Strained graphene: tight-binding and density functional calculations

R M Ribeiro, Vitor M Pereira, N M R Peres, P R Briddon and A H Castro Neto

1 Department of Physics and Center of Physics, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal
2 Department of Physics, Boston University, 590 Commonwealth Avenue, Boston, MA 02215, USA
3 School of Natural Sciences, University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, UK
E-mail: ricardo@fisica.uminho.pt, peres@fisica.uminho.pt, vpereira@bu.edu and neto@bu.edu

New Journal of Physics 11 (2009) 115002 (11pp)
Received 11 May 2009
Published 2 November 2009
Online at http://www.njp.org/
doi:10.1088/1367-2630/11/11/115002

Abstract. We determine the band structure of graphene under strain using density functional calculations. The \emph{ab initio} band structure is then used to extract the best fit to the tight-binding hopping parameters used in a recent microscopic model of strained graphene. It is found that the hopping parameters may increase or decrease upon increasing strain, depending on the orientation of the applied stress. The fitted values are compared with an available parameterization for the dependence of the orbital overlap on the distance separating the two carbon atoms. It is also found that strain does not induce a gap in graphene, at least for deformations up to 10%.

4 Author to whom any correspondence should be addressed.
1. Introduction

Graphene currently gathers an enormous amount of interest from many fronts. This mostly stems from it being a rare example of a system whose phenomenology spans a broad spectrum of fields. For example, graphene exhibits many uncommon transport signatures—as was established during the earliest experiments following its isolation [1]–[3]—and is an unexpectedly good conductor, despite being a strictly two-dimensional (2D) system. While graphene has many properties typical of hard condensed matter systems [4], it is simultaneously a soft membrane from a structural point of view [5, 6]. In fact, since reliable empirical potentials for carbon are generally available, and graphene isolation is now widely practiced, this system can become a new paradigm in membrane physics because both accurate microscopic modeling [7], and direct comparison with experiments are possible.

The simple fact that graphene is an atomically thick membrane has a high import for the interplay between its electronic and mechanical structures. One particular aspect of this interplay is the extent to which an in-plane strain can modify graphene’s electronic structure and, consequently, its transport characteristics. Strain-induced modifications of the electronic structure are usually negligible in conventional systems because of their 3D nature. Even in the thinnest films grown epitaxially on a mismatched substrate, strain is generally irrelevant for the bulk properties, insofar as it is rapidly and efficiently relieved from layer to layer above the substrate, either elastically, or by the intervention of defects [8]. Graphene, on the other hand, is a single-layer membrane, made out of sp² hybridized carbon bonds [9], which are the strongest in nature. If buckling is disregarded, strain cannot be relieved in the third direction, nor in plane through the generation of defects [8]. Graphene, on the other hand, is a single-layer membrane, made out of sp² hybridized carbon bonds [9], which are the strongest in nature. If buckling is disregarded, strain cannot be relieved in the third direction, nor in plane through the generation of defects [8]. Graphene, on the other hand, is a single-layer membrane, made out of sp² hybridized carbon bonds [9], which are the strongest in nature. If buckling is disregarded, strain cannot be relieved in the third direction, nor in plane through the generation of defects [8]. Graphene, on the other hand, is a single-layer membrane, made out of sp² hybridized carbon bonds [9], which are the strongest in nature. If buckling is disregarded, strain cannot be relieved in the third direction, nor in plane through the generation of defects [8]. Graphene, on the other hand, is a single-layer membrane, made out of sp² hybridized carbon bonds [9], which are the strongest in nature. If buckling is disregarded, strain cannot be relieved in the third direction, nor in plane through the generation of defects [8]. Graphene, on the other hand, is a single-layer membrane, made out of sp² hybridized carbon bonds [9], which are the strongest in nature. If buckling is disregarded, strain cannot be relieved in the third direction, nor in plane through the generation of defects [8]. Graphene, on the other hand, is a single-layer membrane, made out of sp² hybridized carbon bonds [9], which are the strongest in nature. If buckling is disregarded, strain cannot be relieved in the third direction, nor in plane through the generation of defects [8]. Graphene, on the other hand, is a single-layer membrane, made out of sp² hybridized carbon bonds [9], which are the strongest in nature. If buckling is disregarded, strain cannot be relieved in the third direction, nor in plane through the generation of defects [8]. Graphene, on the other hand, is a single-layer membrane, made out of sp² hybridized carbon bonds [9], which are the strongest in nature. If buckling is disregarded, strain cannot be relieved in the third direction, nor in plane through the generation of defects [8]. Graphene, on the other hand, is a single-layer membrane, made out of sp² hybridized carbon bonds [9], which are the strongest in nature. If buckling is disregarded, strain cannot be relieved in the third direction, nor in plane through the generation of defects [8].
extract the Gruneissen parameters of graphene, which can be potentially quite useful, for one can use a simple Raman measurement to directly identify and quantify strain profiles in graphene. Another seminal step was given by Kim and collaborators, who have investigated transport properties of graphene under strain, achieved by depositing samples on stretchable substrates [12].

From the theoretical front, a vital question is whether small and easily achievable strain can induce a bulk spectral gap in graphene’s spectrum. If so, this would have enormous consequences in the context of a graphene device with a tunable electronic structure. An early density functional theory (DFT) calculation [14] advanced that any arbitrarily small amount of uniaxial strain opens a gap in graphene’s spectrum, whose magnitude varies non-monotonically with the amount of strain. These findings were apparently seconded by another ab initio calculation [15], although there was strong disagreement between the magnitude of the gap among those two calculations, for the same amount of strain. Recently, however, Pereira and collaborators [17], using a tight-binding approach and treating deformations within linear continuum elasticity, challenged those conclusions. They showed that a spectral gap is achievable only for uniaxial deformations in excess of 20%, and that the effect strongly depends on the direction of the deformation with respect to the underlying lattice. These results are consistent with the investigations of Hasegawa et al [18] which show that the gapless Dirac spectrum is robust with respect to arbitrary (and not exceedingly large) changes in the nearest-neighbor hoppings. Also Wunsch and collaborators [27] using tight-binding found that the semimetallic phase is realized for an extended region of the hopping parameter space. Recent developments from the ab initio front [16, 19] have shown results in agreement with the gapless scenario put forth in [17]. The apparent contradiction among different ab initio calculations can be traced to the peculiarities of the electronic spectrum in graphene. In particular, the fact that, under strain, the Dirac point drifts away from the high-symmetry points of the lattice [17] was overlooked in the interpretation of the earliest results, and led to the erroneous conclusion that a gap seemed possible for any amount of strain. Another somewhat related DFT work was the calculation of strain up to 2% in graphene nanoribbons, by Faccio et al [28].

Given that strain is now perceived as a new avenue of research in the physics of graphene, and given the importance of simple microscopic models that reliably describe the evolution of the electronic system under strain, we intend to further clarify these issues by pursuing two complimentary goals. We perform an ab initio calculation of the band structure of graphene under uniaxial strain, for deformations up to 10%. The calculated bandstructure allows us to establish the absence of a spectral gap in the spectrum. Subsequently, we fit the tight-binding model used in [17] to the bandstructure obtained here ab initio, in order to ascertain its range of validity, and to extract the model parameters. We conclude that the parameterization for the hopping integrals used in the cited reference is generally applicable in the entire range of deformations used in our study.

This paper is organized as follows. We start the next section by discussing the general features of strain in the honeycomb lattice, and the tight-binding parameterization that will be fitted to our ab initio bandstructure. In section 3, we present the details of our DFT calculations, followed, in section 4, by the procedure used here to study the electronic structure as a function of strain. The calculated bandstructures and their fitting to the tight-binding dispersion are shown and discussed in section 5. In section 6, we analyze the variation in the tight-binding hopping integrals, as fitted to the ab initio bands, and compare their strain dependence with the analytical form proposed in [17].

New Journal of Physics 11 (2009) 115002 (http://www.njp.org/)
Figure 1. Illustration of the honeycomb lattice with the A and B sublattices, the lattice vectors $\delta_i$ ($i = 1, 2, 3$), and the hopping parameters $t_1$, $t_2$ and $t_3$. The abscissas are along the zigzag edge (horizontally in the figure). Also shown are the primitive vectors $a$ and $b$ used in the DFT calculation, and $a_0$ is the equilibrium carbon-carbon distance.

2. General considerations on deformed graphene

In figure 1, we represent the unit cell of graphene, depicting the next nearest-neighbor vectors, $\delta_i$ ($i = 1, 2, 3$), and the hopping parameters, $t_i$. The primitive vectors, $a$ and $b$, used in the DFT calculations are also shown. In this study we consider only two types of uniaxial strain: (i) along the $x$-direction—corresponding to strain parallel to the zigzag edge of the ribbon; (ii) along the $y$-direction—corresponding to strain along the armchair edges of the ribbon. These correspond to two particular orientations of the more general uniaxial case discussed in [17], where an arbitrary orientation with respect to the lattice was considered. For small strain (appropriate for our study), the length of the vectors $\delta_i$ (in units of $a_0$) is given by [17]

$$|\delta_1| = |\delta_3| = 1 + \frac{3}{4} \varepsilon - \frac{1}{4} \varepsilon \sigma,$$

$$|\delta_2| = 1 - \varepsilon \sigma,$$

for zigzag and armchair deformations, respectively. In our notation, $\varepsilon$ represents the longitudinal strain and $\sigma = 0.165$ is the Poisson ratio, as measured for graphite [20], or $\sigma = 0.10$–0.14 for graphene as calculated in [19]. It is clear from equation (1) that both $t_1$ and $t_3$ will change upon stress by the same value, since the corresponding change in $\delta_1$ and $\delta_3$ is the same. In [17] it was found that:

1. For stress along the zigzag edge, $t_1$ and $t_3$ decrease and $t_2$ increase upon increasing strain.
2. For stress along the armchair edge, all $t_i$ decrease, with $t_2$ being smaller than $t_1$ and $t_3$.

These findings result from a combination of equation (1) with a parameterization for the change of the hopping parameters with the bond length given by [21]

$$V_{pp\pi} = t_0 e^{-\delta_i (l/a_0 - 1)},$$

*New Journal of Physics* 11 (2009) 115002 (http://www.njp.org/)
where $t_0$ is the hopping integral in free-standing graphene, $l$ the bond length and $\beta_i$ a number of order $\beta_i \sim 3$. One of our goals is to verify to which extent this parameterization (2) is valid, starting from a full DFT calculation of graphene’s bands under stress. With that purpose, we shall compare quantitatively the above parameterization for the variation of $t_i$ with the values of $t_i$ obtained from adjusting the tight-binding and DFT bands. For our DFT calculations it is convenient to write the primitive vectors of the unit cell as (see figure 1):

$$a = a e_x,$$

$$b = \frac{a}{2} e_x + \frac{\sqrt{3}}{2} b e_y. \quad (4)$$

The parameter $a$ was varied when stress was applied along the $x$-axis, and likewise for $b$, when stress is applied along the $y$-direction.

3. Details of the DFT calculations

In our study of the spectrum of graphene under stress, DFT calculations were performed with an ab initio spin-density functional code (AIMPRO) [22], along with the local density approximation (LDA).

The Brillouin zone (BZ) was sampled for integrations according to the scheme proposed by Monkhorst–Pack [23]. A grid of $12 \times 12 \times 1$ $k$-points was generated and folded according to the symmetry of the BZ. An increase in the number of points did not result in a significant total energy change. However, a careful choice of the sampled $k$-points is necessary in this study (see more below).

We use pseudo-potentials to describe the ion cores. Lower states (core states) are accounted for by using the dual-space separable pseudo-potentials by Hartwigsen et al [24]. The valence states are expanded over a set of s-, p-, and d-like Cartesian–Gaussian Bloch atom-centered functions, and the states are filled according to the Fermi–Dirac distribution using a value of $k_B T = 0.01$ eV, a procedure known to accelerate the convergence of the calculations. The Gaussian functions are labeled by p or d, meaning that all angular momenta are allowed up to maxima p ($l = 0, 1$) and d ($l = 0, 1, 2$). Following this nomenclature, the basis set used for the carbon atoms was pdddp. Kohn–Sham states are expressed as linear combinations of these basis functions, which were optimized for graphite.

Graphene was modeled in a slab geometry by including a vacuum region in a unit cell containing two carbon atoms. In the normal direction (z-direction), the vacuum separating repeating slabs has more than 30 Å ($c = 31.75$ Å). The size of the cell in the $z$-direction was optimized to make sure there was no interaction between repeating slabs. The size of the unit cell in the plane direction was optimized, and the lattice parameter after relaxation is $a = 2.4426$ Å. The tolerance for stopping structural optimization was $10^{-6}$ Ha. The tolerance for self-consistency was $10^{-6}$ Ha.

4. Bandstructure calculations under strain

Our calculations implement the deformation of the lattice along the following steps: the unit cell of graphene was first strained in the $x$-direction and no relaxation was first allowed in the $y$-direction, which is at first sight a reasonable approximation if the strain is small (this hypothesis
is confirmed by the DFT calculations. This is validated by the small Poisson ratio for graphene, \( \sigma \sim 0.10–0.14 \), calculated in [19] for much larger strains. Later, we have allowed the lattice to relax along the \( y \)-axis, probing the energy landscape as a function of different bond lengths along \( y \) thus locating in this way the energy minimum of the relaxed lattice. The reasons for studying both the relaxed and unrelaxed lattice are given below. This allowed us to extract a Poisson ratio of \( \sigma \sim 0.13–0.15 \), calculated in [19] for much larger strains. The band structure of strained graphene was then calculated using DFT, for a fixed value of \( \epsilon \). The resulting DFT valence band around the \( K \) point was subsequently used to find the best values of \( t_i \) that fit the tight-binding bandstructure. Our choice of the valence band to fit the hopping parameters is motivated by the documented lack of accuracy of DFT in describing empty states. In the fitting procedure the bands were cut-off at 0.2 eV, well inside the validity of the Dirac cone approximation for unstrained graphene. A fit for the values of \( t_i \) valid over the full energy range of the DFT graphene bands was found to be unsatisfactory using the simple equation (5). This is not surprising because equation (5) neglects details like the overlap factors of the orbitals, and other details discussed in [25]. In addition, the expression used for the tight-binding energy includes only hopping to the first neighbors, albeit with different values for the parameters \( t_1, t_2 \) and \( t_3 \) [4]:

\[
E = \pm |t_2 + t_3 e^{-ik(a+b)} + t_1 e^{-ikb}|. \tag{5}
\]

If the lattice is strained only along the two chosen directions, \( x \) and \( y \), symmetry imposes that \( t_3 = t_1 \). The above procedure was then repeated for stress along the armchair direction.

5. DFT versus tight-binding

Figure 2 presents a fitting of equation (5) to the DFT results (points), together with the fitting (solid line) of the tight-binding equation (5). The fit of the numerical data to equation (5) was done for momenta around the \( K \) point for all the values of strain. As can be seen in figure 2, for finite strain the touching of the valence and conducting bands does not happen at the \( K \) point. This was shown explicitly in [17] and, as a result, any plot of the bandstructure in the close vicinity of \( K \) will inevitably show a fictitious gap. In reality the system remains gapless, as can be seen from the DFT density of states (DOS) plotted in figure 2.

To fit the tight-binding dispersion we used twenty LDA points from each side of the \( K \) point in the direction \( \Gamma-K \). As mentioned earlier, the fit was done only for the valence band, although figure 2 also shows the DFT data for the conduction band together with the tight-binding spectrum using the values of \( t_i \) from the fit to the valence band. The agreement is excellent. The 41 momentum points used for the fitting span a reciprocal length in momentum space of the order of 0.08 rad bohr\(^{-1}\). A few notes are worth discussing here. As strain is induced in graphene, the hexagonal symmetry is lost and the \( K \) points do not retain their original position in the BZ. As an example, one of those symmetry points lies at the position given by the general expression:

\[
K = \left( \frac{c_{1y} c_{2y}^2 + c_{2y} c_{1x} c_{2x} - c_{1x} c_{2x} c_{2y} - c_{1y} c_{2y}^2}{2 c_{1y} c_{2x} - c_{1x} c_{2y}} + \frac{c_{1x}}{2} \right), \tag{6}
\]

where

\[
c_1 = \left( c_{1x}, c_{1y} \right), \tag{7}
\]
Figure 2. Fitting of the DFT data (circles) to the tight-binding expression in equation (5) (solid line), for 1% strain (deformation along the x-direction). The fit is performed around the $K$ point in the BZ, and along the $\Gamma-K$ direction. Note, however, that under strain the bands do not touch at the $K$ point anymore [17]. The system remains gapless, as can be seen on the right panel, where the DOS, as computed from DFT data for the same strain as in the left panel, is given. Also depicted in the right panel are the positions of the two Van Hove singularities in unstrained graphene (dashed lines).

$c_{2} = (c_{2x}, c_{2y})$

are the primitive vectors of the BZ, associated with the distorted unit cell (see figure 1). We have calculated the coordinates of the $K$ point for each value of the strain, and verified that the valence and conduction bands do not touch each other at this point. As found previously in [17] using a tight-binding approach, the $K$ point and the point in momentum space where the valence and conduction bands touch do not coincide. Our calculations show no gap opening in graphene, which agrees with the calculations of the cited reference, and also the DFT calculations of [19].

This point is indeed crucial for the discussion of the bandstructure under strain, since computing the spectrum around the $K$ point may only lead to the erroneous conclusion that strain opens a spectral gap [15], a fact not supported by a more detailed analysis [16, 19], and our current results. DFT methods, inevitably use a finite grid of momentum values over the BZ, which are used to sample the spectrum and the corresponding DOS. Using too coarse a sampling of the BZ is most likely bound to miss the precise momenta at which the valence and conduction bands touch. This would produce a DOS featuring an artificial non-existing gap, a consequence of an aliasing effect [15].

6. Tight-binding hopping parameterization

Figure 3 shows the variation of the hopping parameters as graphene endures stress along the zigzag direction (upper panel). We have strained graphene’s unit cell up to 10%, although...
Figure 3. Variation of hopping parameters, $t_1 = t_3$ and $t_2$, as functions of the strain $\varepsilon$ determined from fitting equation (5) to the DFT valence band (points). The upper panel shows the case where the lattice is deformed along the zigzag direction, while the lower panel refers to strain along the armchair direction. The solid lines represent the hopping computed using equations (1) and (2) and the parameterization given in table 1. The dashed line with triangles in the upper panel is the value of $t_2$ when the length of the corresponding bond is kept constant. The maximum amount of strain was 10%. The error bars are of the size of the points.

experiments seem to indicate that the material can support reversible strains up to 20% [26]. The hopping parameter $t_2$ is perpendicular to this direction, and according to equations (1) should have, in this case, a small variation due to the small value of the Poisson coefficient. Consequently, we have studied two cases for stress along the zigzag direction: (i) keeping constant the bond distance associated with $t_2$; (ii) allowing this distance to vary, such that the energy of the strained lattice is minimum. The study (i) allows us to discuss whether the change in $t_2$ is only due to the bonding length modification or is also controlled by the redistribution of the electronic density around the carbon atoms. It is worth noticing that, according to the simple tight-binding description of equations (1) and (2), the change in the value of $t_2$ is due to the modification of the bond length alone, a result not observed in our DFT calculations, where $t_2$ varies with strain, even under the approximation of keeping the corresponding bond length constant (the variation of $t_2$ is, nevertheless, very small). Additionally, as graphene is strained along the zigzag direction the hopping parameters $t_1$ and $t_3$ decrease, certainly due to the change of the bond length associated with these parameters. The overall results can be understood as follows: strain along the zigzag direction increases the bond length along $t_1$ and $t_3$ directions and...
Table 1. Results for the parameter $\beta_i$ in equation (2) for stress along the zigzag ($x$-direction) and armchair ($y$-direction) directions, both considered in the text.

| Stress      | $t_i$ | $\beta_i$ |
|-------------|-------|-----------|
| $x$-direction | $t_1 = t_3$ | 3.15 |
|             | $t_2$ | 4.0       |
| $y$-direction | $t_1 = t_3$ | 2.6    |
|             | $t_2$ | 3.3       |

reduces the electronic density along these same bonds, additionally it increases the electronic density on the bond length associated with $t_2$, even if no deformation is allowed for this bond. Consequently, $t_1$ and $t_3$ are reduced and $t_2$ increases slightly. This redistribution of electronic density among the several bonds is effectively included in the tight-binding description by allowing a change of all bond lengths, but this is not strictly necessary to observe the effect. We are then forced to conclude that the change in $t_2$ stems from a combination of the two effects: electronic density redistribution among the bonds and change in the bond length. This is in line with the fact that the relative orientation of the orbitals is also affected by the deformation and the resulting re-hybridization alone contributes to a modification of the effective hopping, even if the bond length remains unmodified. It is worth noticing that the values of $t_2$ for the relaxed and unrelaxed lattice are essentially the same for strain up 3%, as seen in the upper panel of figure 2. The points for strains below 1% were obtained without relaxation in the direction perpendicular to the strain. The agreement of these points to the parameterization confirms our assumption that the relaxation is not important for small values of strain.

The situation is different for strain applied along the armchair direction (see lower panel of figure 3), because in this case all three bonds are deformed, up to first order in $\varepsilon$ without any contribution from the Poisson coefficient, as can be seen from equation (1). Since the bond associated with $t_2$ decreases considerably more than the other two, this hopping decreases faster upon strain, an effect seen in figure 3.

In either the zigzag or armchair cases, the bandstructure in the neighborhood of the neutrality point is seen to be well described by the parameterization used in the tight-binding analysis of [17], and given by equation (2). This fact is documented by the agreement between the solid lines and points in both panels of figure 3. In table 1, we present the values of the parameter $\beta_i$ (equation (2)) associated with each bond, extracted for the different cases studied here.

7. Conclusions

We have calculated the bandstructure of graphene under uniaxial strain ab initio, within the LDA approximation. The spectrum remains gapless for all strain configurations studied, and up to the maximum value of longitudinal deformation (10%) used in our calculations, tallying with recent similar investigations [16, 19]. The ab initio bandstructures were used to fit a tight-binding parameterization of the dispersion, from where we extracted the effective nearest-neighbor hopping parameters, and their dependence with the magnitude of deformation. As is generally known, hopping parameters calculated using DFT are lower than the experimental ones, which
is also seen in our calculations that show an unstrained hopping of 2.6 eV. Nevertheless DFT is accurate when calculating energy differences, and thus we believe that the slopes $\beta_i$ of the hopping parameters calculated above should be close to the experimental values. Moreover, the behavior seen for the dependence of $t_i$ on $\varepsilon$ follows rather well the trend given by equation (2). We expect that the results found for $\beta_i$ can be extrapolated to large values of $\varepsilon$ with a certain degree of confidence.

Acknowledgments

We acknowledge the support of the Fundação para a Ciência e a Tecnologia (FCT) under the SeARCH (Services and Advanced Research Computing with HTC/HPC clusters) project, funded by FCT under contract CONC-REEQ/443/2005. VMP and NMRP are supported by FCT via grant reference PTDC/FIS/64404/2006. AHCN acknowledges the partial support of the US Department of Energy under the grant DE-FG02-08ER46512.

References

[1] Novoselov K S et al 2004 Science 306 666
[2] Novoselov K S et al 2005 Nature 438 107
[3] Katsnelson M I, Novoselov K S and Geim A K 2006 Nat. Phys. 2 620
[4] Castro Neto A H, Guinea F, Peres N M, Novoselov K S and Geim A K 2009 Rev. Mod. Phys. 81 109
[5] Meyer J C et al 2007 Nature 446 60
[6] Kim E-A and Castro Neto A H 2008 Eur. Phys. Lett. 84 57007
[7] Fasolino A, Los J H and Katsnelson M I 2007 Nat. Mater. 6 858
[8] Matthews J W and Blakeslee A E 1974 J. Cryst. Growth 27 118
[9] Peres N M R 2009 Graphene: new physics in two dimensions Europhys. News 40 17–20
[10] Lee C, Wei X, Kysar J W and Hone J 2008 Science 321 385
[11] Liu F, Ming P and Li J 2007 Phys. Rev. B 76 064120
[12] Kim K S et al 2009 Nature 457 706
[13] Ni Z H et al 2008 ACS Nano 2 2301
Ni Z H et al 2008 Phys. Rev. B 77
Yu T et al 2008 J. Phys. Chem. C 112 12602
Robinson J A et al 2009 Nano Lett. 9 964
Berciaud S et al 2009 Nano Lett. 9 346
Mohiuddin T M G et al 2009 Phys. Rev. B 79 205433
Huang M et al 2008 arXiv:0812.2258
[14] Gui G, Li J and Zhong J 2008 Phys. Rev. B 78 075435
[15] Ni Z et al 2008 ACS Nano 2 2301
[16] Ni Z et al 2009 ACS Nano 3 483
[17] Pereira V M, Castro Neto A H and Peres N M R 2009 Phys. Rev. B 80 045401
[18] Hasegawa Y, Konno R, Nakano H and Kohmoto M 2006 Phys. Rev. B 74 033413
[19] Farjama M and Rafii-Tabar H 2009 arXiv:0903.1702
[20] Blaksele L, Proctor D G, Selldin E J, Stence G B and Wen T 1970 J. Appl. Phys. 41 3373
[21] Papaconstantopoulos D A, Mehl M J, Erwin S C and Pederson M R 1998 Tight-Binding Approach to Computational Materials Science ed P Turchi, A Gonis and L Colombo (Pittsburgh, PA: Materials Research Society) p 221
[22] Rayson M J and Briddon P R 2008 Rapid iterative method for electronic-structure eigenproblems using localised basis functions Comput. Phys. Commun. 178 128–34

New Journal of Physics 11 (2009) 115002 (http://www.njp.org/)
[23] Monkhorstand H J and Pack J D 1976 *Phys. Rev.* B **13** 5188
[24] Hartwigsen C, Goedecker S and Hutter J 1998 *Phys. Rev.* B **58** 3641
[25] Reich S, Maultzsch J, Thomsen C and Ordejón P 2002 *Phys. Rev.* B **66** 035412
[26] Liu F, Ming P and Li J 2007 *Phys. Rev.* B **76** 064120
[27] Wunsch B, Guinea F and Sols F 2008 *New J. Phys.* **10** 103027
[28] Faccio R, Denis P A, Pardo H, Goyenola C and Mombru A W 2009 *J. Phys.: Condens. Matter* **21** 285304