# The Hall conductivity of graphene

© *Hamze Mousavi*[∗+¶], *Samad Behroozi*[∗]

[∗] Department of Physics, Razi University,
Kermanshah, Iran
[+] Nano Science and Nano Technology Research Center, Razi University,
Kermanshah, Iran

Sensitivity of the Hall conductivity of graphene plane to gas molecule adsorption is investigated within the coherent potential approximation for the tight-binding model Hamiltonian. The results show that the Hall conductivity of system have a limit change when finite triatomic and tetratomic gas molecules adsorb and act as acceptors or donors.

Carbon nanotubes (CNTs) is one of the promising nanoscale molecular sensors used to detect gas molecules with fast response time and high sensitivity [1–3]. Similar to CNT, graphene based device is the first truly 2D material and a promising candidate for gas sensing applications [4–13]. Recently, a graphene sample has been used as a very sensitive possibility of detecting individual $H_2O$, $CO$, $NO_2$ and $NH_3$ molecules [6]. The working principle of graphene devices as gas sensors is based on the changes of their electrical conductivity. The change of conductivity could be attributed to the changes of charge carrier concentration in the graphene, therefore a little change of carrier concentration can cause a notable variation of electrical conductivity. Hence the sensor property could be based on changes in the conductivity due to adsorbed molecules on the graphene sheet that act as acceptors or donors [4–14]. In this work, using the tight-binding approach, Green's function technique and the coherent potential approximation (CPA), we consider the system under a weak magnetic field perpendicular to the graphene plane. In the limit of a weak magnetic field, the Hall conductivity of quantum transport theory agrees with the Boltzmann result [13-16]. We present the sensitivity of the Hall conductivity of system to finite triatomic and tetratomic (in the general form denoted by $XY_2$ and $XY_3$ respectively) gas molecule adsorption in the Boltzmann transport theory, when $XY_2$ acts as acceptors and $XY_3$ acts as donors. These are similar to $NO_2$ and $NH_3$ adsorption.

Let us consider the Hamiltonian of system as a random tight-binding model,

$$H = -\sum_{ij\alpha\beta} t_{ij}^{\alpha\beta} c_i^{\alpha\dagger} c_j^{\beta} + \sum_{i\alpha} (\varepsilon_i^{\alpha} - \mu)\hat{n}_i^{\alpha}, \qquad (1)$$

where $\alpha$ and $\beta$ refer to the $A_m$ or $B_m$ sites inside of the graphite Bravais lattice unit cell. Here $m = 1, 2, 3$ and 4 used for triatomic gas adsorption and $m = 1, 2, 3, 4$ and 5 used for tetratomic gas adsorption. We note that each Bravais lattice site includes two nonequivalent sites that are indicated by $A_1$ and $B_1$ (Fig. 1). Also $c_i^{\alpha\dagger}$ ($c_i^{\alpha}$) is the creation (annihilation) operator of an electron on Bravais lattice site $i$, $t_{ij}^{\alpha\beta}$'s are the usual hopping integrals between the sub-sites $\alpha$ and $\beta$ in the Bravais lattice unit cell $i$ and $j$, $\hat{n}_i^{\alpha} = c_i^{\alpha\dagger} c_i^{\alpha}$ is the number operator, $\mu$ is chemical potential and $\varepsilon_i^{\alpha}$ is the random on-site energy for sub-site $\alpha$ in the Bravais lattice unit cell. We work in units where $m_e = e = c = \hbar$ are set equal to unity.
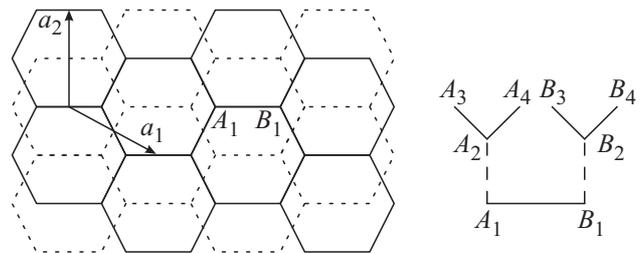


**Figure 1.** A schematic of graphene sheet. The light dashed lines illustrate the Bravais lattice unit cell. Each cell includes two nonequivalent sites, which are denoted by $A_1$ and $B_1$. $\mathbf{a}_1$ and $\mathbf{a}_2$ are the primitive vectors, $|\mathbf{a}_1| = |\mathbf{a}_2| = a = a_0\sqrt{3}$ where $a_0 = a_{cc} = 1.42\,\text{Å}$. Also figure illustrates general form of two triatomic gas molecule adsorption.

Using the Eq. (1) and the Green's function technique, the equation of motion for the electrons can be written as,

$$\sum_l [(E\mathbf{I} - \varepsilon_i + \mu\mathbf{I})\delta_{il} + \mathbf{t}_{il}]\mathbf{G}(l, j; E) = \mathbf{I}\delta_{ij}, \qquad (2)$$

where $\mathbf{G}(l, j; E)$ is the random Green's function matrix and $E = \mathscr{E} + \iota 0^+$. Because of the existence eight atoms and ten atoms in the Bravais lattice unit cell for adsorption of triatomic and tetratomic gas molecules, the Green's function needs to be written as $8 \times 8$ and $10 \times 10$ matrixes respectively.

Since in the Eq. (2) the random Green's function matrix, $\mathbf{G}(i, j; E)$, could not be calculated exactly, it should be expanded in terms of clean system Green's function matrix, $\mathbf{G}^0(i, j; E)$, and random potential [15],

$$\mathbf{G}(i, j; E) = \mathbf{G}^0(i, j; E) + \sum_{ll'} \mathbf{G}^0(i, l; E)\mathbf{V}_{ll'}\mathbf{G}(l', j; E),$$

$$(3)$$

[¶] E-mail: hamze.mousavi@gmail.com

where $\mathbf{G}^0(i, j; E)$ is given by,

$$\mathbf{G}^0(i, j; E) = \frac{n_c}{N} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}_{ij}} (E\mathbf{I} - \epsilon_{\mathbf{k}})^{-1}, \qquad (4)$$

where $n_c$ is number of atoms of a Bravais lattice site, $\mathbf{k} = k_x\mathbf{e}_x + k_y\mathbf{e}_y$ is a two-dimensional wave vector, $\mathbf{r}_{ij}$'s are three vectors that connect a $A_1$ ($B_1$) site to it's nearest neighbor sites, $\epsilon_{\mathbf{k}}$ is the Fourier transformation of $\mathbf{t}_{il}$ and $\{\mathbf{e}_x, \mathbf{e}_y\}$ are unit vectors in $xy$ graphene plane. Also, the random potential matrix, $\mathbf{V}_{ll'}$, is defined by, $\mathbf{V}_{ll'} = \varepsilon_l\delta_{ll'} + \delta\mathbf{t}_{ll'}$ and $\delta\mathbf{t}_{ll'} = t_{ll'} - t_{ll'}^0$ is hopping integral matrix deviation with respect to clean system. For adsorption of triatomic gas molecules, if in the random potential matrix, hopping to the nearest neighbors is allowed and if the molecules are adsorbed by $A_1$ and $B_1$ sub-sites, the nonzero elements of random potential matrix can be defined by,

$$\delta t_{\langle ij\rangle}^{A_1A_2} = \delta t_{\langle ij\rangle}^{A_2A_1} = \delta t_{\langle ij\rangle}^{B_1B_2} = \delta t_{\langle ij\rangle}^{B_2B_1} \equiv \delta_1, \qquad (5)$$

$$\delta t_{\langle ij\rangle}^{A_1A_3} = \delta t_{\langle ij\rangle}^{A_3A_1} = \delta t_{\langle ij\rangle}^{A_1A_4} = \delta t_{\langle ij\rangle}^{A_4A_1} = \delta t_{\langle ij\rangle}^{B_1B_3}$$

$$= \delta t_{\langle ij\rangle}^{B_3B_1} = \delta t_{\langle ij\rangle}^{B_1B_4} = \delta t_{\langle ij\rangle}^{B_4B_1} \equiv \delta_2, \qquad (6)$$

$$\delta t_{\langle ij\rangle}^{A_2A_3} = \delta t_{\langle ij\rangle}^{A_3A_2} = \delta t_{\langle ij\rangle}^{A_2A_4} = \delta t_{\langle ij\rangle}^{A_4A_2} = \delta t_{\langle ij\rangle}^{B_2B_3}$$

$$= \delta t_{\langle ij\rangle}^{B_3B_2} = \delta t_{\langle ij\rangle}^{B_2B_4} = \delta t_{\langle ij\rangle}^{B_4B_2} \equiv \delta_3, \qquad (7)$$

$$\delta t_{\langle ij\rangle}^{A_3A_4} = \delta t_{\langle ij\rangle}^{A_4A_3} = \delta t_{\langle ij\rangle}^{B_3B_4} = \delta t_{\langle ij\rangle}^{B_4B_3} \equiv \delta_4. \qquad (8)$$

Also we define $\varepsilon_1$ as different between on-site energies of host carbon atom and adsorbed gas $X$ atom and $\varepsilon_2$ as different between on-site energies of $X$ atom and $Y$ atoms. The chemical potential takes, $\mu = 0$, which is corresponding to contribution of one electron per carbon atom in the graphene system. Just nearest neighbors hopping are allowed and neglected others, so the nonzero elements of hopping matrix can be written as, $t_{\langle ij\rangle}^{A_1B_1} = t_{\langle ij\rangle}^{B_1A_1} \equiv t \simeq 2.7\,\text{eV}$.

The Dyson equation for the average Green's function corresponding to Eq. (3) can be written as,

$$\bar{\mathbf{G}}(i, j; E) = \mathbf{G}^0(i, j; E)$$

$$+ \sum_{ll'} \mathbf{G}^0(i, l; E)\mathbf{\Sigma}(l, l'; E)\bar{\mathbf{G}}(l', j; E), \qquad (9)$$

where the self-energy, $\mathbf{\Sigma}(l, l'; E)$, is defined by,

$$\sum_{l'} \mathbf{\Sigma}(l, l'; E)\bar{\mathbf{G}}(l', j; E) = \sum_{l'} \langle \mathbf{V}_{ll'}\mathbf{G}(l', j; E)\rangle. \qquad (10)$$

Here, $\langle\cdots\rangle$ denotes configurational averaging. The Fourier transformation of Eq. (9) is as following,

$$\bar{G}(i, j; E) = \frac{n_c}{N} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}_{ij}} \left\{ \left[\mathbf{G}^0(\mathbf{k}; E)\right]^{-1} - \Sigma(\mathbf{k}; E)\right\}^{-1}, \qquad (11)$$

where $\Sigma(\mathbf{k}; E)$ is the Fourier transformation of the self-energy.

In general there is no analytical solution for such random systems, hence it should be solved approximately. Since the gas molecules are adsorbed randomly by the graphene's atoms, the Green's function in the equation of motion is random and the local behavior could be different from whole system behavior, hence we should calculate configurational average properties. We treat this in the CPA formalism to take the average over all possible adsorbed molecule configurations. In the CPA method, inter-site correlations are neglected and each lattice site is replaced by an effective site except one, which is called the impurity site and is denoted by $i$. Then the self-energy is local and takes the same value for all sites, $\Sigma(i, j; E) = \Sigma(E)\delta_{ij}$, so the Eqs. (10) and (11) at impurity site reduce to the following,

$$\Sigma(E)\bar{\mathbf{G}}(i, i; E) = \langle \mathbf{V}_{ii}\mathbf{G}_{\text{imp}}(i, i; E)\rangle, \qquad (12)$$

$$\bar{\mathbf{G}}(i, i; E) = \frac{n_c}{N} \sum_{\mathbf{k}} \left\{ \left[\mathbf{G}^0(\mathbf{k}; E)\right]^{-1} - \mathbf{\Sigma}(E)\right\}^{-1}. \qquad (13)$$

Using Eqs. (3) and (9), the impurity Green's function, $\mathbf{G}_{\text{imp}}(i, i; E)$, relates to the average Green's function, $\bar{\mathbf{G}}(i, i; E)$, by,

$$\mathbf{G}_{\text{imp}}(i, i; E) = \bar{\mathbf{G}}(i, i; E)$$

$$+ \bar{\mathbf{G}}(i, i; E)\left[\mathbf{V}_{ii} - \mathbf{\Sigma}(E)\right]\mathbf{G}_{\text{imp}}(i, i; E). \qquad (14)$$

Finally, the new average Green's function, $\bar{\mathbf{G}}(i, i; E)$, is obtained by taking average over all possible impurity site configurations,

$$\bar{\mathbf{G}}(i, i; E) = \langle \mathbf{G}_{\text{imp}}(i, i; E)\rangle. \qquad (15)$$

The Eqs. (3)–(15) should be solved self-consistently to provide average Green's function, $\bar{\mathbf{G}}(i, i; E)$, in the CPA approach.

Now we address the question of the Hall conductivity on the basis of the Kubo formula [17]. When an electric field is applied to a graphene plane subject to a perpendicular magnetic field, $\mathbf{B} = B_0\mathbf{e}_z$, a current in the direction perpendicular to the electric field is observed. The current is called the Hall current and the Hall conductivity, $\sigma_{xy}$, is the ratio of the current to the electric potential. Our starting for Hall conductivity formula is from [17], $\sigma_{xy} = \int_{-\infty}^{+\infty} d\mathscr{E}\left[-\partial_{\mathscr{E}}f(\mathscr{E})\right]\sigma_{xy}(\mathscr{E})$, where $f(\mathscr{E})$ is Fermi–Dirac distribution function and energy-dependent Hall conductivity, $\sigma_{xy}(\mathscr{E})$, is given by the Boltzmann transport equation [18],

$$\sigma_{xy}(\mathscr{E}) = \frac{4B_0}{3\pi\Omega} \sum_{\mathbf{k}} \left\{ \left[v_x(\mathbf{k})^2 M_{yy}^{-1}(\mathbf{k}) - v_x(\mathbf{k})v_y(\mathbf{k})M_{xy}^{-1}(\mathbf{k})\right]\right.$$

$$\left. \times \left[-\Im\bar{G}(\mathbf{k}; E)\right]^3\right\}, \qquad (16)$$

here $B_0$ is a weak magnetic field perpendicular to the graphene plane, $\Omega$ is the total volume of the system

and $v_\mu$ is a Cartesian component of the velocity operator that can be calculated by, $v_\mu = \partial_{\mathbf{k}_\mu} \mathscr{E}_0(\mathbf{k})$. Also

$$\mathscr{E}_0(\mathbf{k}) = \pm t \left\{ 3 + 2 \left[ \cos(\mathbf{k} \cdot \boldsymbol{\rho}_1) + \cos(\mathbf{k} \cdot \boldsymbol{\rho}_2) + \cos(\mathbf{k} \cdot \boldsymbol{\rho}_3) \right] \right\}^{\frac{1}{2}},$$

where $\boldsymbol{\rho}_1$, $\boldsymbol{\rho}_2$ and $\boldsymbol{\rho}_3$ vectors are defined by $\boldsymbol{\rho}_1 = \mathbf{a}_2$, $\boldsymbol{\rho}_2 = \mathbf{a}_1 + \mathbf{a}_2$, $\boldsymbol{\rho}_3 = \mathbf{a}_1$. We note that the mass operators are defined by, $M_{yy}^{-1}(\mathbf{k}) = \partial_{k_y} v_y(\mathbf{k})$ and $M_{xy}^{-1}(\mathbf{k}) = \partial_{k_x} v_y(\mathbf{k})$ that calculated as,

$$M_{yy}^{-1}(\mathbf{k}) = -\frac{a^2 t^2}{4\mathscr{E}_0(\mathbf{k})} \left\{ \Delta(\mathbf{k}) - \left( \frac{t}{\mathscr{E}_0(\mathbf{k})} \right)^2 [\xi(\mathbf{k}) + \xi(\mathbf{k})]^2 \right\}, \tag{17}$$

$$M_{xy}^{-1}(\mathbf{k}) = -\frac{\sqrt{3} a^2 t^2}{4\mathscr{E}_0(\mathbf{k})} \left\{ \Lambda(\mathbf{k}) - \left( \frac{t}{\mathscr{E}_0(\mathbf{k})} \right)^2 [\xi^2(\mathbf{k}) - \xi^2(\mathbf{k})] \right\}, \tag{18}$$

where

$$\xi(\mathbf{k}) = \sin(\mathbf{k} \cdot \boldsymbol{\rho}_1) + \sin(\mathbf{k} \cdot \boldsymbol{\rho}_2),$$
$$\zeta(\mathbf{k}) = \sin(\mathbf{k} \cdot \boldsymbol{\rho}_1) - \sin(\mathbf{k} \cdot \boldsymbol{\rho}_3),$$
$$\Delta(\mathbf{k}) = 4\cos(\mathbf{k} \cdot \boldsymbol{\rho}_1) + \cos(\mathbf{k} \cdot \boldsymbol{\rho}_2) + \cos(\mathbf{k} \cdot \boldsymbol{\rho}_3)$$

and

$$\Lambda(\mathbf{k}) = \cos(\mathbf{k} \cdot \boldsymbol{\rho}_2) - \cos(\mathbf{k} \cdot \boldsymbol{\rho}_3).$$

So the energy-dependent Hall conductivity of system can be written as,

$$\sigma_{xy}(\mathscr{E}) = \sigma_0 \sum_{\mathbf{k}} \left\{ \left[ \left( \frac{\sqrt{3}[\xi(\mathbf{k}) - \zeta(\mathbf{k})]^2}{\mathscr{E}_0(\mathbf{k})^3} \right) \right. \right.$$
$$\times \left[ \Delta(\mathbf{k}) + \left( \frac{t}{\mathscr{E}_0(\mathbf{k})} \right)^2 (\xi(\mathbf{k}) + \zeta(\mathbf{k}))^2 \right] - \left( \frac{\xi(\mathbf{k})^2 - \zeta(\mathbf{k})^2}{\mathscr{E}_0(\mathbf{k})^3} \right)$$
$$\left. \left. \times \left[ \Lambda(\mathbf{k}) + \left( \frac{t}{\mathscr{E}_0(\mathbf{k})} \right)^2 (\xi(\mathbf{k})^2 - \zeta(\mathbf{k})^2) \right] \right] [-\Im \bar{G}(\mathbf{k}; E)]^3 \right\}, \tag{19}$$

here $\sigma_0$ is a constant value. Also the average Green's function, $\bar{G}(\mathbf{k}; E)$, should be calculated in the CPA formalism (Eqs. (3)–(15)).

As we mentioned, the gas molecules are adsorbed randomly by the graphene's atoms, so the Green's function should be calculated in the configurational average method. By calculation of the average Green's function in the CPA based on the tight-binding model, the effects of finite triatomic and tetratomic gas molecule adsorption on the Hall conductivity of graphene are studied. To compare our conclusions with the theoretical and experimental results, we vary the hopping integral deviations and on-site energies. Also we set the hopping integral deviations and on-site energies for two cases of $XY_2$ as charge acceptors and $XY_3$ as charge donors. Then using by these parameters we investigate the sensitivity of the Hall conductivity of system to finite gas molecule adsorption. First we set the on-site energies and hopping integral deviations, $\varepsilon_1 = -0.15t$,

$\varepsilon_2 = -0.12t$, $\delta_1 = -0.10t$, $\delta_2 = -0.05t$, $\delta_3 = +0.10t$ and $\delta_4 = +0.05t$, when $XY_2$ is identified as charge acceptors. Fig. 2, $b$ illustrates our results in this case. For small concentrations of gas adsorption, $c = 0.010$ and $c = 0.020$, we
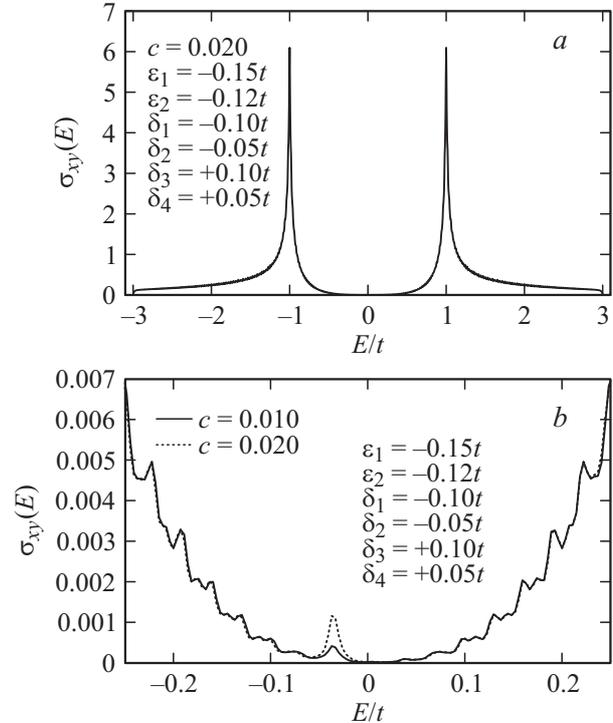


**Figure 2.** Show the energy-dependent Hall conductivity of graphene, when triatomic gas molecules are adsorbed. $a)$ — in full range of energy, concentration of gas adsorption is $c = 0.020$. The on-site energies and hopping deviations are chosen to be $\varepsilon_1 = -0.15t$, $\varepsilon_2 = -0.12t$, $\delta_1 = -0.10t$, $\delta_2 = -0.05t$, $\delta_3 = +0.10t$ and $\delta_4 = +0.05t$. $b)$ — concentrations of gas adsorption are $c = 0.010$ and $c = 0.020$. The Hall conductivity have a change caused by the adsorption of these molecules.
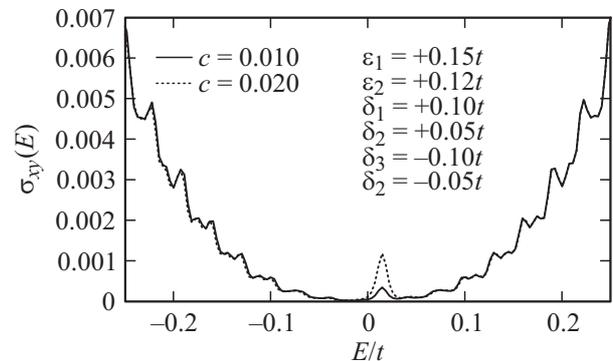


**Figure 3.** The energy-dependent Hall conductivity of graphene when tetratomic gas molecules are adsorbed. The on-site energies and hopping deviations are chosen to be $\varepsilon_1 = +0.15t$, $\varepsilon_2 = +0.12t$, $\delta_1 = +0.10t$, $\delta_2 = +0.05t$, $\delta_3 = -0.10t$ and $\delta_4 = -0.05t$. Concentrations of gas adsorption are $c = 0.010$ and $c = 0.020$. The Hall conductivity have a change caused by the adsorption of these molecules.

found that the Hall conductivity is sensitive to the adsorption of these gases. This is consistent with the reported results for $NO_2$ adsorption [6]. Second we use the on-site energies and hopping integral deviations, $\varepsilon_1 = +0.15t$, $\varepsilon_2 = +0.12t$, $\delta_1 = +0.10t$, $\delta_2 = +0.05t$, $\delta_3 = -0.10t$ and $\delta_4 = -0.05t$, while $XY_3$ acts as charge donors. Concentrations of gas adsorption are $c = 0.010$ and $c = 0.020$. Fig. 3 shows that the Hall conductivity of graphene is sensitive to the adsorption of these gases. This is similar to $NH_3$ adsorption [6]. In conclusions, we found that when the adsorbed gas molecules are identified charge acceptors or charge donors, the Hall conductivity of the graphene have a limit change caused by the adsorption of these molecules. Our results are in agreement with the theoretical and experimental reports for $NO_2$ and $NH_3$ adsorption.

## References

[1] P.G. Collins, K. Bradley, M. Ishigami, A. Zettl. Science, **287**, 1801 (2000).
[2] J. Kong, N.R. Franklin, C. Zhou, M.G. Chapline, S. Peng, K. Cho, H. Dai. Science, **287**, 622 (2000).
[3] S. Peng, K. Cho. Nano Letth., **3**, 513 (2003).
[4] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov. Science, **666**, 306 (2004).
[5] K.S. Novoselov, D. Jiang, F. Schedin, T.J. Booth, V.V. Khotkevich, S.V. Morozov, A.K. Geim. Proc. Nat. Acad. Sci. USA, **102**, 10 451 (2005).
[6] F. Schedin, A.K. Geim, S.V. Morozov, E.W. Hill, P. Blake, M.I. Katsnelson, K.S. Novoselov. Nature Mater., **6**, 652 (2007).
[7] T.O. Wehling, K.S. Novoselov, S.V. Morozov, E.E. Vdovin, M.I. Katsnelson, A.K. Geim, A.I. Lichtenstein. Nano Lett., **8**, 173 (2008).
[8] O. Leenaerts, B. Partoens, F.M. Peeters. Phys. Rev. B, **77**, 125 416 (2008).
[9] O. Leenaerts, B. Partoens, F.M. Peeters. Microelectron. J., **40**, 860 (2009).
[10] O. Leenaerts, B. Partoens, F.M. Peeters. Appl. Phys. Lett., **92**, 243 125 (2008).
[11] I. Zanella, S. Guerini, S.B. Fagan, J.M. Filho, A.G.S. Filho. Phys. Rev. B, **77**, 073 404 (2008).
[12] D. Henwood, J.D. Carey. Phys. Rev. B, **75**, 245 413 (2007).
[13] Y. Hatsugai. Phys. Rev. B, **79**, 075 429 (2009).
[14] Y. Zheng, T. Ando. Phys. Rev. B, **65**, 245 420 (2002).
[15] R.J. Elliot, J.A. Krumhansl, P.L. Leath. Rev. Mod. Phys., **46**, 465 (1974).
[16] H. Mousavi. Sol. St. Commun., **150**, 755 (2010).
[17] B. Velicky. Phys. Rev., **184**, 614 (1969).
[18] H. Fukuyama. Progr. Theor. Phys., **42**, 1284 (1969).

*Редактор Т.А. Полянская*