Scattering Resonances in bilayer graphene

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Abstract. We present density functional calculation of the empty states of graphene single-
and bi-layer. Particular attention is given to the recently discovered scattering resonances of
graphene. When two layers are assembled, these states hybridize, giving rise to more complex
states that are strongly localized in the interlayer regions. These states are at the origin of
bands of graphite that show a pronounced dispersion in the direction perpendicular to the
planes and have been observed over decades in experiments.

1. Introduction
The electronic structure of free-standing graphene and of graphene based materials has been
intensively investigated. Most of these investigations have been concerned with the occupied energy
levels, or have covered a limited energy range above the Fermi level ($E_F$), say, of the order of a few
eV [1-6]. Therefore, the knowledge of the unoccupied energy bands is still largely lacking and appears
important for the understanding of the interfacial properties of graphene on substrates [7,8]. In
particular, the electronic structure of free-standing graphene has been intensively inspected by
countless approaches, ranging from tight-binding methods to density functional theory (DFT) codes,
and it has been recently classified using group theory algebra [5,6]. At energies above the vacuum
level some studies [6] have predicted the existence of two-dimensional (2D) discrete states embedded
in the three-dimensional (3D) continuum, showing that electrons in these confined 2D states have a
non-negligible probability to escape into the vacuum, thus turning the states into resonances.

To study how the peculiar 2D properties of graphene are reflected in 3D derived systems, recently
we considered the local density DFT band structure of graphene and graphene grown on Ni(111) [8].
We focused on the unoccupied energy levels up to 50 eV above $E_F$, and compared their energy-
momentum dispersions with available Angle Resolved Secondary Electron Emission (ARSEE)
observations [7,8]. Indeed, experiments of secondary electron emission have been proven to be very
well suited for the characterization of surfaces and nanomaterials [8-11]. We showed how the
dispersions obtained in ARSEE experiments on graphene/Ni(111) can be related to hybridized energy
states found in DFT calculations, discussing the capability of SEE to probe the interfacial coupling of
2D materials with a substrate. Our results provided a first evidence of the scattering resonance
predicted in ref. [6], showing that its dispersion is only slightly modified by the interaction with the
substrate.

As a part of our research effort in understanding the properties of the unoccupied electronic
structure of graphene based materials, we performed also state of the art density functional
theory (DFT) calculations of the electronic band structure of graphene few-layers and graphite,
focusing on the unoccupied energy levels above the Fermi level. Here we present the calculated band structure for graphene bilayer. Similarly to the case of graphene on nickel [8], the calculations show the sensitivity of the scattering resonance to the environment surrounding the plane. When two layers are assembled, these states hybridize, giving rise to more complex states. The dispersion of these states is similar to that observed in graphene and also to that of states of 3D graphite that have been observed in LEED and ARSEE experiments.

2. Calculations
We performed ground state (GS) calculations on 1-3 layer graphene slabs and graphite, using a DFT approach based on the local density approximation (LDA) [12] for the exchange and correlation part of the total Hamiltonian, as implemented in the Abinit code [13,14]. We used the plane-wave basis set (with a cut-off energy of 25 Hartree) to expand the valence electron density, while the core electrons of the carbon atoms were replaced by Troullier-Martins norm-conserving pseudo-potentials [15]. The few-layer graphene structures were obtained by superimposing graphene sheets with the ABAB stacking of graphite at the graphite interlayer spacing, namely 3.354 Å. The separation distance between the repeated systems in the perpendicular direction was large enough to exclude interaction between the replicas, i.e., we kept the same total volume in all slab calculations, and adopted a vacuum distance d larger than 30 Å. Brillouin Zone (BZ) integrations were performed over unshifted 60 × 60 × 1 and 30 × 30 × 17 Monkhorst-Pack grids [16], for 2D-slab and 3D calculations, respectively. The converged electron density was finally used to compute the one electron Kohn-Sham (KS) eigenstates and eigenvectors on selected k-points along high-symmetry BZ-paths.

3. Results
The calculated band structure of Graphene in Fig.1a is in agreement with other calculations found in literature (see for example refs.[1,6]).

![Figure 1. (a) Energy bands of graphene (red solid lines), and 2D free-electron bands (blue dashed lines) along the ΓKΜ path. (b) Projected k-DOS of graphene: the darker regions mark states with a large localization onto the graphene plane.](image)

We can identify the Dirac cone at the K point, formed by the π and π* bands that touch at \( E_F = 0 \). The empty part is composed by a quasi-continuum of states (which extrapolates to a continuum in the \( d \to \infty \)-limit) starting at about 4 eV with a parabolic-like dispersion vs \( k_\parallel \). The quasi-continuum produces 5 high density regions (dashed blue lines), dispersing as: \( \frac{k_\parallel^2|g_{j}\rangle^2}{2m} + \varphi \). These are 2D free
electron bands typical of the hexagonal honeycomb lattice, where $\mathbf{G} \parallel$ is a surface reciprocal lattice vector and $\varphi = 4.6 \text{ eV}$ is the energy of the vacuum level relative to $E_F$. Similar parabolic dispersions have been observed experimentally as intensity patterns in SEE from graphene layers grown on SiC [17]. Superimposed to the continuum there are discrete states typical of the graphene sheet [5,6]. The lowest lying of these states enter the continuum from below and are clearly seen to retain their individuality. At higher energies the discrete states are fully immersed into the continuum and some of them are no longer visible. To detect them with sufficient accuracy, we focused on the localization of the KS wave-function $\psi_{n,k}(x,y,z)$ on the graphene plane, for the sampled wave-vectors $\mathbf{k}$ and band-energies $E_n(\mathbf{k})$. Accordingly, we considered the probability densities $\rho_{k,n}(z) = \int_{\text{UC}_{2D}} dx \, dy \lvert \psi_{k,n}(x,y,z) \rvert^2$ associated to the KS-states along the out of plane direction $\hat{z}$, where the in-plane integration was performed over the 2D unit cell of the graphene layer ($\text{UC}_{2D}$). In the attempt to improve the visualization as a whole of the band structure of graphene, we further integrated the $\rho_{k,n}(z)$ over an interval $\delta z = 4\AA$ centered at the graphene plane. The resulting energy distributions were convoluted with a Gaussian function $G_\sigma$ of standard deviation $\sigma = 0.5 \text{ eV}$. In this way, we could introduce a $\mathbf{k}$-resolved density of states projected onto the C atoms:

$$\mathbf{k}\text{-DOS}(E) = \sum_n G_\sigma(E - E_n(\mathbf{k})) \int_{-\delta z/2}^{\delta z/2} \rho_{k,n}(z) dz.$$  

In Fig.1b we report a false color plot of the projected $\mathbf{k}$-DOS obtained by sampling the $\Gamma KM$ path in the BZ. This representation improves the visualization of discrete states according to their localization on the graphene plane. The darker regions correspond to states with larger localization integrals. With the aim of studying the transition from a pure 2D material as graphene to graphite we performed similar $\mathbf{k}$-DOS calculations on few-layers graphene. In the following we will discuss the $\mathbf{k}$-DOS for the bilayer, reported in Fig.2, where the integration of the probability density has been carried out over an interval containing the whole slab.

4. Discussion

We start our analysis with the graphene $\mathbf{k}$-DOS in Fig.1b; some wave functions are strongly concentrated near the graphene plane, whereas others show a more extended tailing into the vacuum. Particularly visible in Fig.1 are, for instance, the states labeled by $\sigma^*$ and $\pi^*$ which at the $\Gamma$ point are found at 8.4 eV and 11.4 eV, above the Fermi level. Looking at the $\mathbf{k}$-DOS for 2-layer in Fig. 2, we recognize features similar to those present in graphene. In particular, Fig.2 shows that the dispersion of the states that are more strongly localized on the graphene plane, like for instance the $\sigma^*$ and $\pi^*$ states, are not changed by the interlayer interaction. Due to the strong localization of their wave-functions on each graphene plane, these states are preserved in shape with increasing number of layers (even though there is a correspondence between the states in single-layer graphene and in fewlayer graphene each band in graphene gives rise to multiples bands in a fewlayer slab, the number being equal to the number of layers in the slab). These states can be connected to similar bands in graphite that show negligible dispersion in the direction perpendicular to the carbon planes [18]. On the other hand, the interaction between the graphene planes leads to substantial changes in those states that are less localized on the planes, and determines the onset of new states that are not observed in single-layer graphene.
Figure 2: Projected k-DOS of 2-layer graphene. The yellow crosses mark the energy-momentum positions of the states used for the $\rho_{n,k}(z)$ plots in Fig. 3.

A strongly dispersive band labeled SC is observed in Fig. 1b, extending from $\sim 28$ eV at the $\Gamma$ point to $\sim 13$ eV at the K point. The dispersion of the SC-band corresponds to the narrow line of maximum probability for electron transmission, associated to the lowest lying dispersing branch of the scattering resonance of graphene (see Fig. 4 of Ref. [6]). The SC-probability densities are presented in Fig. 3a for two representative $k$-points along the $\Gamma K$ path of the BZ, namely the $\Gamma$ point ($E - E_F \approx 28.5$ eV) and the point lying at $k = 1.02 \, \text{Å}^{-1}$ ($E - E_F \approx 15.7$ eV). They become zero at the graphene plane, and have two maxima at some $z$-values in the middle of the interlayer spacing in graphite. Their shapes then recall those of the $\pi^*$ band states, but their widths are almost double. Thus, the SC-states are expected to show strong modifications when the graphene layers are assembled to form few-layer slabs or graphite. Indeed, a closer look at Fig. 2 shows that, unlike the mono-layer graphene case, two high density bands having a nearly parallel dispersion, starting at $25 - 28$ eV at $\Gamma$ and dispersing towards $13 - 15$ eV at $K$, are observed in 2-layer graphene. A sample of their probability densities is given in Fig. 3b for 2-layer graphene, where a wave-vector $k = 0.77 \, \text{Å}^{-1}$ along the $\Gamma K$ line is chosen and the two bands are clearly resolved in energy (to 17.9 eV and 19.8 eV above the Fermi level, respectively).

Figure 3: (a) Probability density profiles for the SC state of graphene at two representative $k$-points along the $\Gamma K$ path. (b) The two states generated from the SC in 2-layer graphene are given at $k_{||} = 0.77 \, \text{Å}^{-1}$.
These high energy features find correspondence in graphite, as bands with a pronounced $k_\perp$ dispersion and probability density strongly concentrated in the interlayer region [18]. These states of graphite have been observed in several ARPES and ARSEE experiment, as well as other techniques [19,20], and clearly resolved as two features in VLEED [18]. In all these experiments strongly dispersive bands from about 28 eV at $\Gamma$ to 13 eV at $K$ have been spotted, that are reminiscent of the dispersion of the scattering resonance in the mono-layer graphene given in Fig.1. Furthermore, similar spectral features have been observed as prominent ones also on graphene layers grown on SiC [17] and Ni(111) [21], as well as on other metal substrates [22].

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