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Charge transfer in the vertical structures formed by two-dimensional layers

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Electronic structures of superlattices and encapsulated layers are obtained by Green's function method. The simple scheme for estimation of interlayer charge transfer is proposed. As an example, layers of graphene and graphene-like compounds are considered.

Keywords: 2D structure, superlattice encapsulated layer

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After the advent of graphene topics the intensive search for new two-dimensional (2D) compounds and heterostructures based on them was initiated [1–3]. Now there are hundreds of known 2D-materials [4–6] possible in theory and different schemes to grow superlattices (SL) of 2D-layers (hereinafter referred to as 2DSL) [7–9]. In [10] proposed a simple scheme to describe the electron spectrum of 2DSL making it possible to take into account the interlayer interaction. In this work we use results of [10] to determine the charge transfer between the layers of 2DSL.

Let us consider a vertical structure composed of alternating sheets 1 and 2 that can be described in the isolated form by Green's functions $G_{1,2}(\boldsymbol{\kappa}_{1,2};\ \omega)$, where ω is the energy variable, $\boldsymbol{\kappa}_{1,2}$ are wave vectors for the electron movement in the plane (x, y, pd) of the sheet ($p = 0,\ 1,\ 2,\dots\ N$; d is the distance between layers in the 2DSL). Now we include the interlayer interaction V. In the mode of weak interplanar coupling in the diagonal approximation (see [10]) Green's functions $\tilde{G}_{1,2}(\boldsymbol{\kappa}_{1,2}k_z;\omega)$ of the 2DSL layers can be written as follows

$$\begin{aligned}\tilde{G}^{-1}_{1,2}(\boldsymbol{\kappa}_{1,2}, k_z;\omega) &= G^{-1}_{1,2}(\boldsymbol{\kappa}_{1,2};\omega)\\ &- 4\cos^2(k_z d)\Lambda_{2,1}(\omega) + i0^+,\end{aligned} \qquad (1)$$

where $\Lambda_{1,2}(\omega) = V^2 \int\limits_{-\infty}^{\infty} \rho_{1,2}(\omega')(\omega-\omega')^{-1}d\omega'$ are energy-shift functions of layer 2 (1) under the influence of layer 1 (2) [10], $\rho_{1,2}(\omega) = \pi^{-1}N^{-1}_{\boldsymbol{\kappa}_{1,2}} \sum\limits_{\boldsymbol{\kappa}_{1,2}} \mathrm{Im}G(\boldsymbol{\kappa}_{1,2})$ are densities of states of free layers 1 and 2 ($N_{\boldsymbol{\kappa}_{1,2}}$ are numbers of states $\boldsymbol{\kappa}_{1,2}$), k_z is the wave vector for the electron movement in vertical direction (along the SL). As far as we are not aimed here at obtaining precise results, but only estimating the charge transfer between layers, we average expression (1) over k_z. Then, instead of (1) we get

$$\begin{aligned}\langle \tilde{G}^{-1}_{1,2}(\boldsymbol{\kappa}_{1,2}, k_z;\omega)\rangle_{k_z} &= \bar{G}^{-1}_{1,2}(\boldsymbol{\kappa}_{1,2};\omega)\\ &= G^{-1}_{1,2}(\boldsymbol{\kappa}_{1,2};\omega) - 2\Lambda_{2,1}(\omega) + i0^+.\end{aligned} \qquad (2)$$

Note that this substitution is reasoned in the mode of weak coupling interaction, because the z-band can be considered narrow (dispersion-free) as compared to 2D-band.

Let us consider graphene (Gr) and graphene-like compounds (GLC) as layers that compose the 2DSL. In the low-energy approximation the density of states of free-standing GLC and shift function $\Lambda_{\mathrm{GLC}}(\omega)$ can be respectively written as follows

$$\rho_{\mathrm{GLC}}(\Omega) = \begin{cases} 2|\Omega|/\xi^2, & \Delta \leqslant |\Omega| \leqslant R,\\ 0, & |\Omega| < \Delta,\ |\Omega| > R,\end{cases}$$

$$\Lambda_{\mathrm{GLC}}(\Omega) = \frac{2V^2\Omega}{\xi^2}\ln\left|\frac{\Omega^2-\Delta^2}{\Omega^2-R^2}\right|, \qquad (3)$$

where $\Omega = \omega - \varepsilon$, $\xi = \sqrt{2\pi\sqrt{3}}t$, $R = \sqrt{\xi^2+\Delta^2}$, t is the electron hopping energy between the nearest atoms in a layer, 2Δ is the band gap width of the free-standing GLC, ε is the energy of the band gap center [11]. Assuming $\Delta = 0$ and $\varepsilon = \varepsilon_D$, where ε_D is the Dirac point, we get the density of states of the free-standing graphene $\rho_{Gr}(\omega)$. Let us consider that the density of states of lattice layers $\bar{\rho}_{\mathrm{GLC}}$ is determined by expression (3), where Ω is to be replaced with $\bar{\Omega} = \omega - \bar{\varepsilon}$, where $\bar{\varepsilon} = \varepsilon + 2\Lambda_{n.n.l.}(\omega)$ and $\Lambda_{n.n.l.}(\omega)$ is the shift of electron states caused by the nearest neighboring layer. Let us make the approximation, which is widely used in the theory of adsorption [12] and assume $\bar{\varepsilon} = \varepsilon + 2\Lambda_{n.n.l.}(\varepsilon)$. Occupation numbers of atoms in layers at zero temperature are $\bar{n}_{1,2} = 2\int\limits_{-\infty}^{\mu}\bar{\rho}_{1,2}(\omega)d\omega$, where μ is the chemical potential, which position is determined from the charge conseervation condition $\bar{n}_1 + \bar{n}_2 = n_1 + n_2$, where $n_{1,2}$ are occupation numbers of layers without interaction. The charge transfer between layers is $\nu_{1,2} = \bar{n}_{1,2} - n_{1,2}$, from which we get $\nu_1 = -\nu_2$.

Let's start from the lattice formed by layers Gr and GLC, and let's consider Gr and GLC undoped, so that $n_1 = n_2 = 1$. If $\bar{\varepsilon}_D < \bar{\varepsilon} - \Delta$, electrons transfer from GLC layers to Gr layers. In this case $\nu_{Gr} = 2(\mu - \bar{\varepsilon}_D)^2/\xi_{Gr}^2$ and $\nu_{\mathrm{GLC}} = -2(\mu - \bar{\varepsilon})^2/\xi_{\mathrm{GLC}}^2$, from which

$$\mu = \frac{\bar{\varepsilon}_D \xi_{\mathrm{GLC}} + \bar{\varepsilon}\xi_{Gr}}{\xi_{Gr} + \xi_{\mathrm{GLC}}},$$

$$\nu_{Gr} = 2\frac{(\bar{\varepsilon} - \bar{\varepsilon}_D)^2}{(\xi_{Gr} + \xi_{\mathrm{GLC}})^2}. \tag{4}$$

If $\bar{\varepsilon}_D > \bar{\varepsilon} + \Delta$, electrons transfer from Gr layers to GLC layers. Then $\nu_{Gr} = -2(\mu - \bar{\varepsilon}_D)^2/\xi_{Gr}^2$ and $\nu_{\mathrm{GLC}} = 2(\mu - \bar{\varepsilon})^2/\xi_{\mathrm{GLC}}^2$, from which we again get expression (4) for μ, and for ν_{Gr} a plus to minus change is needed. In the case when $\bar{\varepsilon} - \Delta < \bar{\varepsilon}_D < \bar{\varepsilon} + \Delta$, no charge transfer occurs. If $\varepsilon = \varepsilon_D$ (which approximately corresponds to graphene and hexagonal boron nitride [10]), there is no charge transfer between layers as well. Estimates of t_{Gr} and t_{GLC}, Δ for $\mathrm{A_4B_4}$ and $\mathrm{A_3B_5}$ 2D-compounds are presented in [13], values of $-\varepsilon$ and $-\varepsilon_D$ with respect to the vacuum are equal to corresponding work functions. Due to the variety of parameters, the conclusion on how exactly the consideration of coupling interaction affects the charge transition can only be made for specific 2DSLs.

For 2DSLs composed of GLC1 and GLC2 layers, $\nu_{1,2} = \pm 2(\mu - \bar{\varepsilon}_{1,2})^2/\xi_{1,2}^2$, so that

$$\mu = \frac{\bar{\varepsilon}_1 \xi_2 + \bar{\varepsilon}_2 \xi_1}{\xi_1 + \xi_2},$$

$$\nu_1 = 2\frac{(\bar{\varepsilon}_1 - \bar{\varepsilon}_2)^2}{(\xi_1 + \xi_2)^2}. \tag{5}$$

If $\bar{\varepsilon}_1 - \Delta_1 < \bar{\varepsilon}_2 - \Delta_2$, electrons transfer from GLC2 layers to GLC1 layers, and if $\bar{\varepsilon}_1 + \Delta_1 > \bar{\varepsilon}_2 + \Delta_2$, the reverse process takes place. If $\varepsilon_1 = \varepsilon_2$ (which is approximately valid for AlN and GaN sheets [10]), there is no charge transfer.

Now let us estimate the charge transfer in planar encapsulated structures. For this purpose let us consider N vertically arranged arbitrary 2D-layers enclosed between massive top and bottom slabs. Using the results of [14], we get the following representation for Green's functions of layers $g_p(\omega)$, where p is the layer number

$$\begin{gathered} g_N^{-1}(\omega) = \omega - \varepsilon_N(\boldsymbol{\kappa}_N) - \Lambda_{top}(\omega) - \Lambda_{N-1}(\omega) + i0^+, \\ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \\ g_p^{-1}(\omega) = \omega - \varepsilon_p(\boldsymbol{\kappa}_p) - \Lambda_{p+1}(\omega) - \Lambda_{p-1}(\omega) + i0^+, \\ 1 \leqslant p \leqslant N-1, \\ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \\ g_1^{-1}(\omega) = \omega - \varepsilon_1(\boldsymbol{\kappa}_1) - \Lambda_2(\omega) - \Lambda_{bot}(\omega) + i0^+, \end{gathered} \tag{6}$$

where $\Lambda_{top(bot)}(\omega)$ is the shift of electron states induced by the top (bottom) slab. Let us consider as an example an encapsulated layer of graphene located between the top metal slab (contact pad) and bottom slab — a substrate made of semiconductor (for example, Si, SiC) or dielectric material (for example, BN, $\mathrm{SiO_2}$). In case of nonmagnetic transition metal (TM) we can write the following

$$\rho_{\mathrm{TM}}(\omega) = \begin{cases} 10/W_d, & |\Omega_m| \leqslant W_d/2, \\ 0, & |\Omega_m| > W_d/2, \end{cases}$$

$$\Lambda_{\mathrm{TM}}(\omega) = (\Gamma_m/\pi)\ln\left|\frac{\Omega_m + W_d/2}{\Omega_m - W_d/2}\right|, \tag{7}$$

where $\Omega_m = \omega - \varepsilon_m$; $\Gamma_m = 10\pi V_m^2/W_d$; ε_m is the energy of the center of d-band of the TM, which width is W_d; V_m is the matrix element of metal–graphene interaction (Friedel model) [15]. For the semiconductor (dielectric) we can write the following

$$\rho_{\mathrm{SC}}(\omega) = \begin{cases} \rho_s, & |\Omega_s| \geqslant E_g/2, \\ 0, & |\Omega_s| < E_g/2, \end{cases}$$

$$\Lambda_{\mathrm{SC}}(\omega) = (\Gamma_s/\pi)\ln\left|\frac{\Omega_s - E_g/2}{\Omega_s + E_g/2}\right|, \tag{8}$$

where $\Omega_s = \omega - \varepsilon_s$, $\Gamma_s = 4\pi V_s^2/W_s$; W_s is the width of the conduction band and the valence band; ε_s is the energy of the band gap center E_g; V_s is the matrix element of the substrate–graphene interaction (Haldane–Anderson model) [16]. Assuming $\bar{\varepsilon}_D = \varepsilon_D + \Lambda_{\mathrm{TM}}(\varepsilon_D) + \Lambda_{\mathrm{SC}}(\varepsilon_D)$, we get $|\nu_{Gr}| = 2(\mu - \bar{\varepsilon}_D)^2/\xi_{Gr}^2$, where the position of μ is determined by the slabs. If $\mu < \bar{\varepsilon}_D$, we have $\nu_{Gr} < 0$, i.e. outflow of electrons from the graphene layer; if $\mu > \bar{\varepsilon}_D$, we have $\nu_{Gr} > 0$, i.e. inflow of electrons into the graphene layer. Also, a case is possible when $\Lambda_{\mathrm{TM}}(\varepsilon_D) + \Lambda_{\mathrm{SC}}(\varepsilon_D) = 0$ and $\bar{\varepsilon}_D = \varepsilon_D$.

Thus, a simple scheme to estimate the charge transfer is proposed in the work that allows obtaining analytical results. The weak-coupling regime (van der Waals interaction) was considered not only because of simplicity considerations, but also on the ground that Gr and GLC retain their original properties in this case only.

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Conflict of interest

The authors declare that they have no conflict of interest.

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