Interdistance Effects on Flat and Buckled Silicene Like-bilayers

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Abstract.   Using ab intio numerical calculations based on the all-electron full-potential local-orbital minimum-basis scheme FPLO9.00-34, we discuss the interdistance effect on the energy gap of two parallel layers of the silicone systems. The like- bilayer systems we dealt with here are relying on a dynamic monolayer of silicene located at distance d along the normal direction z forming with a static one a (AA) stacking arrangement. In particular, we investigate the effect of the dynamic layer by varying the distance d starting from a distance around the bond length of Van der Waals. More precisely, we consider the flat and two buckled geometries in (AA) arrangements. The flat geometry is associated with the usual (AA) configuration appearing in the pure graphene material. For buckled geometry, we can distinguish two configurations. The first one corresponds to the usual buckled configuration that keeps the same vertical distance between the two layers atoms while the remaining one is obtained by reversing one silicene layer. We show that the band gap can be opened by simply varying the distance, starting around a Van der Waals distance, between two parallel silicene for flat and buckled geometries due to an electronic transition of electrons living in pz orbital states. Furthermore, we study the stability between the buckled and the flat configuration in the mono and bilayer system.

1. Introduction

The study of two dimensional materials (2DM) with honeycomb structure has been considered as a subject of great interest in lower energy physical models [1-10]. It becomes the most promised research topics in the condensed matter physics and related areas including high energy physics. A special interest is to investigate the electronic structure of some particular materials composed of atoms appearing in the fourth group of Mendeleev chemistry table [11,12]. It has been shown that honeycomb-structured models play a crucial role placed in nano-science and they could be considered as the most stable material systems used in the semiconductor electronic applications [5,13,14].

In the recent years, many efforts have been devoted to study the physics of such materials using different methods with appropriate approximations. Besides that, some theoretical and analytic developments have been also given supporting the obtained experimental results found in 2DM with success in isolating single layer material. This includes the discovery of the graphene

from bulk natural graphite by Noveselov et al [1]. The very nice feature of this material is that near the so-called Dirac points the valence and the conduction bands intersect, exhibiting linear energy dispersion [15]. This research area has received an intense attention because the graphene behaves like a semiconductor with zero energy gap. Analytically, the corresponding low energy excitations are described by the Dirac equation dealing with 2 dimensional massless fermions [16].

On the other hand, there has been also a great interest in studying the silicene since it involves properties similar to those of the graphene [5,6,10]. For this reason, the silicene, which is a monolayer of the silicon atoms forming a 2D honeycomb lattice, can be also viewed as an alternative potential candidate for nanotechnology applications. This material has been synthesized and modeled using different approaches [17-21].

The results of single layer studies of 2DM with honeycomb structure have been extended to multi-layers systems. Special emphasis is put on bilayer like systems relying on inter-interactions between two parallel layers [22]. In such systems, the electronic and transport properties can be modified radically according to layer stacking arrangements [23]. It turns out that there are various types of layer arrangements where the most symmetric configurations are the direct (AA) and Bernal (AB) stacking. The latter appears in three dimensional geometries describing the graphite natural configurations, which have received quite important deeper studies [24]. However, the (AA) stacking arrangement has been also synthesized and observed in few layer configurations including the bilayer hexagonal systems [25-28].

More recently, many efforts have been devoted to the study of the opening energy gaps in both single and multilayers of 2D honeycomb-structured materials using different approaches. In particular, methods based on exciton interactions [29], the application of the magnetic field [15,16], and curved geometries [15] have been well developed using various numerical calculation codes [30,31,32]. More precisely, the opening of the band gap in the graphene and the silicene has been investigated using first principle calculations by the help of quantum chemistry methods. In this context, the low-bucked structure in the silicene has been studied by turning on spin orbit interactions in the quantum spin Hall effect physics [33,34,35]. It is worth noting that experiments have also shown, recently, that the band gap can be opened up in a bilayer system by applying an electric field [36].

In this paper, we use Ab-initio calculations to discuss the band gap energy variation based on the effect of the inter-distance between two parallel layers of silicene separated by distance d. In particular, we consider a dynamic monolayer of the silicone located at distance d along the normal direction z forming with a static one a (AA) stacking arrangement. Here, we treat the planar and buckled geometries in (AA) arrangements, see figure 1. These buckled geometries involve two kinds of the configurations. The first one is associated with the usual (AA) configuration that keeps the same vertical distance between the two layers atoms, while the remaining one is obtained by reversing one the layer of the silicene. For both configurations, the starting distance is taking around the van der waals length. We show that the band gap can be opened by simply varying the distance, starting from a distance around the bond length of Van der Waals, between two parallel silicene for flat and buckled configurations. Furthermore, we study the stability between the buckled and the flat configuration in the mono and bilayer systems.

2. Building models and method

Before presenting the computation method, we first build the model. In fact, the systems we consider here are described by a static single layer of the silicone interacting with an extra dynamic layer. The latter is located at a distance d along the normal direction z forming with the first one a (AA) stacking arrangement as plotted in figure 1. The main object of this work is to see the effect of this extra layer of silicone by varying the distance d starting from a
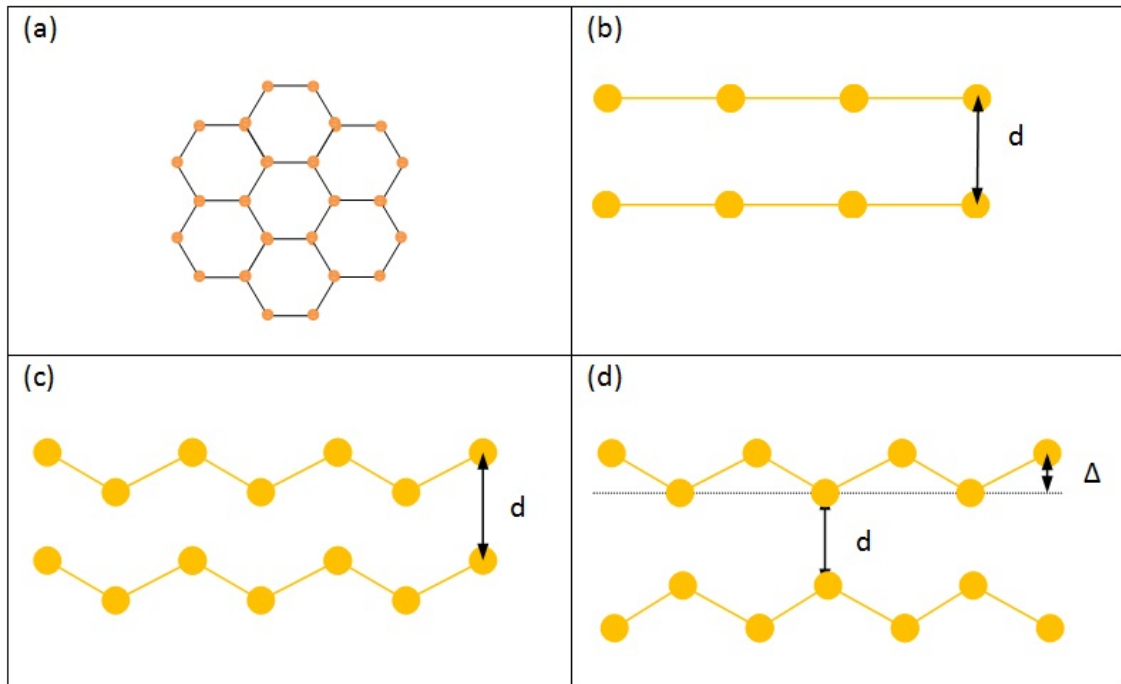
Figure 1. (a) hexagonal structure of silicene. (b) Two parallel flat silicene separated by distance d (c) buckled AA1 (d) buckled AA2 geometry.

distance around the van der Waals bond length. Here, we have performed ab intio calculations based on the all-electron full-potential local-orbital minimum-basis scheme FPLO9.00-34 [37,38]. This has been used to solve the Kohn-Sham equations using the scalar-relativistic scheme. The parameterization of the exchange-correlation energy has been done within the local density approximation [39]. To ensure a high accuracy in the performed computations, we have used both self-consistent criterions of the energy and the density together with a precision of 10^{-8}Ha and 10^{-6} respectively. To accurate the Brillouin zone integrations, we have used the tetrahedron scheme and the centered 48x48x1 K-point mesh. The valence basis state sets are (2s,2p,3s,3p,3d,4s,4p).

The lattice equilibrium parameters $a = b$ and the buckled parameter Δ has been determined from the relaxation method.

3. Numerical results and discussions
In this section, we discuss the distance variation effect on silicene like-bilayers with various geometries. First, we start with the flat case, and then we move to investigate the buckled geometries. A comparative between the studied geometries will be given and discussed.

3.1. Monolayer of the honeycomb-structured materials
Before performing the calculation corresponding to the effect of the inter-distance interaction on silicene like-bilayers, we have first checked the method for the case of the single layer of the silicene with flat and buckled geometries. In order to compute the density of states, we have first relaxed the planar lattice parameters ($a = b$) and the parameter Δ controlling the buckled geometries. Indeed, the total energy of the system is computed using the DFT method depending on the nucleon positions, hence one can minimize the energy functional with respect
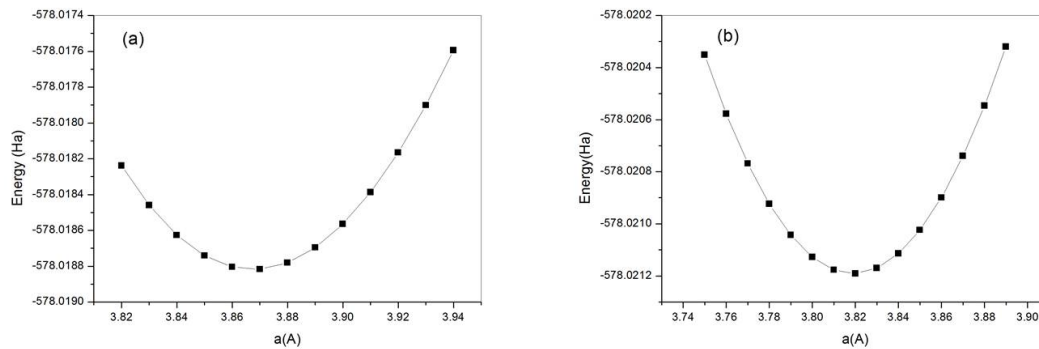
Figure 2. (a) Total energy as a function of lattice parameter a for flat (a) and buckled (b) silicene monolayer with LDA approximation.

Table 1. Lattice equilibrium positions for the silicene for flat and buckled for monolayers corresponding to LDA approximation.
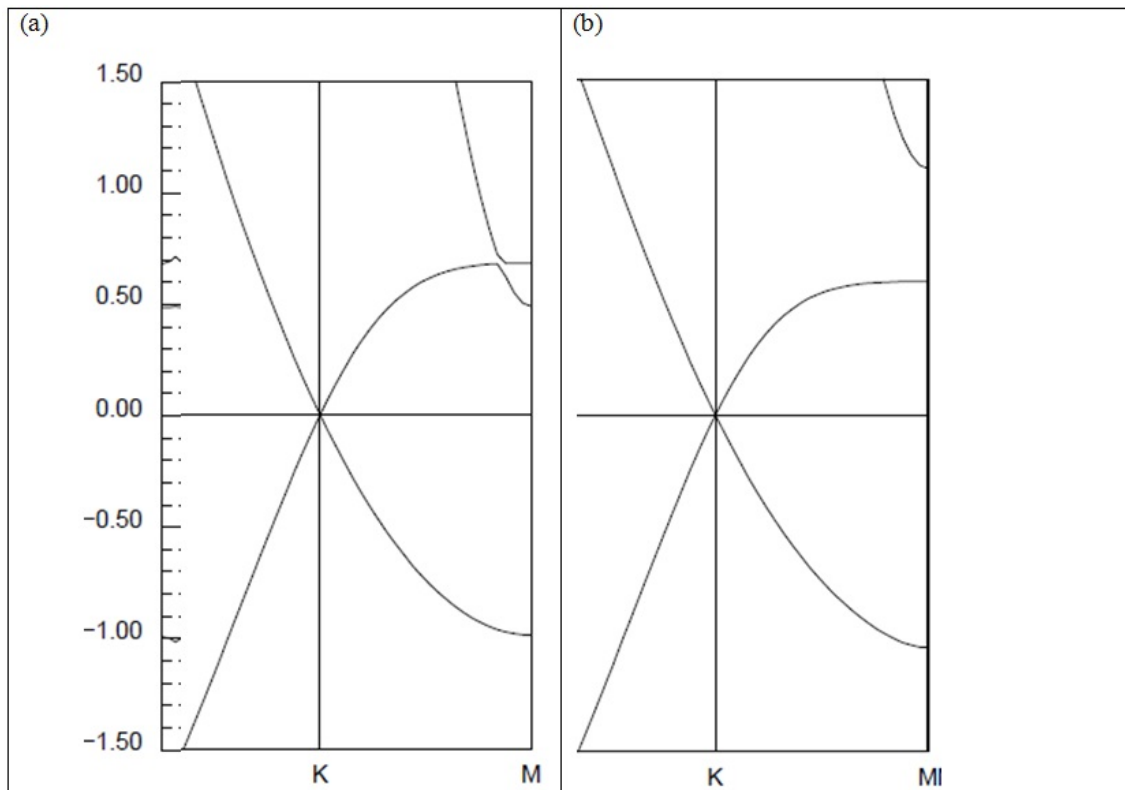
	Flat	Buckled
$\Delta(\mathring{A})$	0	0.504
$a_{eq}(\mathring{A})$	3.87	3.82

to the positions. As usually, the total energy is a function of the lattice parameter a which has been calculated using method given in [40] based on FPLO9.00-34 with LDA approximations. Fitting the obtained result with respect to a generic polynomial of the second order, the lattice equilibriums and the buckled parameter of the silicene for both configurations are listed in the table 1. These values are comparable to those obtained recently in the literature [10]. Indeed, we can find that the buckled geometry is more stable than the flat one, see figure 2.

Considering the equilibrium positions, we have calculated the band structure around K-point for the silicene. The results are shown in the figure 3(a,b) for planar and buckled geometries respectively showing similar results obtained by other groups [10,19,41]. In particular, near the so-called Dirac points the system has a linear energy dispersion i.e

$$E = \pm h v_F k$$

where k and v_F are the momentum and Fermi velocity respectively. Linear dispersion behavior indicates that the charge carriers near the Dirac point become like massless Dirac obeying the relativistic Dirac-like equation. This is a good agreement allowing the validation of the modeling approximations based on FPLO9.00-34 code using the above mentioned parameterizations. It is recalled that the vanishing of the energy gap is intimately related to pz orbitals where the electrons can move freely. This is due to the fact that such orbitals are not interacting with extra ones. In order to reduce the high mobility of the electrons living on such orbitals, a new layer moving on the z direction should be introduced to build like bilayer systems. This extra layer may lead to new correlations between the electrons of pz orbitals placed in the two parallel layers of the silicene. At this level one may ask the following question. Do these correlations modify the band structure? This question will be addressed in the following subsection.

Figure 3. Monolayer Band Structure of silicon around K-point: (a) flat geometry and (b) buckled

3.2. Bilayers of silicene

In this subsection, we study the inter-effect of two layers system by changing the distance d between two parallel layers for planar and buckled geometries with the (AA) arrangement. For the buckled geometry, we distinguish two sorts of configurations. The first one corresponds to the usual (AA) configuration that keeps the same vertical distance between bilayer atoms, while the second one is obtained by reversing one buckled layer of the silicene. In the usual (AA) geometry, the buckled Si atoms of the top layer are faced with the buckled atoms living in the bottom layer (referred AA1). While in the reversed one, the buckled Si atoms of the top layer are faced to flat atoms of the bottom layers (referred AA2).

Varying the distance d, we have calculated the total energy in both configurations. These results are plotted in figure 4 (a,b and c) for buckled AA1, AA2 and flat geometries respectively. From these figures, we have found the equilibrium distance positions corresponding to the minimal energy for flat and two buckled geometries. The obtained results are listed in the table 2. From this table, we observe that we have two minima energies for flat geometry at the inter layers distances $4.2\mathring{A}$ and $2.4\mathring{A}$ which correspond to the Van der Waals and covalent bond length, respectively. However, it is shown clearly that, among these two minima the most stable minimum is related to the covalent distance $2.4\mathring{A}$ which is in a good agreement with the value reported in [42]. It follows that the minimal energy corresponding the minimal distance for two buckled geometries is less than the one associated with flat configuration. More precisely, the calculation indicates that the first buckled geometry is the most stable one.

Now we move to study the distance variation effect on the behavior of the opened energy gap and the electronic structure for the three possible configurations mentioned before. As we

Table 2. Equilibrium distance positions corresponding to the minimal energy for each configuration.

geometries	Equilibrium distance (Å)	Energy (Ha)
Buckled AA1	$d_{min} = 2.62$	$E_{min} = -1156.06276$
Buckled AA2	$d_{min} = 3$	$E_{min} = -1156.06249$
Flat	$d_{min1} = 2.4 \ d_{min2} = 4.2$	$E_{min1} = -1156.06155 \ E_{min2} = -1156.04003$

mentioned above, we can distinguish two zones that are related to the inter layer distance for the Van der Waals and covalent bond length. In fact, we focus, essentially, on the distance variation effect starting from the Van der Waals bond length. This choice is motivated from the fact that this bond is the weak one appearing in the two separated two layers system.

The present calculations show that the band energy gap can be opened up due to the influence of the variation of the distance d for the flat and buckled geometries for the inter layer distance staring from the Van der Waals bond length. This result, which has been obtained from the distance corresponding to a maximal gap, is shown in figure 5. In particular, we see that the band gap varies exponentially with the distance d. It has been also observed that the obtained values of the band energy of AA1 and flat geometries are bigger than the ones obtained in the case of the AA2 geometry. This difference of the energy gap values between the two configurations is due the interaction between two the silicene layers. This can be understood in terms of the distance between two opposite atoms, of the two layers, in both configurations. Indeed, for the AA1 configuration, the opposite atoms have the same distance allowing the maximum gap simultaneously. However, for theAA2 configuration, the opposite atoms do not have the same distance so the system cannot reach the maximum gap at the same distance.

To understand the origin of such an opening energy gap variation, we have calculated the band structure around K-point at the maximal gap distance for each geometry. The corresponding results are depicted in the figures 5(a,b,c,) for flat AA, buckled AA1 and AA2 respectively.

The distance variation shifts the pz orbital states to the valence band for small distance. For large distances, however, the system behaves like single layer of the silicene. It has been seen that the px and py orbitals are not changed. It is known that the electrons located at the valence band contribute to the local cohesion between neighboring atoms and they form localized states. Based on this observation, the variation of the distance has an influence on states of the pz orbital electrons. Taking small values of d, the pz states get stable situations forming a consistent bilayer system. This can be supported from the computed total energy depending on the distance d.

This stabilization can be understood in terms of an electronic structure transition in pz orbitals. It is a transition from delocalized to localized states allowing the opening of the energy gap. One possible explanation of this behavior can be given in terms of the coupling interaction between two parallel material planes caused by varying the interbilayer distance.

In the end of this work, we would like to make contact with many works dealing with the graphene like bilayers. Concerning the opening of energy gap, the buckled silicene like -bilayers share similar behaviors appearing in the case of the graphene only for the distance greater than Van der Waals bond length. The results obtained in this work may support the buckled silicene to be a potential candidate for the nanoscience applications.
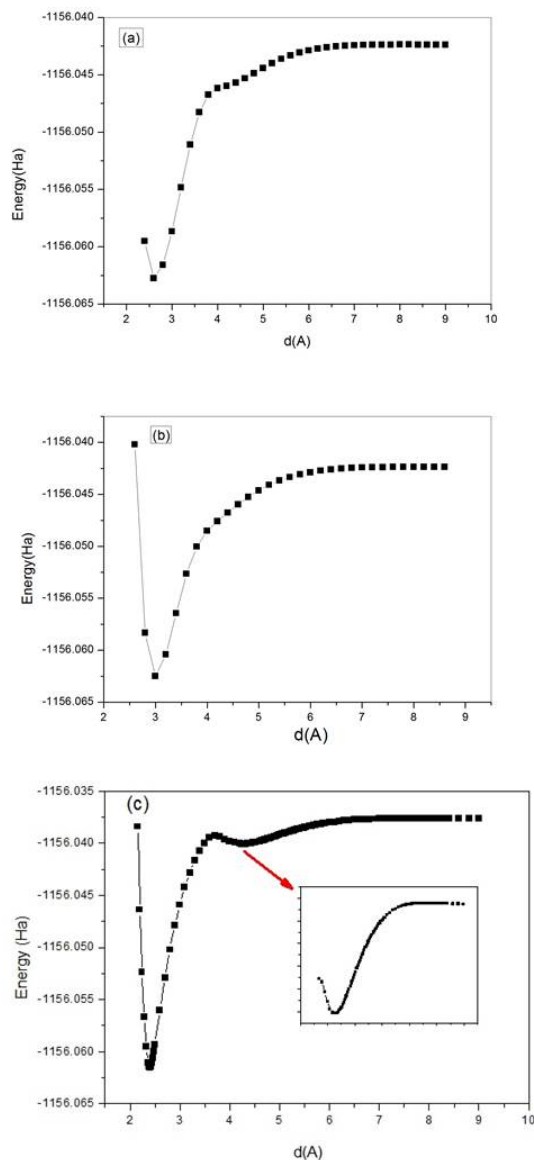
Figure 4. Total energy as function of distance d: (a) AA1 geometry, (b) AA2 geometry and (c) Flat geometry.
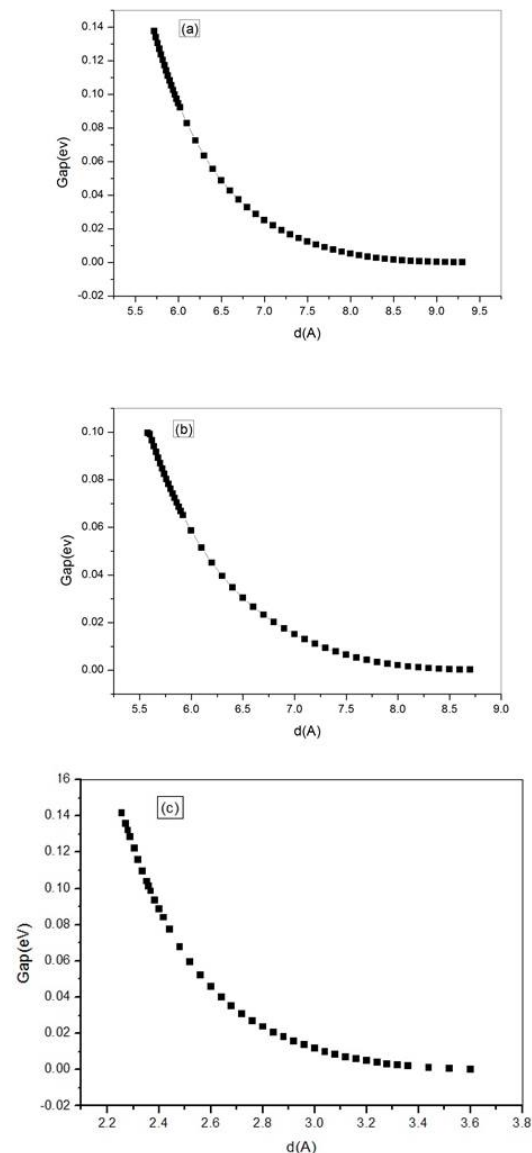
Figure 5. Band gap energy as function of distance: (a) for AA1 geometry , (b) AA2 geometry and (c) Flat geometry.

4. Conclusion

In this work, we have discussed the electronic band structure of two parallel planes of silicene having hexagonal geometries using DFT methods by help of first principal calculations based on FPLO9.00-34 code. We have presented an explicit computational study of a static single layer of silicene interacting with an extra dynamic one. The later is located at distance d along the normal direction z forming with the first one a (AA1) and reversed (AA2) stacking arrangements. It has been shown that band gap can be opened by simply varying the distance between two parallel layers of silicone only for the distance greater than Van der Waals bond length. The existence of the energy gap behavior is due to the transition from delocalized to localized states in pz orbitals. We believe that the obtained results present the first systematical

study on silicene like bilayers.

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