Effective band structure of H-graphene

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Abstract

A band structure unfolding procedure based on the spectral function is introduced, and the weight formula suitable for non-othogonal tight-binding model is presented. Unfolded band structures are shown for hydrogenated graphene using supercell calculations corresponding to HC_{50} and HC_{98}.

Introduction

Graphene has unique electronic properties, and it is expected to have important applications [1]. However, it is a gapless semiconductor, which presents a limitation for electronics applications. Functionalization by hydrogen atoms has been one of the ways proposed to turn graphene into an insulator. Consequently, many investigations have been made regarding the electronic structure of H-graphene. Angle-resolved photoemission spectroscopy (ARPES) experiments have made an important contribution to the understanding of the band structure of H-graphene [2]. In particular, hydrogen adsorption leads to band gap opening and the appearance of a midgap impurity band, as shown by theoretical calculation as well as experiments. However, the calculations must rely on the supercell approach to treat defected systems, which yield heavily folded bands. Such bands are complicated to understand and are not suitable for comparison with ARPES spectra. Therefore, it is very useful to be able to unfold supercell bands back to the primitive cell description. In this paper, we discuss the method of band structure unfolding and present the effective band structure of H-graphene.

Theory

The tight-binding hamiltonian of graphene, with nearest-neighbor hopping, is given by

$$H = -t \sum_{\langle i,j \rangle} c_i^\dagger c_j, \tag{1}$$

with $t = 2.7$ eV as the hopping energy between nearest neighbor carbon atoms. Hydrogen adsorbs on graphene by binding on top of a carbon atom, which in this model has properties quite similar to a vacancy. A slightly more detailed description involves adding the perturbation

$$H' = \varepsilon_h d^\dagger d + \gamma_h H (c_0^\dagger d + d^\dagger c_0) \tag{2}$$

to the graphene hamiltonian, where $\varepsilon_h = -0.2$ eV is the onsite energy of H orbital, and $\gamma_h = -5.2$ eV is the hopping between H and C. A more detailed model uses the LCAO or non-orthogonal tight-binding method, which goes beyond nearest neighbor hopping, and includes overlap integrals between the orbitals.
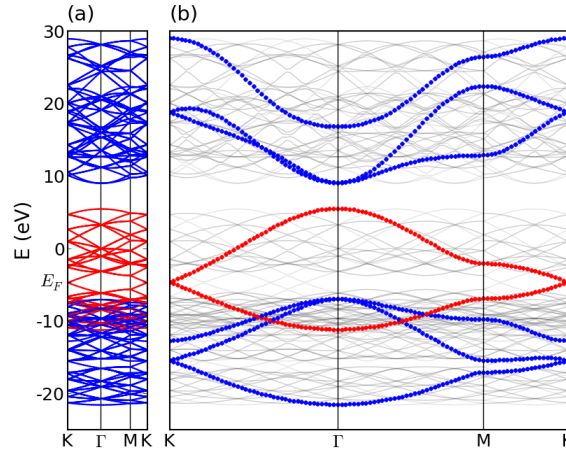
Figure 1: Band structure of graphene based on a 5×5 supercell calculation. (a) Folded bands in supercell Brillouin zone. (b) Unfolded bands in primitive cell Brillouin zone. The folded bands (light grey) are plotted for comparison. The σ and π bands are colored blue and red, respectively.

Band structures are obtained by solving the generalized eigenvalue equation,

$$HC = ESC, \tag{3}$$

where S is the overlap matrix, which is the identity matrix in the orthogonal case. For a periodic system, the eigenvalue problem is reduced by Bloch's theorem to the number of atoms in a unit cell, and the band structure is determined by $E_n(\mathbf{k})$, where n is the band index, and $\mathbf{k}$ is the crystal momentum, which may be restricted to the first Brillouin zone. In supercell calculations used to treat defected systems, a larger unit cell than the primitive unit cell of the underlying system is used. This imposes an artificial periodicity which allows the calculation of band structure, but the supercell wavevectors, $\mathbf{K}$, are now confined to a smaller Brillouin zone while the number of bands are increased proportionately. This renders the band structure complicated and less useful, which makes it desirable to unfold the bands back to the primitive cell description.

Unfolding can be accomplished by using the fact that the information about band structure is contained in the spectral function, $A = -1/\pi \operatorname{Im} G$, where G is the retarded one-particle Green's function. An effective band structure can be derived from the diagonal elements of the spectral function, $A(\mathbf{k}, \omega)$. Indeed ARPES experiments measure just the spectral function in the extended zone which is equivalent to the unfolding procedure.

The unfolding formula obtained in this way consists of both an energy eigenvalue and an unfolding weight given by [3–5],

$$W^{\mathbf{K}J} = \frac{1}{\mathcal{N}} \sum_{MN} C_N^{\mathbf{K}J*} U_{NM}(\mathbf{k}) C_M^{\mathbf{K}J}, \tag{4}$$

where

$$U_{NM}(\mathbf{k}) = \sum_{\mathbf{r}} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_M)} S_{0N,\mathbf{r}m_M}. \tag{5}$$

Here $\mathcal{N}$ is the number of primitive cells contained in a supercell, and uppercase and lowercase letters refer to supercell and primitive cell quantities, respectively. The sum in (5) is over all the primitive lattice vectors, while the pair $\mathbf{r}_M, m_M$ describes mapping of the Mth orbital of the supercell to a primitive cell description. In the case of orthogonal orbitals based on Wannier
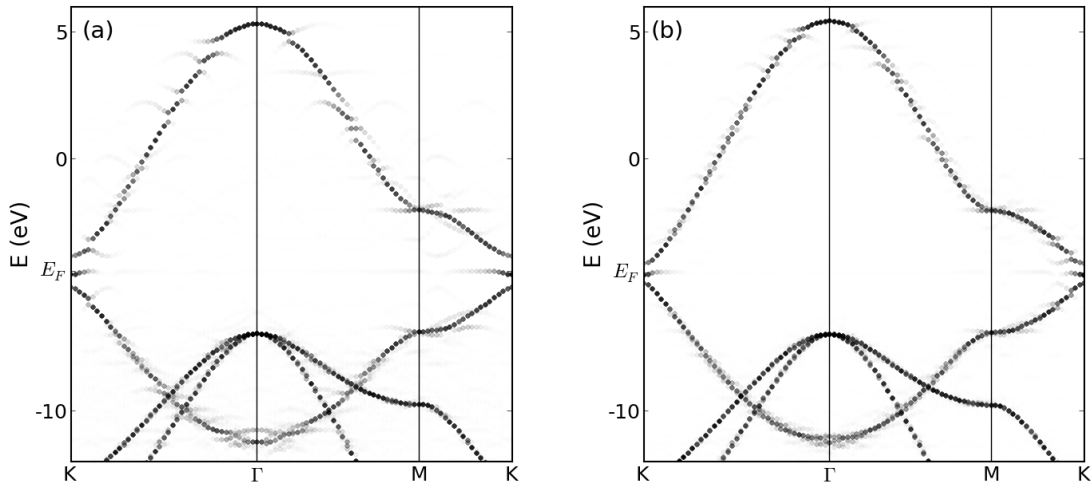
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Figure 2: Effective band structures of hydrogenated graphene. Single H (a) on 5×5 supercell, and (b) on 7×7 supercell corresponding to H concentrations of 2% and 1%, respectively.

functions the unfolding formula simplifies to,

$$U_{NM}(\mathbf{k}) = e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_M)} \delta_{n_N, m_M}. \tag{6}$$

Results

A convenient way of generating a non-orthogonal tight-binding model is via density-functional based tight-binding (DFTB) method. Thus the DFTB+ code [6] was used to obtain the folded band structures of 5×5 and 7×7 supercells of graphene with one hydrogen adsorbate, which correspond to HC_{50} and HC_{98}, respectively. In Fig. 1, a calculation is shown for perfect graphene to compare folded and unfolded band structures, and to see the great simplification that can be achieved. The separation of σ and π bands is based on the Mulliken analyis of the orbital populations. Figure 2 shows unfolded band structures of H graphene, where we can see band gap opening and the appearance of a midgap band.

In summary, band structure unfolding was discussed and applied to two concentrations of H on graphene. The results show the usefulness of the procedure, especially, for comparison with ARPES experiments.

References

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