Theory of the electronic structure of grain boundaries in graphene

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Graphene presents frequently grain boundaries and defect lines, which occur spontaneously in the process of growth or can be created on demand [1,2]. Grain boundaries have been measured to affect both the electronic transport and the magnetic properties of graphene because they present localized states with energies at or close to the Fermi level [3-6]. Such states allow also for the decoration of defect lines with adsorbates, opening a route for nanosensor applications. As the electronic properties of graphene are modified by the localized states at the grain boundaries, the final control of graphene-based devices requires the tailoring and engineering of such defect lines. However, the relation between the geometry of grain boundaries and the induced electronic localized states has not been so far understood.

Defect lines in graphene can be seen as the outcome of matching of two graphene sheets with different edges, which produces localized states. Recently, general rules to predict the existence of edge-localized states and flat bands at the Fermi level in graphene nanoribbons with arbitrary shape of the edges have been given [7]. The localization at defect lines built of octagonal rings has also been understood as a consequence of the zigzag nature of the graphene edges forming the defect lines [8]. Here we bring into contact these ideas about localized states in graphene edges to give a more comprehensive explanation of states appearing in extended defect lines in graphene. We classify the energy spectra of grain boundaries into three types only, relating them directly to the basic classes of spectra of graphene edges [7]. These classes are presented in Fig. 1. We have found a simple formula, based on the topology of grains, which allows to obtain the number of interface bands with energies in the gap and close to the Fermi level. When two graphene edges are connected forming a grain boundary, the pairs of states localized at different edges strongly hybridize and split, usually reaching the energy band continua. The remaining unpaired states (which originate from one edge only) constitute the grain boundary localized bands with energies close to the Fermi level. An example for the grain boundary formed by joining a pure zigzag edge and a chiral edge defined by the edge-translation vector (4,1), is shown in Fig. 2.

Our method to find localized bands around the Fermi energy provides a new understanding on states localized at grain boundaries, showing that they are derived from the edge states of graphene, and allowing for the prediction of their electronic characteristics without performing numerical calculations. Such knowledge is crucial for defect engineering towards practical electronic and optoelectronic applications based on graphene and carbon nanotubes, which strongly depend on the spectrum near the Fermi energy.

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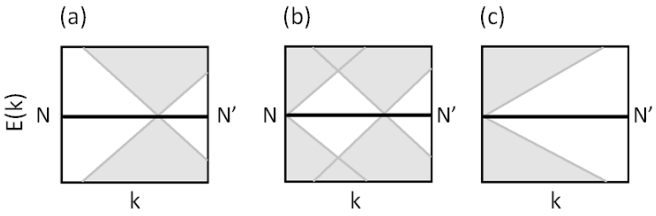

Figure 1. Three possible band structures E(k) for periodic grain boundaries in graphene. k is along the direction corresponding to the grain boundary. Gray areas schematically represent the band continua. Solid horizontal lines represent gap bands with energies close to the Fermi level and localized at grain boundary. The number of such bands is uniquely determined by the topology of the grain boundary. In cases (a) and (b) the numbers N and N' of the bands at the left- and right-hand side of the Dirac cone may be different (can be even equal to zero).

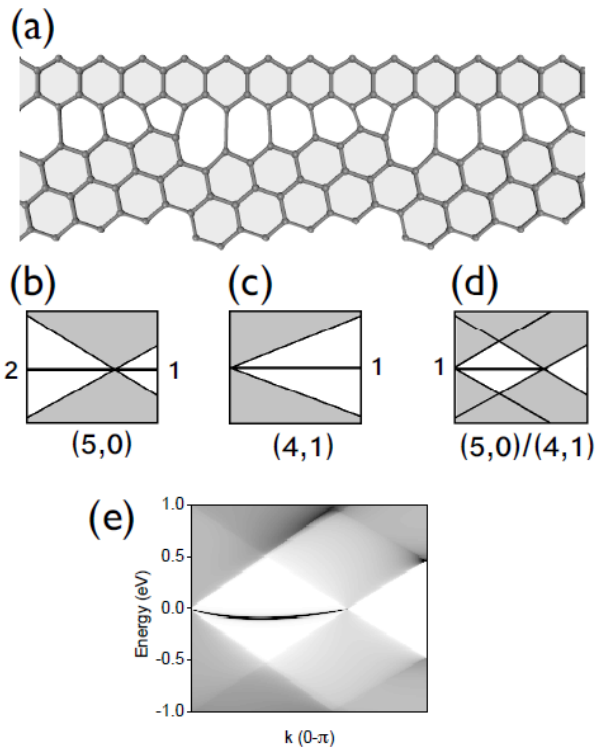

Figure 2. (a) Geometry of the grain boundary formed by joining pure zigzag edge (upper one) with the chiral edge defined by translation vector (4,1). Periodicity of the zigzag edge is adjusted to the chiral edge (4,1) and equals (5,0). (b) and (c): Schematic energy spectra of the chiral (4,1) and zigzag (5,0) edges, respectively. (d) Schematic spectrum of the (5,0)/(4,1) boundary, in good agreement with (e) the calculated density of states (DOS) at the (5,0)/(4,1) boundary. Darker color indicates a larger DOS value. One zero-energy band localized at the zigzag (5,0) edge hybridizes with the band localized at the chiral (4,1) edge; they strongly split and merge the band continua. The remaining band, which extends from k=0 to the Dirac cone, originates from the zigzag edge and constitute the final band localized at the grain boundary.