Symmetry-induced gap opening in graphene superlattices

Rocco Martinazzo, Simone Casolo and Gian Franco Tantardini
Department of Physical Chemistry and Electrochemistry, University of Milan, V. Golgi 19, 20133 Milan, Italy and CIMATE, Interdisciplinary Center of Nanostructured Materials and Interfaces, University of Milan. E-mail: rocco.martinazzo@unimi.it

We study \(nnn\) honeycomb superlattices of defects in graphene. The considered defects are missing \(p_z\) orbitals and can be realized by either introducing C atom vacancies or chemically binding simple atomic species at the given sites. Using symmetry arguments we show how it is possible to open a gap when \(n = 3m + 1, 3m + 2\) (\(m\) integer), and estimate its value to have an approximate square-root dependence on the defect concentration \(x = 1/n^2\). Tight-binding calculations confirm these findings and show that the induced-gaps can be quite large, e.g. \(\sim 100\) meV for \(x \approx 10^{-3}\). Gradient-corrected density functional theory calculations on a number of superlattices made by H atoms adsorbed on graphene are in good agreement with tight-binding results, thereby suggesting that the proposed structures may be used in practice to open a gap in graphene.

The recent fabrication of graphene[1], a one atom thick layer of carbon atoms arranged in a honeycomb lattice, has triggered a wealth of studies in both fundamental and applied science. Graphene is a zero-gap semiconductor with a linear dispersion at the Fermi level in which low-energy excitations mimic the behaviour of relativistic massless fermions[2, 3] (see [4, 5] for reviews). This gives rise to a number of interesting phenomena such as an anomalous Quantum Hall effect[2, 3] and quasirelativistic Klein tunneling[6]. Its unconventional transport properties offer the possibility of high-performance interconnects in hypothetical carbon-based nanoelectronics. However, since conductivity cannot be turned completely off, pristine graphene cannot be used as a transistor in logic applications, where high on/off ratios are required[9, 10]. Field-switching capabilities depend on the presence (and size) of a gap in the electronic structure. Electron confinement can be used to open a gap inversely proportional to the confinement length when rolling up graphene into single-walled nanotubes or cutting its edges to form nanoribbons. Both these possibilities have been exploited, and promising carbon nanotube/nanoribbons field-effect transistors realized[9].

In this Letter we explore a different possibility made available by recent progresses in patterning graphene with lithographic techniques[11, 12]. Specifically, we study \(nnn\) honeycomb superlattices of defects on graphene (defined to be periodic structures of defects arranged to form a honeycomb lattice commensurate with the substrate) and use symmetry arguments to design semiconducting structures. We show that a gap can be opened by preserving graphene symmetry. We estimate that an inverse proportionality to the (super)lattice constant \(n\) approximately holds for the gap size in these structures, and use tight-binding and first-principles calculations to validate these predictions. The computed gaps are sizable and compare favourably with those found in nanoribbons at the same length scale[13].

In the following we first present our symmetry arguments and derive general rules to open a gap in the considered superlattices. We then estimate its value and present the results of numerical calculations.

Graphene’s unconventional electronic properties are strictly related to its \(D_{3h}\) point symmetry. The \(k\)-group at the \(K\) (\(K'\)) high-symmetry points \((D_{3h})\) allows for doubly degenerate irreducible representations, and Bloch functions built with \(p_z\) orbitals of the \(A\) and \(B\) sublattices span one of its two-dimensional irreducible representation (irrep), namely \(E\). This is enough for the \(\pi - \pi^*\) degeneracy at the \(K(K')\) point and for the unusual linear dispersion relation, irrespective of the level of approximation[14]. These properties are captured by the simple tight-binding (TB) model Hamiltonian

\[
H = -t \sum_{\langle i,j \rangle} a_i^\dagger b_j + H.c. - t' \sum_{\langle i,j \rangle} a_i^\dagger a_j - t' \sum_{\langle i,j \rangle} b_i^\dagger b_j
\]

where \(a_i^\dagger(b_i^\dagger)\) is the creation operator for an electron on site \(i\) of the \(A\) (\(B\)) sublattice, the first sums run over nearest neighboring sites in the honeycomb lattice and the second sums over sites which are nearest neighbors in the triangular sublattices. The hopping \(t\) has been estimated to be \(\sim 2.7\) eV whereas \(t' \ll t\) has different values depending on the parametrization. When \(t' = 0\) the Hamiltonian describes a bipartite system, and we assume that this approximately holds for graphene. The consequences of relaxing this approximation will be addressed numerically at the end of this Letter.

Bipartitism has a large impact on the electronic structure via the induced electron-hole symmetry. For instance, it has long been known that in bipartite systems, at half filling, sublattice imbalances due to vacancies strongly affect the energy spectrum at the Fermi level through the introduction of midgap states[15]. In graphene, such states have a semidealocated nature with \(1/r\) dependence on the distance from the defect[16]. By introducing an equal number of defects on each sublattice one restores balance, eliminates midgap states and a gap possibly opens. In general, however, there is no guarantee that the gap opens at \(K\) and does not close somewhere else in the Brillouin zone (BZ). Therefore, we focus here on \(nnn\) honeycomb pat-
terms of defects only, in such a way to constrain (by symmetry) the changes in the band structure and possibly reduce accidental degeneracies. In these structures the high-symmetry points where degeneracy is expected are the $\Gamma$ and $K$ points, that is where the $k$-groups ($D_{6h}$ and $D_{3h}$, respectively) allow for doubly degenerate irreps. In the following we use $E$ ($A$) for a generic two- (one-) dimensional irreducible representation, and denote as $K_n$ the $K$ point of the $nxn$ superlattice BZ. For a strictly bipartite system at half-filling, degeneracy at the Fermi level occurs only. The overall result is given in Table I where the symmetry points $\Gamma$ and $K_n$ point of the corresponding BZ.

To show that this is indeed possible, we consider a generic $nxn$ supercell and count the number of $A$ and $E$ irreps generated by the carbon atoms in cell (the so-called atomic representations). To this end, it is sufficient to consider that half of the cell which has $D_{3h}$ symmetry with respect to its center $I$ (see Fig. 1), the remaining half behaving similarly. These two half-cells ($\alpha$ and $\beta$ in the following) play the role of $A$ and $B$ type of sites in the honeycomb superlattice. In each of them, the set of C atoms may be grouped in classes of equilateral triangles $\Delta_{\alpha,\beta}$ ($\Delta_{\alpha,\beta}$), plus a possible atom at $I_{\alpha}(I_{\beta})$ as it happens when $n = 3m + 1$ and $n = 3m + 2 (m \text{ integer})$. Each triangle spans an $A + E$ irrep of the $D_{3h}$ group (centered at $I$) which behave as $s$ and $(p_x,p_y)$ orbitals centered on $I$; the atom at $I$, when present, spans of course an $A$ irrep. Then, by considering Bloch functions built with these $s$- and $(p_x,p_y)$-like orbitals it is possible to count the number of $A$ and $E$ irreps for each case. At $\Gamma$ the Bloch functions built with $s$-like orbitals centered on $I_{\alpha}$ and $I_{\beta}$ span two $A$ representations, whereas $(p_x,p_y)$-like functions span two $E$ irreps; at $K$ the first generate an $E$ irrep whereas the latter span $2A + E$. These are also the irreps generated by the $p_z$ orbitals of the C atoms as long as we discriminate between $A$ and $E$ type only. The overall result is given in Table I where the symbol $n_\alpha = \bar{0},\bar{1},\bar{2}$ identifies the three (congruence) classes modulo 3, i.e. the sequences $n = 3m, 3m + 1$ and $3m + 2$, respectively.

It follows from Table I that with the full atomic set (i.e. considering pure graphene) degeneracy occurs at the $K_n$ points when either $n \in \bar{1}_3$ or $n \in \bar{2}_3$. This is consistent with the folding $K(K' \rightarrow K_n(K'_n)$ and $K(K' \rightarrow K'_n(K_n)$, respectively. In the case $n \in \bar{0}_3$ both $K$ and $K'$ folds to $\Gamma$ and therefore a 4-fold degeneracy occurs; this can be considered accidental in this context as it cannot be predicted by the number of $E$ irreps only. More interestingly, two important results concerning the introduction of $p_z$—vacancies are easily proved.

I. By removing a $\Delta_{\alpha,\beta}$ pair only is not generally possible to open a gap. Here, $2(A + E)$ irreps are removed both at $\Gamma$ and at $K_n$, and no modification occurs on the parity of the $E$ sets. Exceptions to this rule are, of course, those cases where degeneracy is accidental (as pure graphene in the $\bar{0}_3$ case which does show a gap after removal of one such pairs, see below).

II. When $n \in \bar{1}_3$ or $n \in \bar{2}_3$ removal of the atoms at $I_{\alpha}$ and $I_{\beta}$ does open a gap. In these cases, the atomic basis spans $2A$ at $\Gamma$ and $E$ at $K_n$, thereby turning the number of $E$ irreps to be even at both special points. Also in this case, exceptions of residual accidental degeneracy are possible.

The second result provides a very simple way for opening a gap in two thirds of the cases, that is by introducing a $p_z$ vacancy at $I_{\alpha}$ and $I_{\beta}$. In practice, this can be realized by either removing substrate atoms or using them to covalently bind simple adsorbates such as H atoms. In the latter case, indeed, the C atoms involved in the chemisorption process turn their hybridization to $sp^3$ and effectively get out of the $\pi - \pi^*$ band system. In this Letter we focus on the simplest defective superlattices, i.e. those with vacancies at $I_{\alpha}$ and $I_{\beta}$ only, and call them $(n,0)$-honeycombs. In general, the pair of integers $(n,p)$ ($p = 0, \ldots , \text{int}(n^2/3)$) can be used to identify a $nxn$ honeycomb superlattice with $2p$ equilateral triangles symmetrically removed from the unit supercell, in addition to the atoms at their centers $I_{\alpha}$ and $I_{\beta}$ when $n \in \bar{1}_3 \cup \bar{2}_3$. Fig. II shows an example, the $(4,0)$-honeycomb.

It is possible to estimate the size of the induced gap at the $K_n$ point of these $(n,0)$-honeycombs. To this end, we perform a lattice renormalization by making use of the
bipartite nature of the Hamiltonian $H = H_{AB} + H_{BA}$. This simplifies the problem by halving the state space of interest. Indeed, since $H$ only allows transitions from the A to the B subspaces ($H_{BA}$) and vice versa ($H_{AB}$), it is sufficient to consider the problem in the A space only with Hamiltonian $H_{AA} = H_{AB} + H_{BA}$. For any non-zero eigenvalue $E_i$ and eigenvector $|\psi_{A,i}\rangle$ of this Hamiltonian there exist two solutions of the original problem with eigenvalues $E_i = \pm \sqrt{E_i}$ and eigenvectors $|\psi_{A,i}\rangle = \pm |\psi_{B,i}\rangle$, where $|\psi_{B,i}\rangle$ is defined to be $|\psi_{B,i}\rangle = E_i^{1/2} H_{BA} |\psi_{A,i}\rangle$; if $E_i = 0$, $|\psi_{A,i}\rangle$ is already a $H$ eigenvector. The converse is also true, namely from any eigenvector $|\psi_i\rangle$ the two projections $|\psi_{A,i}\rangle$ and $|\psi_{B,i}\rangle$ onto the A and B subspaces satisfy $H_{BA} |\psi_{A,i}\rangle = E_i |\psi_{B,i}\rangle$ and $H_{AA} |\psi_{A,i}\rangle = E_i^{3/2} |\psi_{A,i}\rangle$; that is, studying $H_{AA}$ one only misses possible zero eigenstates in the B subspace [20]. In graphene the renormalized Hamiltonian $H_{AA}$ describes a triangular lattice with on-site energy $t^2Z$ (where $t$ is the hopping term of $H_{1}$ and $Z = 3$ is the coordination number of A atoms in the original honeycomb lattice) and hopping $t^2$ between neighbors in the triangular lattice. Defects are of two kinds: while A vacancies translate simply into A vacancies in the renormalized lattice, B vacancies modify both the coordination number and the hopping between A sites. The renormalized $(n,0)$-honeycomb for $n = 4$ is shown in the left panel of Fig.2 whereas the right panel of the same figure displays its SBZ along with the graphene BZ. The state space at $K_{a}$ is given by its $n^2$ replicas within BZ and comprises $K$ or $K'$ depending on whether $n \in \mathbb{Z}_3$ or $n \in \mathbb{Z}_9$. Quasi-degenerate perturbation theory is necessary to estimate the ground-state energy $E_0(K_{a})$ (and hence the gap $\epsilon_{gap} = 2\sqrt{E_0}$), but it becomes intractable at large $n$ (i.e., at very small defect concentration $x = 1/n^2$) because a huge number of $K_{a}$ replicas gets close to the $K$ and $K'$ points. Therefore, we consider $x$ sufficiently small that the defects are isolated from each other, but large enough that a few state calculation is reliable. The smallest set of $K_{a}$ replicas contains $K$ and the $k_i$ vectors ($i = 1 - 3$) shown in Fig.2(right panel) for the case $n = 4$, and corresponds to the set of Bloch functions $|\psi_0\rangle = |\psi_{k}\rangle$ and $|\psi_{i}\rangle = |\psi_{k+i}\rangle$ built with $p_{z}$ orbitals at A sites; the case $n \in \mathbb{Z}_3$ is analogous except that $K$ is replaced with $K'$. $|\psi_0\rangle$ spans the $A''_2$ irrep of the $k$-group at $K_{a}$ ($D_{3h}$), whereas $\{|\psi_i\rangle\}$ span $A'_2 + E'$. Thus it is possible to set up a two dimensional problem in the $A''_2$ subspace. The corresponding Hamiltonian matrix can be obtained from the $H_{AA}$ matrix elements between (graphene) Bloch states, Eq.2

$$\langle \psi_{k'}|H_{AA}|\psi_{k}\rangle = t^2 \delta_{k,k'} (3 + F(k') - x^2 \delta_{k,k'} + \sum_{g} e^{i\delta_{g}k'} f(k')^* f(k)$$

Here $F(k') = \sum_{i=1}^{3} e^{-ik_{i}}$, $f(k') = \sum_{i=1}^{3} e^{-ik_{i}}$ (where $\delta_{i}$ and $\delta_{i}'$ are the vectors joining AA and AB nearest-neighbors, respectively), $g$ is a reciprocal superlattice vector and $\delta_{A}, \delta_{B}$ are the position vectors of the defects in the unit supercell. In deriving Eq.2, periodicity of the super-lattice has been used and the defects have been considered as isolated ($n > 2$). With the help of Eq.2, and of the symmetry properties of $F(k)$ and $f(k)$, the Hamiltonian matrix in the above $A''_2$ space reads as

$$t^2 \begin{bmatrix} 3x & -x\sqrt{3}F_x \\ -x\sqrt{3}F_y & 3 + F_x - 9x(2 + F_y) \end{bmatrix}$$

where $F_x = F(k_1) \sim -3 + 3(2\pi/3)^2 x - \sqrt{3}(2\pi/3)^3 x^{3/2}$. The lowest eigenvalue $E_0 (\sim 3x^2 (0.561 - 0.961\sqrt{3}) )$ allows us to estimate the energy gap $\epsilon_{gap}$ at the $K_{a}$ point.
This is plotted in Fig. 4 as a function of $x$ along with the results of tight-binding calculations. The importance of including a larger number of $K_n$ replicas close to $K(K, K')$ is evident at small $x$ where the energy gap decreases slightly faster than $\sqrt{x}$; the best-fit to the numerical results gives an exponent $\sim 0.66$. Tight-binding calculations reveal that the minimum gaps occurs either at $M$ or $\Gamma$ (see inset of Fig. 3) depending on $x$ and on the sequence considered, but behave similarly to the gaps at $K_n$. Differences between the two sequences appear at large $x$ and reflect the different shape of the low-energy bands (not shown). A best-fit of $\epsilon_{\text{gap}} = a x^b (1 + bx^d)$ to the numerical results, also reported in Fig. 3, gives $(a, b, \alpha, \beta) = (3.34, -4.99, 0.65, 1.14)$ for $n \in 1_3$ and $(3.37, +2.9, 0.66, 0.88)$ for $n \in 2_3$. We have also investigated the effect of breaking the electron-hole symmetry by performing tight-binding calculations with $t' \neq 0$. Introduction of the next-to-nearest neighbors interaction only affects the results at small $x$, where the valence and conduction bands start to overlap at some $x_c$ because of the asymmetry introduced in the energy spectrum. The position of this critical value $x_c$ shifts to larger $x$ when increasing $t'$ but remains small for realistic values (for $t' = 0.1t$ used in Fig. 3, $x_c < 10^{-3}$). Notice that the effect of next-to-nearest neighbor interactions is different for the two sequences considered.

To further investigate this point and, more importantly, to address the role of electron correlation we performed gradient-corrected density-functional-theory (DFT) calculations on a number of $(n,0)$-honeycombs of adsorbed H atoms. The details of the calculations are analogous to those reported in a previous work [17], except for the fact that a finer mesh of $k$ points has been used to correctly compute the energy gaps. The results are reported in Fig. 4 up to $n = 14$ ($x \sim 0.005$); for larger values of $n$ DFT calculations become prohibitive. As can be seen from Fig. 4, DFT results show a reduced gap size with respect to TB ones in all the cases considered but the effect is much more pronounced in the $1_3$ sequence than in the $2_3$ one. In particular, DFT results for $n = 5, 8, 11, 14$ closely parallel the TB ones ($t$ has been set to its accepted value, $t = 2.7$ eV), despite the fact that the first refer to a realistic situation where defects are H atoms while in TB calculations defects are modeled by simple $p_z$ vacancies. Discrepancies in the $1_3$ sequence at small $n$ needs further investigation, though it is in line with the introduction of the next-to-nearest-neighbor hopping (Fig. 3). Similar behaviour was found for the gap in armchair graphene nanoribbons where it was explained by the modified nearest-neighbor hoppings for the sites close to the defect [13]. In any case, both the size of the gap and its dependence on $n$ are promising for future applications.

Finally, to underline the role played by symmetry in designing the defective structures, TB results for different superlattices are also reported in Fig. 4. Notice that the $(n,0)$ honeycombs considered in this Letter show the largest gaps with the minimum number of defects per supercell (see the inset of Fig. 4, where the results for a number of $(n,p)$-honeycombs with $n \in 0_3$ are also reported).

To summarize, we have studied graphene superlattices of defects where a gap at the Fermi level opens because of symmetry. Tight-binding and density-functional-theory calculations show that the gap is indeed sizable, thereby suggesting that the proposed structures may play a role in designing future carbon-based electronic devices.

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