sigma_s \) is proportional to the changes in electron surface concentration \( \Delta n_s \) and its surface mobility \( \Delta \mu_s \). First contribution \( \Delta n_s \) is connected with the charge transfer processes between adatoms and substrate, while the second contribution \( \Delta \mu_s \) arises from the extra electron scattering due to adatoms. In the number of papers [11-14] devoted to the metal oxides conductivity variation arises from the adsorption of gases particles has been shown that the change of \( \Delta n_s \) is the dominant factor. Moreover, it is the charge of adatom strictly connected with \( \Delta n_s \), which dictates value and character (sign) of \( \Delta \sigma_s \). Here we consider the charge transfer between the SLG and adsorbed gases atoms and molecules.

THEORY OF ADSORPTION ON SLG

Simple analytical model of adsorption (M-model) has been formulated in [15-18]. Here we briefly describe the M-model features.

Green’s function \( G \) corresponding to the single adatom adsorption on SLG has a form

\[
G^{-1} = \omega - \varepsilon_a - A(\omega) + i\Gamma(\omega) \quad (1)
\]

where the quasilevel half-width \( \Gamma \) and hybridization shift \( A \) functions are

\[
\Gamma(\omega) = \pi V \rho_g \quad (2)
\]

\[
A(\omega) = \frac{1}{\pi} \int \frac{\Gamma(\omega')d\omega'}{\omega' - \omega - \omega'} \quad (3)
\]

\( \omega \) is the energy variable, \( \varepsilon_a \) is the center of quasilevel energy, \( V \) is the adatom-substrate hopping energy, \( \rho_g \) is the SLG substrate Density of States (DOS).

For the SLG DOS we accept the following expression:

\[
\rho_g(\omega) = \begin{cases} 
0, & \omega < -3t; \\
\frac{1}{\omega}, & -3t < \omega < -t; \\
\frac{P_n[|\omega|]}{t}, & -t < \omega < t; \\
\frac{P_n}{\omega}, & t < \omega < 3t; \\
0, & \omega > 3t.
\end{cases} \quad (4)
\]

Here \( t \) is the hopping energy for the nearest neighbor carbon atoms in graphene, 3t is the width of the valence \( \pi \) and conduction \( \pi^* \) bands, \( \omega = 0 \) is the energy of the Dirac point \( K \) in the Brillouin zone and \( P_n = 2/(1+21n3)t \). Then we find \( A(\omega) = \rho_m V^2 \lambda(\omega) \)

where \( x = \omega/t \) and

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Fig. 1: Plot of the reduced SLG DOS $f(x)$ versus reduced energy $x = \omega/t$

Fig. 2: Plot of the reduced shift function $\lambda(x)$ versus reduced energy $x = \omega/t$ and graphical solution of equation $x - \eta_a - \gamma \lambda(x) = 0$ for the Eq. (11)
The reduced SLG DOS \( f(x) = \rho_s(x)/\rho_m \) and shift function \( \lambda(x) \) are shown in Fig. 1 and 2. Thus, the adatom’s DOS and occupation number \( n_a \) (at zero temperature) we obtain

\[
\rho_s(\omega) = \frac{1}{\pi} \frac{\Gamma(\omega)}{(\omega - \varepsilon_a - \Lambda(\omega))^2 + \Gamma(\omega)^2} \\
\]

\[
n_a = \int \rho_s(\omega) d\omega 
\]

where \( \varepsilon_F \) is the Fermi energy. It is more suitable to decompose \( n_a \) to the sum of local state \( \omega_l \leq 3t \) (SLG valence band bottom) contribution \( n_l \) and band states contribution \( n_b \), which are calculated as

\[
n_l = \int \frac{\partial \Lambda(\omega)}{\partial \omega} \lambda(\omega) d\omega \\
n_b = \int \rho_s(\omega) d\omega = \int \lambda(\omega) d\omega 
\]

where \( \gamma = [2/(1 + 2\ln 3)](V/t)^2 \)

\[
\overline{\rho}_s(\omega) = \rho_s(\omega) \cdot t \\
\overline{\varepsilon}_s = \varepsilon_s/t 
\]

The energies of local (\( \omega_l \)) and resonance (\( \omega_b \)) energies can be found from the equation

\[
\omega - \varepsilon_a - \Lambda(\omega) = 0 \\
x - \eta_a - \gamma \lambda(x) = 0 
\]

where \( \eta_a = \varepsilon_a/t \). In Fig. 2 the graphical solution of Eq. (11) is demonstrated.

Note, that the M-model has been successfully applied to the calculation of hydrogen, alkali metals and halogen atoms on SLG [15-18].

**ESTIMATIONS OF THE SINGLE HYDROGEN ADATOM CHARGE**

Atomic hydrogen has been most extensively studied as an adsorbate on grapheme [19-30]. We therefore proceed to determining of H on SLG adsorption parameters.

Let us begin with hopping energy \( t \), using the Harrison’s Bond Orbital Model (BOM) [31]. Then,

\[
t = |V_{pp}| = |\eta_{pp}| \left( \hbar^2/m^2 a^2 \right) 
\]

where coefficient describing \( \pi \)-interaction of the nearest-neighbor \( |p_h| \) carbon orbitals \( \eta_{pp} = -0.63 \), nearest-neighbor distance of carbon atoms \( \alpha = 1.42 \) Å, \( m \) is the free electron mass. So, we find \( t = 2.38 \) eV. The value of the energy \( V \), representing hopping matrix element of the \( \sigma \)-interaction between the \( |s\rangle \) hydrogen orbital the \( |p_h| \) carbon orbital is also determined according to BOM:

\[
V = \eta_{pp}(\hbar^2/m d) \\
d = r(C) + r(H) 
\]

where \( \varepsilon_A \) is the atomic radius of atom A (0.77 Å for C [32] and 0.53 Å for H). This gives \( V = 6.40 \) eV and \( \gamma = 4.53 \).

Now we have only to evaluate the energy \( \varepsilon_a \), which determines the center-of gravity of the adatom quasilevel. The \( \varepsilon_a \) level of free H atom is below the vacuum level by the ionization energy \( I = 13.60 \) eV.

Putting \( \varepsilon_a = \varepsilon_a + \Delta_c \) where Coulomb repulsion upward shift [33, 34] and accepting work function of SLG \( \phi_g = 5.11 \) eV [35], we find \( \varepsilon_a = \phi_g - I + \Delta_c = -5.72 \) eV (\( \eta_a = -2.40 \)). Note, that we consider here undoped SLG, when the Fermi level \( \varepsilon_F \) coincides with the Dirac point.

Figure 3 shows the reduced DOS on hydrogen adatom in the region of the continuous spectrum of SLG. In addition, there is a local level at \( x_1 = 5.39 \), on which adatom’s DOS is \( n_l \approx 0.59 \). Thus, \( n_a \approx 0.69 \) and the hydrogen adatom charge \( Z_a = 1 - n_a \approx 0.31 \).

**ESTIMATIONS OF THE HYDROGEN ADATOM CHARGE FOR SUBMONOLAYER**

For a finite number of adatoms their interaction has to be taken into account. There are three main channels of the adatoms interaction. They are: dipole-dipole repulsion of charged adatoms, indirect interaction
Fig. 3: Reduced DOS in the region of continuous graphene spectrum for hydrogen adatom (exchange) via the substrate electrons, direct interaction (exchange) when orbitals of neighboring adatoms overlap [36].

**Dipole-dipole repulsion of adatoms:** Let us begin with the dipole-dipole interaction. If adatoms are charged due to the electron transfer between substrate and adatom, the dipole-dipole repulsion in the adlayer arises. It was shown [37], that in the presence of such an interaction the single adatom quasi-level $\varepsilon_a$ is shifted to

$$\varepsilon_a(\Theta) = \varepsilon_a - \xi \Theta^{1/2} Z_a(\Theta)$$

(12)

where the dipole interaction constant

$$\xi = 2 \hat{e} d N_{\text{ML}}^{1/2}$$

(13)

Here, the coverage $\Theta = N_a / N_{\text{ML}}$, where $N_a (N_{\text{ML}})$ is the number of adatoms in the submonolayer (monolayer), $\bar{A} = 10$ is a coefficient depending only weakly on the geometry of the adsorbed layer, $Z_a(\Theta) = 1 - \bar{a}_a(\Theta)$ is the hydrogen adatom charge. Since within our scheme hydrogen adatom charge $\bar{Z}_a > 0$ for all the coverages. The increase of $\Theta$ leads to the downward shift of $\varepsilon_a(\Theta)$. This results in the decrease of $\tilde{Z}_a(\Theta)$ or depolarization of adatom. To obtain more quantitative results we will use the simplified picture of hydrogen adsorption.

With some overestimation we may consider that $n_1 >> n_b$. Let us seek for a solution of Eq. (10) for the energy region of $|\omega| >> 3t$. In this region Eq. (3) gives approximately

$$\Lambda(\omega) = \frac{2V^2}{\omega} \int_{\omega_1}^{\omega_2} \rho(\omega') d\omega'$$

(14)

which gives $\Lambda(\omega) = \frac{2V^2}{\omega}$. Now instead Eq. (10) we obtain

$$\omega - \varepsilon_a(\Theta) - \frac{2V^2}{\omega} = 0$$

(15)

which gives

$$\omega_1(\Theta) = \frac{1}{2} \left[ \varepsilon_a(\Theta) \pm R(\Theta) \right]$$

$$R(\Theta) = \left( \varepsilon_a(\Theta)^2 + 8V^2 \right)^{1/2}$$

(16)

where subscripts + and - refer to the antibonding and bonding states of the surface molecule respectively. We are interested only in the occupied states $\omega_1^+(\Theta)$. 
Let us consider small coverage limit $\Theta << 1$ and put $e_i(\Theta) = e_i - \xi^3/2Z_8$, i.e. ignor charge dependence on coverage. It is easy to demonstrate now that

$$\frac{d|e_i(\Theta)|}{d\Theta} = \frac{3}{4} \Theta^{1/2} e_i Z_8 \left(1 - \frac{e_i}{(e_i + 8\sqrt{3})^2}\right)$$

(17)

It was shown in [15], that

$$\frac{d\lambda}{dx} = \ln \left| \frac{x^2}{1-x^2} - \frac{1}{x^2} \ln \left| \frac{1-x^2}{1-(x/3)^2}\right| + \frac{2}{9} - x^2 \right|$$

(18)

Then for $|x^2| > 3$ we obtain $(d\lambda/dx) \approx -1/(x^2)^2$. Inserting this result into Eq. (8), we get

$$n_i = 1 - \frac{1}{(x^2)}$$

(19)

It is clear now that $n_i \sim 1$ and increase with $\Theta$.

**Exchange interaction of adatoms:** We start with the direct exchange that occurs at high coverages when the $|s\rangle$ orbitals of the adjacent hydrogen adatoms begin to overlap. It can be shown that the effect of direct exchange may be demonstrated by considering two interacting adatoms, i.e. dimer [38, 39].

For the dimer DOS (per one atom) $\rho_{\text{dim}}(\omega)$ the following expression can be written [38]:

$$\rho_{\text{dim}}(\omega) = \frac{1}{2} [\rho_+(\omega) + \rho_-(\omega)]$$

(20)

where

$$\rho_\pm(\omega) = \frac{1}{\pi} \frac{\Gamma(\omega)}{(\omega - \varepsilon_+ \pm t_a)^2 + \Gamma^2(\omega)}$$

(21)

where $t_a$ is the direct exchange hopping energy.

Let us again address for simplicity surface molecular model. Then instead of Eq. (15) we get [39]:

$$\omega - \varepsilon_s \pm \frac{2V^2}{\omega} = 0$$

(22)

which gives for the deep local state lying below SLG valence band bottom

$$\varepsilon_s = \frac{1}{2}(\varepsilon_s \pm t_a - R_s)$$

$$R_s = \left(\varepsilon_s^3 + t_a^3 + 8V^2\right)^{1/2}$$

(23)

To estimate $t_a$, we put two hydrogen atoms just upon two adjacent carbon atoms. Then

$$t_a = V_{\text{so}} = |\eta_{\text{ss}}| (\hbar^2/m^2)$$

where $\eta_{\text{ss}} = -1.32$. Then $t_a = 4.99$ eV and we obtain $\omega^+ = -9.42$, $\omega^- = -15.87$ eV. This gives $n_i^+ = 0.34$, $n_i^- = 0.87$. Thus, the local contribution to the occupation number $n_i = (n_i^+ + n_i^-)/2 = 0.61$. Since for the isolated hydrogen adatom $n_i = 0.59$, we have again small but pronounced depolarization effect due to direct exchange.

Note also that it is easy to take into account both direct exchange and dipole-dipole interaction. In the above expressions we simply have to replace $\varepsilon_s$ by $e_s(\Theta)$.

We now proceed to the indirect exchange between two adatoms through the substrate electrons. As was shown in Ref. [38], if we replace hopping energy $t_a$ in the above formulas by the matrix element

$$T(\omega) = V^2 \sum_{k} \exp(ikr_1) \frac{\exp(ikr_2)}{\omega - \varepsilon_n + i\sigma}$$

(24)

where $k$ is the SLG electron wave vector, $r_2$ is the distance between two adatoms, $s = 0^\pm$. Let us analyze expression (24) for low-energy approximation for $\varepsilon_n$ near the Dirac point $K$, which is

$$\varepsilon_n(q) = \pm \frac{3}{2} t_a |q|$$

(25)

where $q = Kk$, sign plus is referred to the $\pi^*$ band ($\omega^+ > 0$), sign minus is referred to the $\pi$ band ($\omega^- < 0$) [1]. When calculating $T$, we will consider the near region assuming $q r_{12} << 1$ and the far region, where $q r_{12} >> 1$.

For the near region ($q r_{12} << 1$), we assume $\exp(q r_{12}) = 1$ and introduce cut-off vector $q_1$. In this case, via the direct calculation, we derive

$$T_{\text{near}}(\omega) = \frac{2V^2}{\xi} \left(\frac{\bar{\xi} + \omega n_{\text{SS}}}{\omega + \frac{2V^2}{\xi}}\right)$$

(26)

where cut-off energy $\bar{\xi} = (3t_a q_1)/2$, the upper sign is referred to the region $\omega > 0$ and lower sign is referred to the region $\omega < 0$. In the limit $\omega \to 0$, we derive

$$T_{\text{near}}(\omega) = \frac{2V^2}{\xi}$$

(27)

In the far region ($q r_{12} >> 1$) at $\omega \to 0$, we find
It should be noted that expression (28) transforms into (27) at $q_{B_{12}} << 1$ if we equate the imaginary exponent to unity. Thus, we can apply expression (28) for both regions. This dependence of the indirect exchange on the distance between two interacting adatoms is similar to the far asymptotic of the RKKY interaction.

In the presented evaluations, we neglect the dependence of $T$ on $\omega$, in our opinion, this introduces no serious error. For example, in the limit $\omega \rightarrow \pm \xi$, we find

$$T_{\text{far}}(\omega) \approx (q_{B_{12}}/2) \exp(iq_{B_{12}}/2)$$

and if there is two-side coverage with alternation in the arrangement of neighboring adatoms on different sides of the graphene sheet, the system is said to be graphane [28, 43]. Note in addition, that the interaction of atomic hydrogen with other carbon nanosystem attracts today much attention [44, 45].

In this paper we have considered hydrogen adsorption for the zero (single adatom) and nonzero (submonolayer) coverages. It was shown that all main channels of the adatom interactions lead to their depolarization. Numerical estimations for all the cases considered give quite reasonable results. However, for the more rigorous theoretical studies additional experimental data is needed.

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