Visualizing the influence of point defects on the electronic band structure of graphene

M Farjam

School of Nano-Science, Institute for Research in Fundamental Sciences (IPM), PO Box 19395-5531, Tehran, Iran

E-mail: mfarjam@ipm.ir

Received 2 December 2013, revised 9 February 2014
Accepted for publication 17 February 2014
Published 27 March 2014

Abstract
The supercell approach enables us to treat the electronic structure of defective crystals, but the calculated energy bands are too complicated to understand or compare with angle-resolved photoemission spectra because of inevitable zone folding. We discuss how to visualize supercell band structures more effectively by incorporating unfolded spectral weights and orbital decompositions into them. We then apply these ideas to gain a better understanding of the band structure of graphene containing various types of point defects, including nitrogen impurity, hydrogen adsorbate, vacancy defects and the Stone–Wales defect.

Keywords: band structure, defects, graphene, unfolding

(Some figures may appear in colour only in the online journal)

1. Introduction

The electronic band structure of a crystal is an important tool in understanding its electronic, optical, transport and magnetic properties. Applied to graphene, the band structure can show many interesting facts about its electronic properties [1, 2]. We can see that graphene is a gapless semiconductor, and its low-energy excitations have linear dispersion, which implies that they have the properties of massless Dirac fermions [3–5].

Defects and impurities have a significant influence on the electronic properties of semiconductors, and can be introduced deliberately to tailor their electronic structure. In graphene, atomic impurities, point and structural defects, edges and substrates can all modify the electronic structure in important ways. Two simple impurities are the substitutional dopants formed by the carbon neighbours in the periodic table, boron and nitrogen, which can turn graphene into a p- or n-type semiconductor, respectively [6]. Two other simple defects of a different type are vacancies and hydrogen adsorbates, which induce midgap states and magnetic moments in graphene [7]. One small structural defect is the 57–57 defect, known as the Stone–Wales (SW) defect [8, 9].

One convenient way of treating point defects is via the supercell approach within density-functional theory (DFT) and tight-binding method calculations. The supercell device allows us to use methods designed for periodic structures to treat relatively isolated defects. However, this workaround has a price: the Brillouin zone (BZ) becomes smaller as the supercell gets larger, which results in the folding of the bands. The complicated bands are difficult to comprehend or to compare with angle-resolved photoemission spectroscopy (ARPES) experiments. This often leaves the density of states (DOS) as the sole option for spectral analysis.

However, there are ways to improve the visualization of band structures. A simplification is made possible by the unfolding method, which allows the plotting of effective bands in the larger BZ of the normal system, i.e. one described in terms of the primitive unit cell [10–14]. Furthermore, an enhancement can be made by incorporating orbital contributions in both supercell and normal cell band structures. Orbital decomposition is more commonly used in obtaining the partial density of states (PDOS) as the sole option for spectral analysis.

In this paper, we develop ways of implementing the above ideas into the visualization
of electronic structure data. We then apply them to the case of graphene containing point defects. Our results are based on density-functional-based tight-binding (DFTB) calculations for 5 × 5 supercells of graphene containing a nitrogen impurity, a hydrogen adsorbate, a vacancy and an SW defect, respectively.

In section 2 we describe the computational details, including the DFTB calculations and the unfolding procedure. In section 3 we present our results and discuss perfect graphene and each type of defect. We then summarize our conclusions in section 4.

2. Computational details

2.1 DFTB calculations

We calculate the requisite electronic structure data for the unfolding method using the DFTB+ code [16], which is an efficient and accurate implementation of the DFTB method [17]. Since the method is based on a small set of non-orthogonal atomic orbitals, 2s, 2p_x, 2p_y, and 2p_z, for carbon and nitrogen, and 2s for hydrogen, the unfolding formula can be described as below.

We use n × n supercells, which encompass N_o = n^2 normal unit cells, or 2n^2 honeycomb lattice sites. This implies for n = 5 a 2% concentration of periodically arranged point defects, which is sufficiently small to consider them as relatively isolated, but large enough to produce visible effects. We need to run the code several times. Having defined a supercell with our choice of defect placed in a tentative position, in a first calculation we allow the atomic positions to relax. Then, using the optimized coordinates, we calculate the DOS and PDOS using a finer k-grid for the desired accuracy. Finally, we use the well-converged charges saved from the previous self-consistent calculation to obtain the data for the band structure along the given paths in the supercell and normal cell Brillouin zones, respectively.

The basic ingredients needed for the unfolding method consist of eigenvector coefficients and overlap integrals. Concomitant with the band structure calculations, we instruct the code to save these data in designated files. To estimate the size of the data, which may grow to be quite large, let N_o be the total number of orbitals in a supercell, which is also the total number of bands, and let N_k be the number of k points used in the calculation of the band structure. The overlap integrals are represented as a sparse matrix [16], so their size can only be estimated to be less than N_R × N_o × N_o × (size of a real number), where N_R is the small number of unit cells required to include non-zero overlaps. On the other hand, the total size of the complex eigenvectors, which is by far the larger set of data, is exactly 2 × N_k × N_o × N_o × (size of a real number).

2.2 Unfolding procedure

We need an unfolding formula that takes into account the non-orthogonality of the atomic orbitals. Such a formula has been derived recently by Lee et al in [13]. In this section, we describe their method from the viewpoint of numerical implementation.

It is customary to use upper and lower cases to refer to the supercell and normal cell variables, respectively, so K and k denote the wavevectors of the supercell Brillouin zone (SBZ) and normal cell Brillouin zone (NBZ), respectively. A given k in the NBZ folds onto exactly one K in the SBZ but, in contrast, each K unfolds back to N_o normal system k vectors in the NBZ. The unfolding method assigns the same energy at a given K to the multiple unfolded ks with proper spectral weights. In practice, this simple procedure can be followed. If we choose a k path in the NBZ, and regard it as a path in the extended zone of the supercell, then each K needs to be unfolded to only a single k = K to achieve the desired band structure representation. We calculate the energy eigenvalues along this path for the supercell system, and determine their spectral weights using the unfolding formula.

It is useful to note some of the properties of the non-orthogonal orbitals. The normalization of an eigenvector, \( |KJ\rangle \), in terms of its expansion coefficients, is given by

\[
\sum_{MN} C^M_N S_{NM}(K) C^K_M = 1, \tag{1}
\]

where \( S(K) \) is the overlap matrix of the Bloch orbitals,

\[
S_{NM}(K) = \sum_R \exp(iK \cdot R) S_{NM}(R). \tag{2}
\]

Here, the overlap integrals are defined by

\[
S_{NM}(R) \equiv S_{0\eta,RM} = \langle 0\eta | R M \rangle. \tag{3}
\]

In (1), J and N (or M) are band and orbital indices, respectively, and are both in the range 1 to N_o. Breaking down the contributions in (1), we can write the orbital populations for an eigenstate as

\[
P^K_N = \text{Re}\left\{ \sum_{M} S_{NM}(K) C^K_M \right\}. \tag{4}
\]

The unfolding procedure must uncover the hidden translational symmetry inherited by the supercell system from the normal system. A useful connection between the two systems is expressed by the Fourier relation [10],

\[
\frac{1}{N_o} \sum_{G} \exp(iG \cdot r) = \delta_{r,R}, \tag{5}
\]

where \( R \) and \( r \) are the corresponding lattice vectors, respectively, and the sum is over the set of N_o reciprocal lattice vectors of the supercell system that unfold the SBZ onto the NBZ. An orbital described in the supercell system by the pair \( R,M \) can be described in the normal system through the mapping [13],

\[
R, M \rightarrow R + r_M, m_M, \tag{6}
\]

where \( r_M \) is one of the N_o normal system lattice vectors within a supercell. The range of \( m_M \) is the (possibly variable) number of orbitals in each normal unit cell.

The unfolded spectral weight is given by [13]
where \( k = k + G \), and

\[
U_{NM}(k) = \sum_r \exp[i \mathbf{k} \cdot (r - r_M)] S_{N r, r_M},
\]

which is a particular Fourier sum of overlap integrals that encapsulates the unfolding information. We call this the unfolding matrix. A convenience of this unfolding formula is that it does not require the definition of a virtual crystal for its implementation.

Noting the similarity between \( U(k) \) and \( S(K) \), we write partial unfolded orbital weights as

\[
W_{NM}^{K}(G) = \frac{1}{N} \sum_{M} C_{N M}^{K} U_{NM}(k) C_{M}^{K*},
\]

so that \( W_{NM}^{K}(G) = \sum_{N} W_{NM}^{K}(G) \). We can verify that the unfolding matrix is Hermitean, so the spectral weights are real. This can be shown by writing \( S_{N r, r_M} \) as \( S_{r r, n m} \), and using the symmetry properties of overlap integrals. Another checkpoint is the special case of an orthonormal basis set. We can easily see that orthogonality implies that \( S_{N r, r_M} = \delta_{N n, r r, m m} \), from which we obtain the simpler result [12],

\[
U_{NM}(k) = \exp[i \mathbf{k} \cdot (r_N - r_M)] \delta_{r r, m m}.
\]

The main numerical task pertains to the unfolding matrix in (8). First, there is a sum over the infinite set of lattice vectors, \( r \), but the actual set is sharply restricted by the range of overlap integrals. Second, it must be noted that the overlap integral \( S_{0 N, r M} \) is equivalent to one in the standard form of \( S_{0 N, R M} \), supplied by the electronic structure code.

Figure 1. (a) The band structure of graphene obtained from supercell calculations. (b) The unfolded bands in the normal BZ. The light grey bands are a supercell band structure in the extended zone. (c) The total DOS. (d) Colour map used in the band structure plots. (e) The 5 x 5 unit cell used in the supercell calculations. (f)–(h) The band structure and DOS limited to a window of \( E_F \pm 2 \) eV centred on the Dirac point.
The supercell and normal cell lattice vectors are related by $r = R + r_i$, where $r_i$ is a normal lattice vector within a supercell, while the orbital index $M'$ is determined by the pair of $r, m_M$.

Two sum rules can help us verify the results of our calculations. By using (5), we can prove the first one,

$$\sum_G W^{KL}(G) = 1.$$  (11)

The second one, which is more practical for our procedure, is given by

$$\sum_J W^{KL}(G) = \frac{N_o}{N_v},$$  (12)

where the right-hand side is just the average number of basis orbitals in the primitive unit cell of the normal system. This sum rule is a consequence of the properties of the spectral function.

3. Results and discussion

3.1 Perfect graphene

The band structure of perfect graphene provides a good testing ground for our numerical procedure, since we know exactly what to expect. Furthermore, it allows us to measure the computational load of the unfolding procedure, which is about the same in all of the cases that we consider. Using a Fortran serial code, on a computer with an Intel® Core™ i7-3610QM CPU, the runtime for the unfolding of this example was about 1 min.

We first explain our approach to using additional data consisting of unfolded spectral weights and orbital populations in the visualization of band structures. (A somewhat different approach is described in the supplemental material of [18]). In the (matplotlib) 2D plotting package used here, we can specify the colours and transparency in terms of parameters $r, g, b$ and $\alpha$, respectively, all in the 0–1 range [19].

Figure 2. (a) The band structure of nitrogen-doped graphene obtained from supercell calculations. (b) The unfolded bands in the normal BZ. (c) The total DOS and PDOS of the nitrogen orbitals. (d) Colour map used in the band structure plots. (e) The 5 × 5 unit cell with nitrogen at the centre. (f)–(h) The band structure and DOS plotted in a window centred on the Dirac point. The Fermi level is seen to have shifted because of doping by the extra electron of nitrogen. There is a small band gap opening at the Dirac point.
in the *rgb* colour space, (0,0,0) and (1,1,1) represent black and white, respectively, and these are visible or invisible on a white background. The $\alpha$ parameter controls the transparency, so that $\alpha = 0$ is completely transparent and thus invisible, and $\alpha = 1$ is completely opaque. We adopt a simple scheme and always decompose the orbital contributions into only two sets, which are represented by blue (0,0,1) and red (1,0,0), respectively. We then use the normalized weighted average of the colours to represent the mixing of the two sets, and set $\alpha$ equal to the total spectral weight, which results in the colour map shown in figure 1(d). It is possible to partition the orbitals into more than two sets, but the colour maps become more complicated. We must mention that this continuous range of colours is unnecessary for the present case of perfect graphene, where the weights turn out to be zero or unity, but it will be essential for defective graphene.

Figure 1(a) shows the band structure, using 25 $K$ points along the $\Gamma$KM path in the SBZ. We assigned our two pure colours to the two sets consisting of 2$s$, 2$p_x$, 2$p_y$ orbitals and the 2$p_z$ orbital, respectively. This made the $\sigma$ and $\pi$ bands appear in these colours, since these bands are mutually orthogonal in graphene. However, heavy folding makes it hard to recognize the shape of the bands.

Figure 1(b) shows the unfolded bands. We make the calculations using the same 5 x 5 unit cell along the $\Gamma$KM path in the NBZ of graphene. As this path is five times larger than the one in SBZ, we use 121 $K$ points. The expected bands of graphene emerged, in blue and red, out of the complicated supercell bands, shown in light grey. Figures 1(f)–(h) show the same data as in figures 1(a)–(c), but in the important low energy range.

### 3.2 Nitrogen impurity

We repeated similar electronic structure calculations for a 5 x 5 graphene supercell with a single nitrogen substitutional impurity. The results are shown in figure 2, where we used the same visualization approach discussed in section 3.1, except we...
partitioned the orbital contributions according to the atoms, C and N. The utility of a continuous colour map is demonstrated by the existence of bands with contributions from both C and N orbitals. We note the appearance of the bound states below each of the $\sigma$ and $\pi$ bands because of the presence of nitrogen impurity [20]. In addition, the unfolding shows that the weights of these states have non-uniform distributions in the NBZ.

In figures 2(f)–(h), we show the data for the low-energy spectrum. Because of doping by nitrogen, the Fermi level has shifted above the neutrality point. The presence of the impurity also caused a small gap to open up at the Dirac energy.

3.3 Hydrogen adsorbate

The results of calculations for a single hydrogen adsorbate on a $5 \times 5$ graphene supercell are shown in figure 3. A buckling of the graphene lattice near hydrogen, seen in figure 3(e), indicates the formation of an $sp^3$ defect. Such a defect effectively creates a $\pi$ orbital vacancy, which manifests itself as a midgap state at the Fermi level [21, 22]. We can see the midgap state in all the band structure plots, as well as the DOS plots. Moreover, most of the weight of the midgap band comes from carbon $2p_z$ orbitals. There is a bound state visible in the gap above the $\pi$ bands with contributions from both C and H atoms, see figures 3(a)–(c) [23]. We note, in figure 3(g), that the weight of the midgap band is accumulated near the $K$ point, a fact that has also been observed in the ARPES spectra of hydrogenated graphene [24].

3.4 Vacancy defects

The electronic structure calculation for graphene with a missing atom is shown in figure 4. Although not visible in figure 4(e), the relaxation of atoms results in a Jahn–Teller distortion [7]. There are four missing orbitals at the vacancy site, which can give rise to midgap bands, and other spectral changes [25]. Three midgap bands are clearly displayed in figures 4(f)–(h), where the use of the colour map has also revealed the difference in their orbital decomposition. The two pure colours were assigned to two sets of carbon atoms, those nearest the vacancy site and those on the remaining sites.
Lastly, we performed SW defect calculations. A similar example was recently treated with a different band unfolding methodology in [26], which could provide an interesting comparison. Although the Dirac cone is generally preserved, as pointed out in [26], a small gap appeared at the $K$ point of the unfolded bands, shown in figure 5(g). A close examination of the folded bands, see figure 5(f), shows that there is actually no gap in the energy spectrum, but that the band crossing has slightly shifted from its SBZ $K$ point towards the $\Gamma$ point. In addition, the SW defect has caused much smearing and breaking up of the bands, and the appearance of new bands, especially for the $\sigma$ bands. It can be expected that the magnitude of the defect-induced effects will diminish smoothly as the size of the supercell is gradually increased.

In all cases, we checked that the sum rule, (12), holds. For pure graphene, the SW defect or nitrogen impurity, the sum adds up to $N_d/N_u = 200/25 = 8$, while for hydrogen and vacancy defects it adds up to $201/25 = 8.04$, and $196/25 = 7.84$, respectively. The variety of examples used shows the versatility of our procedure.

### 4. Conclusions

We implemented the unfolding method of Lee et al [13], proposed how to visualize additional data from spectral weights in energy dispersion plots, and demonstrated these for selected defective 2D graphenes. Although the DFTB+ code was used in this work, the unfolding procedure described can more generally be employed for any electronic structure code that uses a basis of non-orthogonal atomic orbitals. It can be predicted that a great number of graphene-based systems, involving defects, impurities, adsorbates and substrates, can take advantage of the methods discussed here. The simplified effective band structures could be more easily comprehended, and supercell calculations may be compared directly with normal cell calculations. The major attraction, however, is the

---

**Figure 5.** (a) The band structure of graphene with a Stone–Wales defect obtained from supercell calculations. (b) The unfolded bands in the normal BZ. (c) The total DOS. (d) Colour map used in the band structure plots. (e) The $5 \times 5$ unit cell with the Stone–Wales defect. (f)–(h) The band structures and DOS in a 4 eV window centred on the Dirac point.

### 3.5 The Stone–Wales defect

Lastly, we performed SW defect calculations. A similar example was recently treated with a different band unfolding methodology in [26], which could provide an interesting comparison. Although the Dirac cone is generally preserved, as pointed out in [26], a small gap appeared at the $K$ point of the unfolded bands, shown in figure 5(g). A close examination of the folded bands, see figure 5(f), shows that there is actually no gap in the energy spectrum, but that the band crossing has slightly shifted from its SBZ $K$ point towards the $\Gamma$ point. In addition, the SW defect has caused much smearing and breaking up of the bands, and the appearance of new bands, especially for the $\sigma$ bands. It can be expected that the magnitude of the defect-induced effects will diminish smoothly as the size of the supercell is gradually increased.

In all cases, we checked that the sum rule, (12), holds. For pure graphene, the SW defect or nitrogen impurity, the sum adds up to $N_d/N_u = 200/25 = 8$, while for hydrogen and vacancy defects it adds up to $201/25 = 8.04$, and $196/25 = 7.84$, respectively. The variety of examples used shows the versatility of our procedure.
correlation of the unfolded band structure with the measurements of ARPES experiments.

Acknowledgments

I have greatly benefited from discussions with Alex Grüneis.

References

[1] Castro Neto A H, Guinea F, Peres N M R, Novoselov K S and Geim A K 2009 Rev. Mod. Phys. 81 109
[2] Wallace P R 1947 Phys. Rev. 71 622
[3] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Science 306 666
[4] Novoselov K S, Geim A K, Morozov S V, Jiang D, Katsnelson M I, Grigorieva I V, Dubonos S V and Firsov A A 2005 Nature 438 197
[5] Zhang Y, Tan Y W, Stormer H L and Kim P 2005 Nature 438 201
[6] Usachov D et al 2011 Nano Lett. 11 5401
[7] Yazyev O V and Helm L 2007 Phys. Rev. B 75 125408
[8] Stone A and Wales D 1986 Chem. Phys. Lett. 128 501
[9] Banhart F, kotakoski J and Krasheninnikov A V 2011 ACS Nano 5 26
[10] Allen P B, Berlijn T, Casavant D A and Soler J M 2013 Phys. Rev. B 87 085322
[11] Boykin T B, Klimeck G 2005 Phys. Rev. B 71 115215
[12] Boykin T B, Kharche N, Klimeck G and Korkusinski M 2007 J. Phys.: Condens. Matter 19 036203
[13] Ku W, Berlijn T and Lee C-C 2010 Phys. Rev. Lett. 104 216401
[14] Lee C-C, Yamada-Takamura Y and Ozaki T 2013 J. Phys.: Condens. Matter 25 345501
[15] Rudenko A N, Keil F J, Katsnelson M I and Lichtenstein A I 2013 Phys. Rev. B 88 081405(R)
[16] Aradi B, Hourahine B and Frauenheim T 2007 J. Phys. Chem. A 111 5678
[17] Elstner M, Porezag D, Jungnickel G, Elsner J, Frauenheim T, Suhai S and Seifert G 1998 Phys. Rev. B 58 7260
[18] Berlijn T, Volja D and Ku W 2011 Phys. Rev. Lett. 106 077005
[19] Lambin Ph, Amara H, Ducastelle F and Henrard L 2012 Phys. Rev. B 86 045448
[20] Mirzadeh M and Farjam M 2012 J. Phys.: Condens. Matter 24 235304
[21] Farjam M, Haberer D and Grüneis A 2011 Phys. Rev. B 83 193411
[22] Haberer D et al 2011 Phys. Rev. B 83 165433
[23] Nanda B R K, Sherafati M, Popović Z S and Satpathy S 2012 New J. Phys. 14 083004
[24] Medeiros P V, Stafström S and Björk J 2014 Phys. Rev. B 89 041407(R)