



# On the band gaps and effective masses of mono and dual doped monolayer graphene



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## ABSTRACT

Herein, we studied the variation of band gaps and effective masses of doped graphene. The gaps of mono and dual doped graphene decay with respect to unit cell size following a curve of the form  $\beta N^\alpha$ . The exponent has a small variation and an average value of  $-3/2$ . The pre-exponential term presents a larger dispersion as the heteroatom is changed. In some cases, such as Si-doped graphene, the gaps could not be fitted to the aforementioned type of curve because the gaps are close to zero. Using these curves for P-doped graphene, we estimated that for a unit cell with 5000 atoms, one P atom is expected to open a gap close to 0.05 eV, as indicated by HSE calculations. The effective masses of holes and electrons also follow a curve of the form  $\beta N^\alpha$ , as the unit cell is increased. Yet, in contrast with the results obtained for gaps, the exponents determined for Si, P and S doped graphene exhibit a larger variation. For dual-doped graphene, the introduction of a second dopant to P-doped graphene (namely, B or N), decreases the effective masses. This result suggests that dual-doped graphene is an interesting material to develop graphene based electronic devices.

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## 1. Introduction

The doping of graphene is among the most explored aspects of this carbon nanostructure. In fact, at the moment of writing this manuscript, 31% of the documents gathered about graphene in Scholar Google, correspond to some sort of doping. In this context, the doping with heteroatoms is at the forefront [1,2]. Some dopants have become the preferred ones because of their potential use in electronics, catalysis and environmental applications, for example. In the p-block, boron [3–5] and nitrogen [4–6], sulfur [7–14], phosphorus [7,8,15–19], silicon [20–23] and selenium [24,25] doped graphene have been shown to display unique properties. The d elements like manganese, cobalt, nickel [26], iron [27,28] and actinides like thorium and uranium [29] motivated thorough studies. However, the incorporation of some elements in the graphene framework remains elusive. For example, to the best of our knowledge, Al has not been incorporated in the graphene framework, notwithstanding the fact that this material should have extraordinary properties [7,8,14,30,31]. Moreover, Beryllium doped graphene which has been studied theoretically, is still waiting to be prepared [32–36]. For 3p elements, it has been confirmed by experimental works that the dopants substitute a

carbon atom, adopting a trivalent structure. For example, trivalent Si atoms were observed by means of transmission electron microscopy and electron energy loss spectroscopy (EELS) [21]. In the same vein, atomically resolved electron energy loss spectroscopy to show that when silicon substitutes a carbon atom it adopts a  $sp^3$  hybridization [20]. The evidence favoring the presence of trivalent 3p dopants is not limited to silicon. In effect, the XPS analysis performed in Ref. [11] for S doped graphene indicated the presence of substitutional sulfur while the Pumera group also confirmed this hypothesis [13]. Finally, a recent work provided the first unambiguously detection of trivalent phosphorus in the graphene framework by means of EELS [19].

One of the most rewarding consequences of the heteroatom doping of graphene is the opening of a band gap which can help develop graphene based electronics. For this reason, the investigation of the electronic structure of graphene is of crucial importance. In a previous work, we analyzed the evolution of the band gaps of P and S doped graphene [37], and observed that P is more effective than S, if one is interested in opening a band gap. In the same line, another enlightening report by Lambin et al. [38], focused on the effect of substitutional nitrogen dopants. These authors demonstrated that the band gap opening at the K point follows a  $V/N^2$  curve, where N is the size of the unit cell ( $N \times N$ ) and V is a parameter of the order of 10. It is important to mention that the gap of the  $3N \times 3N$  unit cells of graphene do not fit in the same

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equation because those cells are particularly small as the K points are folded to the gamma point [39]. Motivated by the interesting variation of the band gaps of doped graphene, in the present work, we have undertaken a DFT investigation on the gap openings for Si, P and S monodoped graphene, using unit cells up to  $14 \times 14$  size. For comparative purposes we also investigated the decay of the band gaps for PB, PN and SiN dual doped graphene. Finally, we calculated the effective masses of the doped graphene systems studied. Our results show that even at a doping concentration of 0.3 at. %, gaps above 0.1 eV can be observed. This is caused by their slow decay as concentration is decreased. We discuss in detail the curves that can be used to scale the band gap with unit cell size. Interestingly, we found that a curve of the form  $\beta N^\alpha$  ( $-1.2 < \alpha < -1.7$ ) provides the best fit for both band gaps and effective masses. We hope that this work may contribute to the understanding of the effects of heteroatom doping on graphene.

## 2. Methods

We studied monodoped and dual doped graphene by means of spin polarized VDW-DF [40], M06-L [41] and HSEH1PBE [42] periodic density functional calculations. Although it is known that most density functionals underestimate band gaps, for 3p atom doped monolayer graphene, the deviation between VDW-DF and HSEH1PBE values is small. Inspection of the values reported in Table 1, confirms this statement. Also, the differences between both methods become smaller as the unit cell size increases.

In the case of the VDW-DF calculations, the double-zeta basis set with polarization functions (DZP) was employed. The orbital confining cut-off was fixed to 0.01 Ry. The split norm used was 0.15. The interaction between ionic cores and valence electrons was described by the Troullier–Martins norm conserving pseudopotentials [43]. The Mesh cut-off was fixed to 200 Ry, which gave converged binding energies within 0.02 eV. The lattice parameters were optimized along the *a* and *b* directions but the *c* axis was maintained frozen at 20 Å. Geometry optimizations were pursued using the conjugate gradient algorithm until all residual forces were smaller than 0.01 eV/Å. Unit cells were sampled using a Monkhorst–Pack *k*-point sampling scheme of  $40 \times 40 \times 1$  *k* points. As for the M06-L and HSEH1PBE calculations, they were carried out using the 6-31G\* basis set [44] and the ultrafine grid. As we have shown in our previous work on monodoped graphene [37], the use of larger basis sets does not alter the band gaps. The unit cells were sampled using 2000 *K* points. Graphene was modeled with a *N* × *N* unit cells, *N* = 5–14 for the VDW-DF calculations, whereas for the M06-L and HSEH1PBE calculations, our computa-

**Table 1**

Comparison between the band gaps computed for  $4 \times 4$ ,  $5 \times 5$ ,  $7 \times 7$  and  $8 \times 8$ , doped monolayer graphene at the VDW-DF/DZP and HSEH1PBE/6-31G\* levels.

	VDW-DF/DZP	HSEH1PBE/6-31G*	$G_{\text{PHSE}} - G_{\text{PM06-L}}$
$4 \times 4$			
Si-doped	0.16	0.09	0.07
P-doped	0.70/0.70	1.14/1.06	0.44/0.36
S-doped	0.58	0.80	0.22
$5 \times 5$			
Si-doped	0.12	0.06	0.06
P-doped	0.62/0.59	0.94/0.82	0.32/0.23
S-doped	0.45	0.61	0.16
$7 \times 7$			
Si-doped	0.08	0.04	0.04
P-doped	0.37/0.35	0.56/0.50	0.19/0.015
S-doped	0.25	0.35	0.10
$8 \times 8$			
Si-doped	0.06	0.03	0.03
P-doped	0.33/0.30	0.48/0.42	0.15/0.12
S-doped	0.21	0.28	0.07

tional resources allowed us to work with up to  $11 \times 11$  unit cells. The largest calculation carried out included 392 atoms in the unit cell, and took one and a half year of CPU time, running in parallel on 12 cores. The VDW-DF calculations were performed with SIESTA [45,46] while the M06-L and HSEH1PBE were conducted with Gaussian 2009 [47].

## 3. Results

### 3.1. Sulfur doped graphene

The band gaps determined for sulfur doped graphene at all levels of theory are presented in Table 2, while the band structures determined for the  $11 \times 11$ ,  $13 \times 13$  and  $14 \times 14$  unit cells are shown in Fig. 1. The band plots are very similar near the K-point, the main difference being the value of the gap opening at the K-point, which is reduced by 0.04 eV when going from *N* = 11 to *N* = 14. At the M point, the conduction band of S-doped graphene is more similar to the one of perfect graphene as compared to the valence band. The variation of the band gaps with respect to unit cell size can be appreciated in Fig. 2. Although three different density functionals were used, all band gaps obtained showed a good correlation when a curve of the form  $\beta N^\alpha$  is fitted. The exponents determined were  $-1.62$ ,  $-1.51$  and  $-1.58$  at the VDW-DF/DZP, M06-L/6-31G\* and HSEH1PBE/6-31G\* levels of theory, respectively. The average value is  $-1.57$ , slightly larger than the exponent suggested by Lambin et al. [38], namely  $-2$ . It is interesting to use our model to determine the band gaps that would be opened for very large unit cells. For  $30 \times 30$  and  $50 \times 50$  unit cells, the predicted band gaps are 0.02 and 0.01 eV, at the VDW-DF/DZP level, whereas the HSEH1PBE/6-31G\* method predicted a gap of 0.015 eV for a  $50 \times 50$  unit cell (5000 atoms).

### 3.2. Phosphorus doped graphene

The band gaps corresponding to P-doped graphene are listed in Table 3 and the band structure calculated for the  $11 \times 11$  unit cell is shown in Fig. 3.

In all cases the gap are larger than those calculated for S-doped graphene. The variation of the band gaps with respect to unit cell size can be appreciated in Fig. 4. For the spin up channels, the values calculated for the exponent  $\alpha$  in our model are  $-1.30$ ,  $-1.27$  and  $-1.30$  at the VDW-DF/DZP, M06-L/6-31G\* and HSEH1PBE/6-31G\* levels of theory, respectively. Considering that  $\alpha$  values determined for P are smaller than those observed for S, the band gaps of P-doped graphene would decrease at a lower rate. Indeed, for  $50 \times 50$  unit cell, the band gap of P-doped graphene is predicted to be 0.045 eV, at the HSEH1PBE/6-31G\* level, about three times the value determined for S-doped graphene. It is worth noting that the good correlation observed at the M06-L/6-31G\* level is only valid when the direct band gaps are used to fit the curve. At the same level of theory, the band gap computed for the  $4 \times 4$  unit cell

**Table 2**

Band gaps determined for sulfur doped graphene, at different levels.

	VDW-DF/DZP	M06-L/6-31G*	HSEH1PBE/6-31G*
$4 \times 4$	0.58	0.66	0.80
$5 \times 5$	0.45	0.52	0.61
$6 \times 6$	0.00		
$7 \times 7$	0.25	0.29	0.35
$8 \times 8$	0.21	0.24	0.28
$9 \times 9$	0.00		
$10 \times 10$	0.14	0.17	0.19
$11 \times 11$	0.12		
$12 \times 12$	0.01		
$13 \times 13$	0.09		
$14 \times 14$	0.08		

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