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To the model description of electronic spectrum for the graphene-like Janus structures

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Model of $C{-}AB{-}D$ Janus structure as the compound formed by the interacting through atoms A and B dimers $A{-}C$ and $B{-}D$, where A and B atoms are in the sites of two-dimensional hexagonal lattice and C and D atoms are on the opposite sides from AB list is proposed. In the scope of tight-binding theory and Green's function method general equation for the dispersion low is obtained. The particular cases of $C{-}AA{-}D$ and $A{-}AB{-}B$ compounds are considered and analytical expressions for their electronic spectra is fulfilled. The effect of the external mechanical deformation on the band parameters including effective masses is examined. Problem of the magnetic states in Janus compounds is discussed.

Keywords: model of interacting dimers, electronic spectrum, effect of deformation, magnetic states.

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1. Introduction

Two-dimensional Janus compounds are structures with top and bottom surfaces built from different atoms or molecules [1–3]. The research of electron spectrum of these structures started in 2009 from graphone–graphene, where every second carbon atom is bonded to a hydrogen atom with the hydrogen atoms laying on one side of the graphene sheet (the same structure can be considered as graphan where hydrogen is deleted from one of its surfaces) [4]. Virtually at the same time an interest has arisen to the structures where the place of hydrogen atoms is occupied by halogen atoms, and graphene is replaced by graphene-like compounds (GLC), such as hexagonal boron nitride (h-BN), silicene, germanene, etc. [5,6]. A great attention is paid to the Janus structures based on dichalcogenides of transition metals [7,8]. A special place is held by the research of magnetic states in Janus structures [4,9,10].

To the author's knowledge, all theoretical works in this field are performed within the framework of DFT (density functional theory). In this paper we suggest a simple model of graphene-like Janus compounds (J-GLC), that makes it possible to get analytical expressions for band characteristics (including effective masses of carriers) and estimate the impact of external mechanical deformation on values of these characteristics. Also, we discuss the issue of J-GLC magnetization.

2. Electron spectrum: general relationships

Structural model of hexagonal fragment of J-GLC is shown in the figure below. In the following we use the results of [11], where a symmetrical graphene-like structure was considered, which is different from the J-GLC structure in that the same C atoms are located on both sides of the GLC-sheet.

As in [11], let us start from a set of two different dimers composed of A, C and B, D atoms related to t_{ac} and t_{bd} transition integrals, respectively. Let us build a hexagonal two-dimensional lattice from these dimers by introducing t_{ab} interaction between the closest atoms A and B. We denote this structure as $C{-}AB{-}D$. Generalizing the results of [11], we get Green functions for J-GLC in the following form:

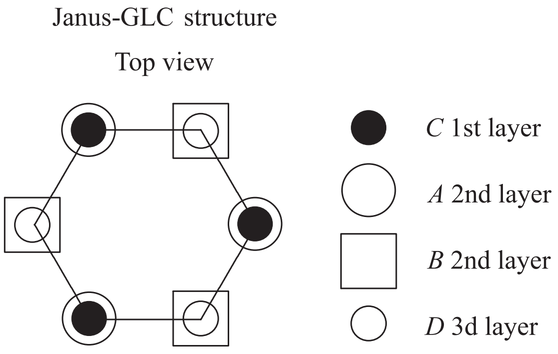
$$G^{AA(BB)}(\omega,\mathbf{k}) = \frac{G^{A(B)}(\omega)}{1 - t_{ab}^2 G^A(\omega) G^B(\omega) f^2(\mathbf{k})},$$

$$G^{A(B)}(\omega) = \frac{g^{A(B)}(\omega)}{1 - t_{a(b)c(d)}^2 g^{A(B)}(\omega) g^{C(D)}(\omega)}, \qquad (1)$$

$$f(\mathbf{k}) = \sqrt{3 + 2\cos(k_x a\sqrt{3}) + 4\cos(k_x a\sqrt{3}/2)\cos(3k_y a/2)}.$$

Here ω — energy variable, $g^I(\omega) = (\omega - \varepsilon_i + i0^+)^{-1}$ — atomic Green function, where ε_i — atom level energy $i = a, b, c, d$; $\mathbf{k} = (k_x, k_y, 0)$ — wave vector for electron motion in the $(x, y, 0)$ plane, a — distance between the closest atoms A and B. The electron spectrum of the system can be obtained from the following equation: $\operatorname{Re} D(\omega, \mathbf{k}) = 0$, where

$$D(\omega,\mathbf{k}) = \left[1 - t_{ac}^2 g^A(\omega) g^C(\omega)\right]\left[1 - t_{bd}^2 g^B(\omega) g^D(\omega)\right] - t_{ab}^2 g^A(\omega) g^B(\omega) f^2(\mathbf{k}), \qquad (2)$$



Hexagonal fragment of structure of a graphene-like Janus compound (J-GLC).

from which we get the following equation

$$(\Omega_a\Omega_c - t_{ac}^2)(\Omega_b\Omega_d - t_{bd}^2) - \Omega_c\Omega_d\, t_{ab}^2 f^2(\mathbf{k}) = 0, \qquad (3)$$

where $\Omega_i = \omega - \varepsilon_i$. With $t_{ac} = t_{bd} = 0$ we get two local atom levels $\omega_{c,d} = \varepsilon_{c(d)}$ and two GLC-bands $\omega_{ab}^{\pm}(\mathbf{k}) = \varepsilon_{ab} \pm \sqrt{\Delta_{ab}^2 + t_{ab}^2 f^2(\mathbf{k})}$, where $\bar{\varepsilon}_{ab} = (\varepsilon_a + \varepsilon_b)/2$ and $\Delta_{ab} = |\varepsilon_a - \varepsilon_b|/2$. With $t_{ab} = 0$ we have four local levels of dimers $A-C$ and $B-D$ with energies $\bar{\omega}_{ac}^{\pm} = \varepsilon_{ac} \pm R_{ac}$ and $\bar{\omega}_{bd}^{\pm} = \varepsilon_{bd} \pm R_{bd}$, where $R_{ij} = \sqrt{\Delta_{ij}^2 + t_{ij}^2}$, $\bar{\varepsilon}_{ij} = (\varepsilon_i + \varepsilon_j)/2$ and $\Delta_{ij} = |\varepsilon_i - \varepsilon_j|/2\Delta_{ij}$. In the general case, the solution to equation (3) is too cumbersome and thus it yields little information. However, it's easy to show that with $\varepsilon_a = -\varepsilon_b$, $\varepsilon_c = -\varepsilon_d$ and $t_{ac} = t_{bd}$ equation (3) becomes a biquadratic equation. Therefore, in the following, we consider special cases and show specific J-GLCs that can be associated with these cases.

3. Special cases and J-GLCs corresponding to them

3.1. $C-AA-D$ compounds

Suppose $\varepsilon_a = \varepsilon_b = 0$, $\varepsilon_c = -\varepsilon_d = e > 0$, $t_{ac} = t_{bd} = t_\perp$, $t_{ab} = t$ (variant 1). Then we get solution to equation (3) in the following form:

$$E_{1\pm}^{\pm}(\mathbf{k}) = \pm\sqrt{\left[B_1(\mathbf{k}) \pm R_1(\mathbf{k})\right]/\mathbf{2}},$$

$$R_1(\mathbf{k}) = \sqrt{\left[e^2 - t^2 f^2(\mathbf{k})\right]^2 + 4t_\perp^2\left[e^2 + t^2 f^2(\mathbf{k})\right]}, \qquad (4)$$

where $B_1(\mathbf{k}) = e^2 + 2t_\perp^2 + t^2 f^2(\mathbf{k})$, upper signs of bands $E_{1\pm}^{\pm}(\mathbf{k})$ correspond to signs before the external root sign, while lower signs correspond to signs before the internal root sign $R_1(\mathbf{k})$. In the following, we focus on low-energy bands $E_{1-}^{+}(\mathbf{k}) = E_{C1}(\mathbf{k})$ and $E_{1-}^{-}(\mathbf{k}) = E_{V1}(\mathbf{k})$, where C and V subscripts are related to conduction band and valence band.

Taking into account that $f(\Gamma) = 3$, $f(\mathrm{M}) = 1$ and $f(\mathrm{K}) = 0$, where Γ, M and K are points of the Brillouin zone in a two-dimensional hexagonal lattice, we get:

$$B_{1\Gamma} = e^2 + 2t_\perp^2 + 9t^2, \quad B_{1\mathrm{M}} = e^2 + 2t_\perp^2 + t^2,$$

$$B_{1\mathrm{K}} = e^2 + 2t_\perp^2, \quad R_{1\Gamma} = \sqrt{(e^2 - 9t^2)^2 + 4t_\perp^2(e^2 + 9t^2)},$$

$$R_{1\mathrm{M}} = \sqrt{(e^2 - t^2)^2 + 4t_\perp^2(e^2 + t^2)}, \quad R_{1\mathrm{K}} = e\sqrt{e^2 + 4t_\perp^2}.$$

Gaps between extreme values of low-energy bands in points of $\Gamma(\mathrm{M},\mathrm{K})$ are equal to

$$\Delta_{1\Gamma(\mathrm{M},\mathrm{K})} = \sqrt{2(B_{1\Gamma(\mathrm{M},\mathrm{K})} - R_{1\Gamma(\mathrm{M},\mathrm{K})})}.$$

Now we demonstrate, that within variant 1 it is possible to approximately describe, for example, the Cl−graphene (Gr)−Br compound. In principle, it is possible to choose appropriate C and D decorating atom pairs and for other two-dimensional hexagonal single-element structures, such as silicene, germanene, etc. known as Xenens [12.13]. Here we restrict the discussion to the case of asymmetrically decorated graphene.

Assuming that σ-bond of carbon atoms (A and B) is implemented by $|sp^2\rangle$-orbitals and taking the energy $\varepsilon_{sp2}(\mathrm{Gr}) = (\varepsilon_s + 2\varepsilon_p)/3 = -11.82\,\mathrm{eV}$ relative to vacuum (we used Herman−Skillman atomic term tables [14]) as the reference point, we get energies of p-levels of chlorine and bromine atoms equal to -0.49 and $0.62\,\mathrm{eV}$, respectively. To determine transition integrals t and $t_\perp$ we use the bond orbital method of Harrison [15]. Then $t = V_{sp2} = 3.2(\hbar^2/m_0 a^2)$, where $\hbar$ — reduced Plank constant, m_0 — free-electron mass. In the following we set all lengths of bonds equal to the sum of radii r_a of atoms [16,17], forming these bonds. Then for Gr we get the length of bond $a = 1.54\,\text{Å}$, which is almost coincides with the value of 1.53 Å, obtained from the numeric calculation for graphone Gr−C [18]. Then we get $t \approx 10.5\,\mathrm{eV}$. We assume the bonds of carbon atoms with halogen atoms as σ-bonds of two $|p\rangle$-orbitals, so $t_\perp = V_{pp\sigma} = 2.22(\hbar^2/m_0 d^2)$, where d is length of the bond. For carbon atom $r_a = 0.77\,\text{Å}$ [16], values of r_a for Cl and Br atoms (according to Pauling) are equal to 0.99 and 1.14 Å, respectively [17]. It gives us $t_\perp = 5.46$ and $4.64\,\mathrm{eV}$ for C−Cl and C−Br bonds, respectively. For further numeric estimates we assume $e = 0.5\,\mathrm{eV}$, $t = 10\,\mathrm{eV}$, $t_\perp = 5\,\mathrm{eV}$. Results of the calculation are summarized in the table, which also contains estimates of widths of allowed state bands $W_C = W_V = W = (\Delta_\mathrm{K} - \Delta_\Gamma)/2$ and gaps between high-energy and low-energy bands $\Delta_{\mathrm{KK}} = E_{+}^{+}(\mathrm{K}) - E_{-}^{+}(\mathrm{K})$.

Since $\Delta_{1\Gamma} < \Delta_{1\mathrm{K}}$, the energy band gap is $E_{g1} = \Delta_{1\Gamma}$. In the vicinity of point Γ dispersions of the conduction band $E_C(\mathbf{k}) = E_{-}^{+}(\mathbf{k})$ and the valence band $E_V(\mathbf{k}) = E_{-}^{-}(\mathbf{k})$ can be represented in the following form

$$E_{C(V)}(\mathbf{k}) = \pm\frac{E_{g1}}{2} + \frac{\hbar^2 k^2}{2m_{1e(h)}}. \qquad (5)$$

Parameters of the model and estimates of band characteristics of J-GLC (All values of energy characteristics are given in eV, strain characteristics are normalized to relative strains of interatomic bonds ξ and ζ, responses of band characteristics to variation of energy e are normalized to ψ. Subscripts 1 for Cl$-$Gr$-$Br and 2 for other compounds are omitted.)

J-GLC	Cl$-$Gr$-$Br	B$-$BN$-$N	Al$-$AlP$-$P	Ga$-$GaAs$-$As	In$-$InSb$-$Sb
t	10	10	5	4.4	3.3
$t_\perp$	5.0	10	5	4.4	3.3
e	0.5	3.0	2.2	1.3	1.5
$\Delta_\Gamma = E_g$	1.89	7.71	4.63	3.26	3.07
$\delta_{2D}\Delta_\Gamma/\xi$	1.30	4.65	0.35	1.17	0.20
$\delta_z\Delta_\Gamma/\zeta$	-2.70	-51	-21	-24	-14
$\delta_e\Delta_\Gamma/\psi$	0.25	1.48	0.80	0.66	0.93
Δ_M	4.22	11.3	5.21	4.98	3.19
$\delta_{2D}\Delta_\mathrm{M}/\xi$	2.82	3.22	0.52	1.45	0.12
$\delta_z\Delta_\mathrm{M}/\zeta$	-6.90	-34	-18	-15	-13
$\delta_e\Delta_\mathrm{M}/\psi$	0.09	-0.92	-0.75	-0.39	-0.50
Δ_K	9.51	17.8	8.68	7.83	5.73
$\delta_{2D}\Delta_\mathrm{K}/\xi$	0	0	0	0	0
$\delta_z\Delta_\mathrm{K}/\zeta$	-10	-19	-9	-8	-6
$\delta_e\Delta_\mathrm{K}/\psi$	-0.24	-0.67	-0.07	-0.30	-0.08
Δ_KK	0.50	2.90	1.84	1.26	0.96
$\delta_{2D}\Delta_\mathrm{KK}/\xi$	0	0	0	0	0
$\delta_z\Delta_\mathrm{KK}/\zeta$	-4	-0.38	-0.56	-0.16	-0.63
$\delta_e\Delta_\mathrm{KK}/\psi$	2	10.8	7.1	4.71	4.76
m_e^*	5	3	8	3	11
$\delta_{2D}m_e^*/m_e^*\xi$	-4.9	-4.0	-4.5	-4.2	-4.5
$\delta_z m_e^*/m_e^*\zeta$	7	30	175	60	208
$\delta_e m_e^*/m_e^*\psi$	0.13	0.83	7.27	4.90	1.13
W	3.81	2.90	2.03	2.20	1.31

where effective masses of electrons (e) and holes (h) are

$$m_{1e} = -m_{1h} = \frac{\hbar^2 E_{g1}}{9t^2a^2C_{1\Gamma}}, \tag{6}$$

$C_{1\Gamma} = r_{1\Gamma}/R_{1\Gamma} - 1$, $r_{1\Gamma} = 9t^2 + 2t_\perp^2 - e^2$. Value of the dimensionless effective mass $m_{1e}^* = m_{1e}/m_0$ is given in the table. With $e^2 \ll t_\perp^2 \ll t^2$ we get $C_{1\Gamma} \approx 2t_\perp^4/81t^4 \ll 1$, and the precise value is $C_{1\Gamma} = 1.36 \cdot 10^{-3}$.

Now let us consider the H$-$Gr$-$Cl compound using Fischer atomic term tables (see [14], v. 2, Appendix 1). Then for carbon atoms (A and B atoms) we have $\varepsilon_a = \varepsilon_b = (\varepsilon_s + 2\varepsilon_p)/3 = -13.84$ eV relative to vacuum. For hydrogen atom (C atom) we have $\varepsilon_c = \varepsilon_s = -I = -13.60$ eV, where I is ionization energy. For chlorine we have $\varepsilon_d = -13.78$ eV. Assume for the sake of simplicity that $\varepsilon_a = \varepsilon_b = \varepsilon_c = \varepsilon_d = -13.7$ eV and take this energy as a reference point. Then, as it is shown before, for the C$-$Cl bond we have $t_{bd} = 5.46$ eV. Assuming the length of C$-$Cl bond equal to 1.30 Å, where atomic radius of hydrogen is taken equal to Bohr radius, we get $t_{ac} = V_{sp\sigma} = 1.42(\hbar^2/m_0d^2) = 6.40$ eV. Let us assume $t_\perp = 6$ eV and, as above, $t_{ab} = t = 10$ eV. Now, instead of equation (3), we have

$$\omega^4 - \left(2t_\perp^2 + t^2 f^2(\mathbf{k})\right) + t_\perp^4 = 0,$$

from which we get the following:

$$E_\pm^\pm(\mathbf{k})' = \pm\sqrt{\left[B'(\mathbf{k}) \pm R'(\mathbf{k})\right]/2},$$

where

$$B_1(\mathbf{k}) = e^2 = 2t_\perp^2 f^2(\mathbf{k})$$

and

$$R'(\mathbf{k}) = tf(\mathbf{k})\sqrt{4t_\perp^2 + t^2 f^2(\mathbf{k})}.$$

Thus, bands $E_\pm^\pm(\mathbf{k})'$ coincide with bands $E_{1\pm}^\pm(\mathbf{k})$ (4) for the Cl$-$Gr$-$Br compound, where in all expressions for $B'_{\Gamma,\mathrm{M,K}}$ and $R'_{\Gamma,\mathrm{M,K}}$ we should assume $e = 0$. Since $e \ll t_\perp, t$ for Cl$-$Gr$-$Br (see the table), and value of $t_\perp = 5$ eV is close to $t_\perp = 6$ eV for H$-$Gr$-$Cl, band characteristics of these two compounds are close to each other as well. Thus, for example, we get $E'_{g1} = \Delta'_{1\Gamma} = 2.31$ eV and $m'^*_{1e} = 3$.

DFT-calculations for H$-$Gr$-D$ compounds (D = F, Cl, Br) were performed in [19,20]. However, these works considered small surface concentrations of hydrogen and halogen atoms that form three-atom islands around hexagons on both sides of the graphone sheet. Depending on configuration of these islands on the graphene surface locations of energy gaps (points Γ and K) and their width (from 0.06 to 1.57 eV) are both changed. Thus, for example, for the H−Gr−Cl compound a value of $E_g = 1.57$ eV was obtained for the energy gap in point Γ. Unfortunately, there is no information on effective masses in [19,20].

3.2. $A{-}AB{-}B$ compounds

Now suppose $\varepsilon_a = \varepsilon_c = e$, $\varepsilon_b = \varepsilon_d = -e$, $t_{ac} = t_{bd} = t_\perp$, $t_{ab} = t$ (variant 2). Then, from (3) we get the following spectrum:

$$E_{2\pm}^{\pm} = \pm\sqrt{[B_2(\mathbf{k}) \pm R_2(\mathbf{k})]/2},$$

$$R_2(\mathbf{k}) = \sqrt{4t_\perp^2[4e^2 + t^2 f^2(\mathbf{k})] + t^4 f^4(\mathbf{k})}, \tag{7}$$

where

$$B_2(\mathbf{k}) = 2(e^2 + t_\perp^2) = t^2 f^2(\mathbf{k}).$$

Characteristic band parameters are equal to:

$$B_{2\Gamma} = 2(e^2 + t_\perp^2) + 9t^2, \quad B_{2\mathrm{M}} = 2(e^2 + t_\perp^2) + t^2,$$

$$B_{2\mathrm{K}} = 2(e^2 + t_\perp^2), \quad R_{2\Gamma} = \sqrt{4t_\perp^2(4e^2 + 9t^2) + 81t^4}.$$

$$R_{2\mathrm{M}} = \sqrt{4t_\perp^2(4e^2 + t^2) + t^4}, \quad R_{2\mathrm{K}} = 2et_\perp,$$

$$\Delta_{2\Gamma,\mathrm{M}} = 2\sqrt{(B_{2\Gamma,\mathrm{M}} - R_{2\Gamma,\mathrm{M}})/2} \text{ and } \Delta_{2\mathrm{K}} = 2\sqrt{e^2 + t_\perp^2 - et_\perp}.$$

It is easy to show that $\Delta_\Gamma < \Delta_\mathrm{K}$, or $2et_\perp < R_{2\Gamma}$, so the energy gap is formed in the Γ point. Width of the conduction band and valence band $W = (\Delta_\mathrm{K} - \Delta_\Gamma)/2$, and the gap is

$$\Delta_{2\mathrm{KK}} = \sqrt{e^2 + t_\perp^2 + et_\perp} - \sqrt{e^2 + t_\perp^2 - et}.$$

Effective masses of carriers can be expressed as follows:

$$m_{2e}^* = -m_{2h}^* = \frac{\hbar^2 E_{g2}}{9t^2 a^2 C_{2\Gamma}}, \tag{8}$$

where $E_{g2} = \Delta_{2\Gamma}$, $C_{2\Gamma} = r_{2\Gamma}/R_{2\Gamma} - 1$, $r_{2\Gamma} = 9t^2 + 2t_\perp^2$.

Variant 2 can be applied to J-GLC of the $A{-}AB{-}B$ type, where AB represent two-dimensional hexagonal compounds III−V, such as, for example, BN, AlP, GaAs and InSb [11,21,22]. As the mean bond length of $A{-}A$ and $B{-}B$ within our scheme is equal to the length of $A{-}B$ bond, i.e. $d = a$, then $t_\perp = t$. We assume that all atoms form σ-bonds of $|sp^3\rangle$-orbitals with energies of $\varepsilon_{sp3} = (\varepsilon_s + 3\varepsilon_p)/4$. Then $t = V_{sp3} = 3.22(\hbar^2/m_0 a^2)$ [15]. Taking $\bar{\varepsilon}_{ab} = (\varepsilon_a + \varepsilon_b)/2$ as a reference point of energy, let us assume $\varepsilon_a = -\varepsilon_b = e$. Results of the calculation are summarized in the table. Here, for comparison, we give the value of $E_g = 2.55$ eV, obtained for F−BN−H compound in [9] — the only work devoted to $C{-}AB{-}D$ compounds known to us.

Based on the results presented in the table, the following conclusions can be made: 1) Cl−Gr−Br and In−InSb−Sb compounds are wide-band semiconductors, B−BN−N, Al−AlP−P and Ga−GaAs−As compounds are isolators; 2) $E_C(\mathbf{k})$ and $E_V(\mathbf{k})$ bands are narrow, the Δ_KK gap separating these bands from $E_+^\pm(\mathbf{k})$ high-energy bands is narrow as well; 3) in the considered J-GLCs effective masses of carriers are heavy. By virtue of assumed simplifications, all the presented estimates of band characteristics should be considered as semiquantitative. The estimates of effective masses are just order estimates, which is caused by the small value of $C \sim 10^{-3}$ parameter, that can result in significant errors in the estimates. The smallness of C emerges due the fact that when expanding the expression $E_C(\mathbf{k}) = -E_V(\mathbf{k})$ in $(ka)^2$, contributions from $B(\mathbf{k})$ and $R(\mathbf{k})$ nearly compensate each other, which results in a little dispersion (causing the narrowness of bands as well) and high effective mass.

It's worth to note that estimates of band parameters for graphane H−Gr−H [23] and fluorographene F−Gr−F [24] (obtained within nearly the same model as that used in this work) are close to the results of this work. Thus, for example, $E_g \approx 5.6$ and 3 eV, $m_e^* = -m_h^* \approx 2$ and 3 for graphane and fluorographane, respectively. On the other hand, according to results of [11], C−BN−C, Si−AlP−Si, Ge−GaAs−Ge and Sn−InSb−Sn symmetric structures are narrow-band semiconductors ($E_g \approx 0.7$ eV for C−BN−C and ~ 0.3 eV for other compounds), widths of bands $W_C = W_V$ and gap Δ_KK are narrow as well.

4. Strain impact on the electron spectrum

Suppose a hexagonal lattice formed by AB atoms is subjected to omniradial stretching or compression (plane strain). We denote $\xi = \delta a/a$ the corresponding relative strain of bond length between the closest neighbors. With such a strain $f(\mathbf{k})$ function remains unchanged, however energy characteristics of bands change. Now suppose, that under a pair of opposite forces along z axis the $A{-}C$ and $B{-}D$ bonds are either stretched or compressed. At the same time the strains δd_{ac} and δd_{bd} of bond lengths must meet the $k_{ac}\delta d_{ac} = k_{bd}\delta d_{bd}$ equation, where k_{ac} and k_{bd} are force constants of the bonds. According to [14,15,25], the central force constant is $k = 4\alpha_c(1 - 2\alpha_p)V_2/d^2$, where $V_2 = t_{ac}, t_{bd}$, $\alpha_c = V_2/\sqrt{V_2^2 + V_3^2}$ and $\alpha_p = V_3/\sqrt{V_2^2 + V_3^2}$ — covalence and polarity of bond, $V_3 = |\varepsilon_{a(b)} - \varepsilon_{c(d)}|/2$. For the special cases under consideration ($d_{ac} = d_{bd}$, $t_{ac} = t_{bd} = t_\perp$ and $V_2 = e/2$) we get $\xi_{ac} = \xi_{bd} = \xi$.

4.1. $C{-}AA{-}D$ compounds

We now proceed with estimates for specific structures and start with $C{-}AA{-}D$ compounds. By introducing parameter $\delta_{2D}L \equiv (\partial L/\partial a)\xi$ for the plane strain, where L is the band characteristic, and taking into account that $t_{ab} \propto a^{-2}$ and $t_{ac(bd)} \propto d_{ac(bd)}^{-2}$, we get:

$$\delta_{2D}B_{1\Gamma} = -36t^2\xi,\ \ \delta_{2D}B_{1\mathrm{M}} = -4t^2\xi,\ \ \delta_{2D}B_{1\mathrm{K}} = 0,$$

$$\delta_{2D}R_{1\Gamma} = \delta_{2D}B_{1\Gamma}(r_{1\Gamma}/R_{1\Gamma}),\ \ r_{1\Gamma} = 9t^2 + 2t_{\perp}^2 - e^2,$$

$$\delta_{2D}R_{1\mathrm{M}} = \delta_{2D}B_{1\mathrm{M}}(r_{1\mathrm{M}}/R_{1\mathrm{M}}),\ \ r_{1\mathrm{M}} = t^2 + 2t_{\perp}^2 - e^2,$$

$$\delta_{2D}R_{1\mathrm{K}} = 0. \tag{9}$$

The change in $\Delta_{1\Gamma,\mathrm{M,K}}$ parameters is:

$$\delta_{2D}\Delta_{1\Gamma,\mathrm{M,K}} = -\delta_{2D}B_{1\Gamma,\mathrm{M,K}}C_{1\Gamma,\mathrm{M,K}}/2\Delta_{1\Gamma,\mathrm{M,K}}, \tag{10}$$

where $C_{1\Gamma,\mathrm{M,K}} = r_{1\Gamma,\mathrm{M,K}}/R_{1\Gamma,\mathrm{M,K}}-1$. The impact of plane strain on the effective masses of carriers is defined by the following expression:

$$\delta_{2D}m_{1e(h)}/m_{1e(h)} = 2\xi + \delta_{2D}\Delta_{1\Gamma}/\Delta_{1\Gamma} + \frac{\delta_{2D}B_{1\Gamma}}{R_{1\Gamma}}\left(1 + \frac{r_{1\Gamma}}{R_{1\Gamma}}\right), \tag{11}$$

from which we get $\delta_{2D}m_{1e(h)}/m_{1e(h)} \approx -5.6\xi$. Results of the calculation for Cl−Gr−Br compounds are given in the table. The same order of values we get for H−Gr−Cl compound as well.. Thus, the plane strain has relatively low impact on the band parameters and effective masses of carriers.

We now proceed with uniaxial strain, for which purpose we define the parameter$\delta_z L \equiv (\partial L/\partial d)\xi$, where $\xi = \xi_{ac}(1 + k_{ac}/k_{bd})$. Then we get

$$\delta_z B_{1\Gamma,\mathrm{M,K}} = -8t_{\perp}^2\xi,$$

$$\delta_z R_{1\Gamma} = \delta_z B_{1\Gamma}(\rho_{1\Gamma}/R_{1\Gamma}),\quad \rho_{1\Gamma} = e^2 + 9t^2,$$

$$\delta_z R_{1\mathrm{M}} = \delta_z B_{1\mathrm{M}}(\rho_{1\mathrm{M}}/R_{1\mathrm{M}}),\quad \rho_{1\mathrm{M}} = e^2 + t^2,$$

$$\delta_z R_{1\mathrm{K}} = \delta_z B_{1\mathrm{K}}(\rho_{1\mathrm{K}}/R_{1\mathrm{K}}),\quad \rho_{1\mathrm{K}} = e^2. \tag{12}$$

Instead of (10) we have

$$\delta_z\Delta_{1\Gamma,\mathrm{M,K}} = \delta_z B_{1\Gamma,\mathrm{M,K}}(1 - \rho_{1\Gamma,\mathrm{M,K}}/R_{1\Gamma,\mathrm{M,K}})/2\Delta_{1\Gamma,\mathrm{M,K}}. \tag{13}$$

from which, taking into account the $e^2 \ll t_{\perp}^2 \ll t^2$ inequation, we get

$$\delta_z\Delta_{1\Gamma} \approx -8t_{\perp}^4\xi/9t^2\Delta_{1\Gamma},\quad \delta_z\Delta_{1\mathrm{M}} \approx -8t_{\perp}^4\xi/t^2\Delta_{1\mathrm{M}},$$

$$\delta_z\Delta_{1\mathrm{K}} \approx -4t_{\perp}^4\xi/\Delta_{1\mathrm{K}},\quad \delta_z\Delta_{1\mathrm{KK}} = 0.$$

Thus, $|\delta_z\Delta_{1\Gamma,\mathrm{M,K}}| \gg |\delta_{2D}\Delta_{1\Gamma,\mathrm{M,K}}|$. For effective masses we get

$$\delta_z m_{1e(h)}/m_{1e(h)} = \delta_z\Delta_{1\Gamma}/\Delta_{1\Gamma} - \frac{\delta_{2D}B_{1\Gamma}}{C_{1\Gamma}R_{1\Gamma}}\left(1 - \frac{r_{1\Gamma}\rho_{1\Gamma}}{R_{1\Gamma}^2}\right). \tag{14}$$

Results of numeric estimates for the Cl−Gr−Br compound are given in the table. Estimates of the same order correspond to the H−Gr−Cl compound. Note that, first, the strains $\delta_{2D}\Delta_{\Gamma,\mathrm{M}} > 0$ $(C_{1\Gamma,\mathrm{M,K}} > 0)$ and they grow when transiting from Γ to M, $\delta_{2D}\Delta_{\mathrm{K}} = 0$; the strains $\delta_z\Delta_{1\Gamma,\mathrm{M,K}} < 0$ $(\rho_{1\Gamma,\mathrm{M,K}}/R_{1\Gamma,\mathrm{M,K}} < 1)$ and they grow as well by modulus when transiting from Γ to K. As for the order of magnitude, all strain characteristics are within the range from 0 to $10\xi(\zeta)$ eV. The strain value is $\delta_{2D}m_{1e(h)}/m_{1e(h)} = -4.9\xi$, because the third term of sum in formula (11) prevails; $\delta_z m_{1e(h)}/m_{1e(h)} = 7\zeta$, since $r_{1\Gamma}\rho_{1\Gamma}/R_{1\Gamma} < 1$. It must be emphasized that the uniaxial strain makes stronger changes in characteristics of the electron spectrum as compared with the plane strain.

4.2. *A−AB−B* compounds

In the case of plane strain, it is easy to show that $\delta_{2D}B_{1\Gamma,\mathrm{M,K}} = \delta_{2D}B_{1\Gamma,\mathrm{M,K}}$, and values of $\delta_{2D}R_{2\Gamma,\mathrm{M,K}}$ are defined by formulae (9) with corresponding replacement of subscript 1 by 2, where $r_{2\Gamma} = 9t^2 + 2t_{\perp}^2$, $r_{2\mathrm{M}} = t^2 + 2t_{\perp}^2$ ($r_{1\Gamma,\mathrm{M}}$ become $r_{2\Gamma,\mathrm{M}}$ at $e = 0$). Formula (10) holds for for $\delta_{2D}m_{2e(h)}$ with substitution of subscripts 1 by subscripts 2. In the case of uniaxial strain we have $\delta_z B_{2\Gamma,\mathrm{M,K}} = -8t_{\perp}^2 e^2$, $\delta_z R_{2\Gamma,\mathrm{M}} = \delta_z B_{2\Gamma,\mathrm{M}}(\rho_{2\Gamma,\mathrm{M}}/R_{2\Gamma,\mathrm{M}})$, $\rho_{2\Gamma,\mathrm{M}} = e^2$, $\delta_z R_{2\mathrm{K}} = -4t_{\perp}e$. Expressions for $\delta_z\Delta_{2\Gamma,\mathrm{M,K}}$ and $\delta_z m_{2e(h)}$ are derived from expressions (13) and (14) through substitution of subscripts 1 by subscripts 2. Results of numeric estimates for two-dimensional hexagonal compounds III−V are summarized in the table. It follows by the table that, first, the response of band parameters to the plane strain is nearly the same as that of Cl−Gr−Br and H−Gr−Cl compounds. As for the response of *A−AB−B* structures to the uniaxial strain, for the characteristics considered in this work and corresponding to Γ and M points of the Brillouin zone, this response is considerably higher (by several times and several tens times), than that for Cl−Gr−Br and H−Gr−Cl compounds. The reason of this inconsistency is that for *A−AB−B* the following ratio holds: $\rho_{2\Gamma,\mathrm{M}}/R_{2\Gamma,\mathrm{M}} \ll 1$ and $(1 - r_{2\Gamma,\mathrm{M}}\rho_{2\Gamma,\mathrm{M}}/R_{2\Gamma,\mathrm{M}}^2) \sim 1$, while for Cl−Gr−Br and H−Gr−Cl we have $\rho_{2\Gamma,\mathrm{M}}/R_{2\Gamma,\mathrm{M}} \sim 1$ and $(1 - r_{2\Gamma,\mathrm{M}}\rho_{2\Gamma,\mathrm{M}}/R_{2\Gamma,\mathrm{M}}^2) \ll 1$. At the same time, for all structures: $C_{1\Gamma} \sim C_{2\Gamma} \ll 1$.

So, in this section we have considered the response of electron spectrum of J-GLC to the strain of bond lengths a and d. However, the obtained results also can be interpreted as immunity of the model to the choice of a and d parameters. In the Appendix we have considered the system response to e energy variation. It should be noted, that lengths and energies of bonds are the only parameters of the bond orbital method of Harrison [14,15] used by us in this work.

5. About magnetic states in J-GLC

The issue of J-GLC magnetization came up in theoretical works [4.10,26], that considered the Gr−H graphone. It was shown that a carbon atom free from H has a large spin moment ($\sim 1\,\mu_{\mathrm{B}}$, where μ_{B} — Bohr magneton). Similar results were obtained in [9] for the H−BN and F−BN compounds: free atoms of nitrogen have a magnetic moment of ~ 0.75 and $1\,\mu_{\mathrm{B}}$, respectively.

To describe spin states in the Hartree−Fock approximation within our model of J-GLC, it is necessary, first, to assign a spin index $\sigma = \uparrow, \downarrow$ to all Green functions in expression (1) and instead of energy ε_i $(i = a, b, c, d)$ introduce energy $\varepsilon_{i\sigma} = \varepsilon_i + U_i n_{i-\sigma}$, where U_i — Coulomb repulsion of electrons with opposite spins in the atom of $I = A, B, C, D$, $n_{i\sigma}$ — occupation number for the level of $\varepsilon_{i\sigma}$ [27,28]. Second, by leaving only atoms of C atoms as decorating atoms, it is necessary to replace in expression (1) the Green function $G^B_\sigma(\omega)$ of dimer $B-D$ by the Green function $g^B_\sigma(\omega)$ of atom B. Then, instead of (3) we get a system of two equations (for $\sigma = \uparrow, \downarrow$) as follows:

$$\Omega_{a\sigma}\Omega_{b\sigma}\Omega_{c\sigma} - \Omega_{b\sigma}t_{ac}^2 - \Omega_{c\sigma}t_{ab}^2 f^2(\mathbf{k}) = 0, \tag{15}$$

where $\Omega_{i\sigma} = \omega - \varepsilon_{i\sigma}$. The same equation can be obtained from (3) by assuming $t_{bd} = 0$ and rejecting the solution $\Omega_d = 0$. In a generic form a self-consistent solution to the system of equations (15) is quite a labor-intensive problem.

For example, let as consider graphone. Taking into account the fact, that lengths of C−C and C−H bonds are equal to 1.50 and 1.16 Å, respectively [9,18], we have $t_{ab} = t \approx 11$ eV and $t_{ab} = V_{sp\sigma} \equiv t \approx 8$ eV [15]. For atoms of carbon $\varepsilon_a = \varepsilon_b = (\varepsilon_s + 2\varepsilon_p)/3 = -13.84$ eV relative to vacuum, where we used Mann atomic term tables [29], also containing value of $U_a = U_b = 11.76$ eV (note, that values of energies ε_s and ε_p from Mann tables are almost the same as values from Fischer tables). For atoms of hydrogen $\varepsilon_c = \varepsilon_s = -I = -13.60$ eV, $U_c = I - A = 12.85$ eV, where I and A — ionization energy and electron affinity energy [16]. We assume $\varepsilon_a = \varepsilon_b = \varepsilon_c = -13.7$ eV, $U_a = U_b = U_c \equiv U = 12.3$ eV. By introducing spin moments $m_i = n_{i\uparrow} - n_{i\downarrow}$ localized on I atom and assuming $\varepsilon_a + U/2 = \varepsilon_b + U/2 = \varepsilon_c + U/2 = 0$, we get $\varepsilon_{i\uparrow} = -U(Z_i + m_i)/2$ and $\varepsilon_{i\downarrow} = -U(Z_i - m_i)/2$, where $Z_i = 1 - n_i$ — charge of the i-the atom. We take into account two additional circumstances: 1) because of charge conservation law we have $\sum_i Z_i = 0$; 2) since there is only one uncompensated spin in the system per one unit cell, which is localized mainly on unpaired $|p_z\rangle$-orbital of carbon atom, we get $\sum_i m_i = 1$. It follows that $\sum_i \varepsilon_i = U$.

Without taking into account the Coulomb interaction $(U = 0)$ from equation (3) we get symmetrical bands of the following form $E^0_0(\mathbf{k}) = 0$ and $E^0_\pm(\mathbf{k}) = \pm\sqrt{t_\perp^2 + 4t^2 f^2(\mathbf{k})}$. At $U \neq 0$ the symmetry is disturbed due to interatomic transition of electrons and presence of spin moments. It is easy to see that even with our considerable simplifications the self-consistent system of equations (15) does not have an analytical solution, thus computerized calculation is required.

6. Conclusion

So, in this work we suggested a model of Janus structure and considered a number of cases for which this model gives simple analytical solution. It should be noted that this model is convenient for express estimates of band parameters (gaps in the spectrum, effective masses), response to external disturbance (mechanical deformation in our case) and, if sufficiently representative set of compounds under examination is considered, for identifying behavior of changes in some physical characteristic. At the same time we did not use any adjustable parameters to determine energies of states using atomic term tables [14,29], interatomic distances — using sum of atomic radii [16,17] and transition integrals — using Harrison scheme [14,15]. In principle we should have a little difficulty in considering here capacitive characteristics of Janus structures, as well as the issue of defects in these structures using the approaches of works devoted to graphane [23], fluorographene [24] and $C-h-AB-C$ graphene-like compounds [11]. We, however, have postponed these research activities until emergence of corresponding experimental data or at least ab initio calculations.

Conflict of interest

The author declares that he has no conflict of interest.

APPENDIX

Let us consider the response of electron spectrum to e energy variations by determining the response of band characteristic L to relative change $\psi = \delta e/e$ as $\delta_e L = (\partial L/\partial e)\psi$.

C−AA−D compounds.

In accordance with expressions for $B_{1\Gamma,\mathrm{M},\mathrm{K}}$ and $R_{1\Gamma\mathrm{M},\mathrm{K}}$ we get

$$\delta_e B_{1\Gamma,\mathrm{M},\mathrm{K}} = 2e^2\psi, \quad \delta_e R_{1\Gamma} = -2e^2(9t^2 - 4t_\perp^2 - e^2)\psi/R_{1\Gamma},$$

$$\delta_e R_{1\mathrm{M}} = -2e^2(t^2 - 4t_\perp^2 - e^2)\psi/R_{1\mathrm{M}},$$

$$\delta_e R_{1\mathrm{K}} = R_{1\mathrm{K}}(1 + e^4/R_{1\Gamma}^2)\psi.$$

For the response of gaps $\Delta_{1\Gamma,\mathrm{M},\mathrm{K}}$, $\Delta_{1\mathrm{KK}}$ and effective masses of carriers $m_{1e} = -m_{1h}$ to the relative change in e energy we get:

$$\delta_e\Delta_{1\Gamma,\mathrm{M},\mathrm{K}} = (\delta_e B_{1\Gamma,\mathrm{M},\mathrm{K}} - \delta_e R_{1\Gamma,\mathrm{M},\mathrm{K}})/2\Delta_{1\Gamma,\mathrm{M},\mathrm{K}}, \tag{A1}$$

$$\begin{aligned}\delta_e\Delta_{1\mathrm{KK}} = {}& (\delta_e B_{1\mathrm{K}} + \delta_e R_{1\mathrm{K}})/\sqrt{(B_{1\mathrm{K}} + R_{1\mathrm{K}})/2} \\ & - (\delta_e B_{1\mathrm{K}} - \delta_e R_{1\mathrm{K}})/\sqrt{(B_{1\mathrm{K}} - R_{1\mathrm{K}})/2}.\end{aligned} \tag{A2}$$

$$\delta_e m_{1e} = -\delta_e m_{1h} = m_{1e}(\delta_e\Delta_{1\Gamma}/\Delta_{1\Gamma} - \delta_e C_{1\Gamma}/C_{1\Gamma}),$$

$$\delta_e C_{1\Gamma} = -\frac{2e^2\psi}{R_{1\Gamma}}\left(1 - \frac{r_{1\Gamma}(9t^2 - 4t_\perp^2 - e^2)}{R_{1\Gamma}^2}\right). \tag{A3}$$

Results of numeric estimates for the Cl−Gr−Br compound are given in the table. For the H−Gr−Cl compound, for which $e = 0$, and, as a consequence, $\delta_e B_{1\Gamma,\mathrm{M},\mathrm{K}} = \delta_e R_{1\Gamma,\mathrm{M},\mathrm{K}} = 0$, we get $\delta_e \Delta_{1,\mathrm{M},\mathrm{K}} = \delta_e \Delta_{\mathrm{KK}} = \delta_e m_{1e(h)} = 0$.

A−AB−B compounds.

In accordance with expressions for $B_{2\Gamma,\mathrm{M},\mathrm{K}}$ and $R_{2\Gamma,\mathrm{M},\mathrm{K}}$ we get

$$\delta_e B_{2\Gamma,\mathrm{M},\mathrm{K}} = 4e^2\psi,$$

$$\delta_e R_{2\Gamma,\mathrm{M}} = 16e^2 t_\perp^2 \psi / R_{2\Gamma,\mathrm{M}}, \quad \delta_e R_{2\mathrm{K}} = R_{2\mathrm{K}}\psi.$$

The responses of gaps $\Delta_{2\Gamma,\mathrm{M},\mathrm{K}}$, $\Delta_{2\mathrm{KK}}$ are defined by formulae (A1) and (A2) with substitution of subscripts 1 by subscripts 2. For effective masses we get

$$\delta_e m_{2e} = -\delta_e m_{2h} = m_{1e}(\delta_e \Delta_{2\Gamma}/\Delta_{1\Gamma} - \delta_e C_{2\Gamma}/C_{2\Gamma}),$$

$$\delta_e C_{2\Gamma} = -r_{2\Gamma}\delta_e R_{2\Gamma}/R_{2\Gamma}^2. \qquad \text{(A4)}$$

Numeric results are presented in the table, from which it follows that changes in almost all considered characteristics in modulus are not greater than ψ. Exceptions are values of $\delta_e \Delta_{2\Gamma}$ for B−BN−N and $\delta_e m_e/m_e$ for Al−AlP−P, Ga−GaAs−As and In−InSb−Sb. It is logically reasonable to estimate the order of magnitude of ψ through the difference of atom level energies ε_s and ε_p given in Mann tables (M) [15] and Herman−Skillman tables (HS) [14]. Estimates of $\psi_{s,p} = 2[\varepsilon_{s,p}(\mathrm{M}) - \varepsilon_{s,p}(\mathrm{HS})]$ show that maximum value of $(\psi_z)_{\max} = 0.17$ takes place for chlorine atoms and maximum value of $(\psi_p)_{\max} = 0.24$ takes place for bromine atoms. Mean values for all atoms composing the considered J-GLCs are equal to $\bar{\psi}_s = 0.07$ and $\bar{\psi}_p = 0.14$.

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