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Energy gap of Kronig-Penney-type hydrogenated graphene superlattices

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The electronic structure of graphene-graphene superlattices with armchair interfaces is investigated with first-principles density-functional theory. By separately varying the widths, we find that the energy gap $E_g$ is inversely proportional to the width of the graphene strip and that the gap increases as the hydrogenated strip becomes wider due to the enhanced confinement effect. It is further demonstrated that, unlike other graphene nanostructures, the superlattices exhibit both direct and indirect band gaps without external perturbations. This peculiarity in the nature of $E_g$ originates from the different connection structures of the symmetrized wave function at the boundary between adjacent unit cells due to the reflection symmetry of the superlattices. These findings suggest that the optical as well as electronic properties of graphene superlattices can be controlled through selective chemical functionalization.

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Carbon-based systems exhibit a rich variety of structures with equally intriguing physical properties in different dimensionality, which arises largely from the remarkable bonding flexibility of carbon atoms. Zero-dimensional fullerenes, one-dimensional (1-D) nanotubes, two-dimensional (2-D) graphene, and three-dimensional graphite are archetypal examples to name a few. Among these, graphene plays a special role because it serves as “the basis for understanding electronic properties in other allotropes” and shows fascinating physical properties such as chiral integer Hall effect, Klein tunneling, and the absence of weak localization. The origin of these exotic behaviors in graphene lies in the fact that the low-lying excitations around the Fermi point are described by massless, chiral Dirac fermions with a linear dispersion at the Fermi velocity $v_F$ instead of the speed of light. Furthermore, since it is now experimentally realizable to form patterned hydrogenation on graphene, which would impact on the electronic properties in the case of KP GSLs, it is of interest to achieve an improved understanding of the geometric effect on the electronic structure of the GSLs both from a fundamental physics standpoint and for future graphene-based applications.

In the present work, we have performed first-principles studies on the electronic structure of KP GSLs with armchair-type interfaces (AGSLs) based on density-functional theory (DFT). AGSLs are modeled with a repeated structure of pure and hydrogenated graphene (i.e., graphane) strips, and calculations are carried out by varying the widths of the pure and hydrogenated parts separately. Our results demonstrate that AGSLs possess finite energy gaps that increase as the graphane region becomes wider due to the enhanced confinement effect. Surprisingly, the band gaps exhibit both direct and indirect character depending on the width of the graphene strip, and we show that the origin of this peculiarity in the band gap lies in the symmetry of AGSLs, which governs the connection structure of the wave functions at the boundary between neighboring unit cells.

All first-principles calculations are performed within DFT as implemented in the Vienna Ab Initio Simulation Package, employing 450-eV plane-wave cutoff, Vanderbilt-type ultrasoft pseudopotentials, and the exchange-correlation energy is treated within the generalized gradient approximation (GGA) of Perdew and Wang. The interlayer separation is kept at 18 Å to avoid spurious interactions between the superlattice layers, and the Brillouin-zone (BZ) integration is carried out by employing the Gaussian smearing approach with a smearing parameter of 0.05 eV. Due to the variation in the cell size, different numbers of irreducible $k$ points ($N_k$) are considered: for the smallest cell, $N_k = 256$ is used, whereas it gradually decreases to 96 as the cell becomes larger.
leads to a 12% increase in the hopping parameter, which was shown to play a critical role in opening the gap. These observations indicate that the gap in AGSLs is the result of the confinement effect due to the potential barrier from the hydrogenated strips and structural relaxation at the interface as well.

We note that the gap is categorized into three different families, as in the case of AGNRs, as is clearly seen from Fig. 1(b). For a fixed $N_H$, the magnitude of $E_g$ is well ordered depending on the values of $N_C$: $E_g(N_C = 3p + 1) > E_g(N_C = 3p) > E_g(N_C = 3p + 2)$, where $p$ are integers. Furthermore, $E_g$ is well fitted with $N_C^\alpha$, where $0.74 < \beta < 0.90$ depending on $N_H$ values. From Fig. 1(b), it is found that $E_g$ increases with $N_H$ for a given $N_C$, due to wider potential barriers provided by the graphane strip with larger $N_H$ values. By computing $\Delta E_g = E_g(N_H = 4, 5) - E_g(N_H = 2, 3)$, it is found that, although there exist three different families in $E_g$, $\Delta E_g$ remain close to each other among them, implying that the confinement effect is very similar. This similarity in $\Delta E_g$ results in the relative increase in the gap of 14 and 6% on average for $N_C = 3p$ and $3p + 1$, respectively, whereas the small gap makes $E_g(N_C = 3p + 2)$ for $N_H = 4.5$ more than doubled from those with $N_H = 2.3$.

The variation in $E_g$ with respect to $N_C$ can also be compared with that of AGNRs. As is seen from Fig. 1(b), $E_g$ of AGSLs is close to the energy gap in AGNRs. For instance, $E_g$ with $N_C = 3p$ and $3p + 1$ for $N_H = 2$ and $3$ is reduced from that of AGNRs by 10 and 19% on average, respectively, whereas the reduction is as large as 83% when $N_C = 3p + 2$. However, the difference is reduced by as low as 4, 14, and 50% for $N_H = 3p, 3p + 1$, and $3p + 2$, respectively, in the case of $N_H = 4$ and 5, due to the wider potential barrier. The similarity in $E_g$ partly implies that the hydrogenated strips isolate the graphene regions so that the electronic structure of the latter resembles that of AGNRs. It should be noted, however, that the periodic nature of the potential barrier significantly differentiates AGSLs from AGNRs, as is discussed below.

In order to better understand the nature of these energy gaps, we plot the band structures of the AGSLs in Fig. 2 for selected ($N_H, N_C$) values. It is clear from Fig. 2 that the bands in the $\Gamma \rightarrow Y$ direction are highly dispersive, whereas they are quite flat along $\Gamma \rightarrow X$. This implies a higher electrical conductivity along than across the potential barrier, leading to an anisotropic behavior in the transport properties.

Surprisingly, unlike AGNRs, in which both the conduction-band minimum (CBM) and valence-band maximum (VBM) occur at the $\Gamma$ point in the Brillouin zone (BZ), the CBM and VBM of AGSLs are located at either the $\Gamma$ or X point in the BZ, depending on the detailed superlattice geometry. As previously mentioned, since the Dirac point of graphene is mapped onto either $\Gamma$ or $2/3 \bar{X}$ in AGSLs, the direct band gap is expected around these points due to the confining potential. This is exactly the case for even $N_H$ values, in which both the VBM and CBM are at the same $k$ point, as shown in Fig 2(a). When $N_H$ assumes odd values, however, indirect as well as direct band gaps are obtained, as presented in Fig. 2(b).

With $N_H = 3$, for instance, the VBM (CBM) occurs at the $X$ ($\bar{X}$), $X$ ($\bar{X}$), and $\Gamma$ ($X$) points when $N_C = 3p, 3p + 1$, and $3p + 2$, respectively, which is the same for $N_H = 7$, whereas...
direct gaps occur when \( N_H = 5 \). We note that the difference in the energy eigenvalues at the \( \Gamma \) and \( X \) points for \( N_H = 9 \) becomes less than 1 meV due to the wide potential barrier, making the dispersion along \( \Gamma \rightarrow X \) flat, essentially resulting in a set of AGNRs. It should be stressed that, while indirect band gaps can be induced in AGNRs by applying an external bias,31 and in bilayer graphene through strain,32 the indirect band gap in AGSLs is an intrinsic effect in the sense that no external perturbation is required.

To understand the origin of the indirect gap in AGSLs for odd \( N_H \) values, we plot the real part of the wave function \( \psi \) at the \( \Gamma \) (\( \psi_\Gamma \)) and \( X \) point (\( \psi_X \)) for \((N_H, N_C) = (3,5)\) and \((5,5)\) in Figs. 3 and 4, respectively. In Figs. 3 and 4, the wave functions for both the top of the valence band (\( \psi_{\Gamma, X}^{VB} \)) and bottom of the conduction band (\( \psi_{\Gamma, X}^{CB} \)) are presented. As is seen from both figures, \( \psi_{\Gamma, X} \) is antisymmetric with respect to the reflection plane \( P_{\rho} \), which is represented with the dotted line in the figures. In fact, \( \psi_{\Gamma, X} \) becomes symmetric and antisymmetric when \( N_C = 4p - 1 \) and \( 4p + 1 \), respectively. This symmetry property of \( \psi_{\Gamma, X} \) is the result of the reflection symmetry of AGSLs for odd \( N_H \) values.

We first note that the reflection \( \sigma \) with respect to \( P_{\rho} \) is a covering operation of the 2-D Hamiltonian of the AGSLs \( \mathcal{H}_{AGSL} \) when \( N_H = 2p + 1 \): \( \sigma \mathcal{H}_{AGSL} = \mathcal{H}_{AGSL} \sigma \). Thus, if \( \psi_{\Gamma, X} \) is a nondegenerate eigenfunction of \( \mathcal{H}_{AGSL} \), which is indeed the case, it is easy to see that \( \sigma \psi_{\Gamma, X} = \pm \psi_{\Gamma, X} \). To show the nondegeneracy of \( \psi_{\Gamma, X} \), let us consider the space group \( \mathcal{G} \) of AGSLs, which is the same as the group of a \( \mathbf{k} \) vector at the \( \Gamma \) and \( X \) points. We find that \( \mathcal{G} \) of the fully relaxed superlattices consists of four elements: \( E \) (identity), \( \sigma \), \( i \) (inversion), and \( C_2 \) (\( \pi \) rotation about the \( x \) axis). Since each of these elements forms its own class, there are four 1-D irreducible representations of \( \mathcal{G} \), which only allows nondegenerate eigenfunctions of \( \mathcal{H}_{AGSL} \).

The symmetrized wave functions form different node structures at the connection regions (the solid rectangles in Figs. 3 and 4) between adjacent unit cells, depending on \( N_H \) values. As is seen from Figs. 3(a) and 3(b), both \( \psi^{VB} \) and \( \psi^{CB} \) for \((N_H, N_C) = (3,5)\) have the same number of nodes \( N_n \) at the \( \Gamma \) point, whereas \( N_n \) is reduced at the \( X \) point, leading to a lowering of the kinetic energy. This change in \( N_n \) thus places the VBM and CBM at the \( \Gamma \) and \( X \) points, respectively. We also computed \( \psi \) for \((N_H, N_C) = (3,7)\) and found that \( N_n \) is increased at the \( X \) point, reversing the result with \((N_H, N_C) = (3,5)\); the VBM occurs at the \( X \) point, whereas the CBM is at the \( \Gamma \) point.

The situation for \( N_H = 5 \) is, however, in sharp contrast with the above case, as depicted in Fig. 4. From Fig. 4(a), it is seen that \( N_n \) is decreasing going from the \( \Gamma \) to the \( X \) point in the VB, which makes the \( \Gamma \) point the VBM. In contrast, \( \psi_{\Gamma}^{CB} \) has...
Recently, superlattice structures with broken inversion symmetry were proposed to induce a finite gap at the Dirac point in graphene.\textsuperscript{13} Our results, however, demonstrate that graphene superlattices can have nonzero band gaps even with the inversion symmetry if a sufficient confining potential is present. We note that, since the energy gaps in the present work were computed within DFT-GGA, beyond-GGA approaches such as hybrid functionals or GW approximation will produce larger gaps. Despite this underestimation, however, the trend in $E_g$ with $N_C$ and $N_H$ values will remain valid even within GGA, as demonstrated elsewhere.\textsuperscript{33}

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