Modeling of gas adsorption on graphene nanoribbons

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(Dated: February 20, 2010)

We present a theory to study gas molecules adsorption on armchair graphene nanoribbons (AGNRs) by applying the results of ab initio calculations to the single-band tight-binding approximation. In addition, the effect of edge states on the electronic properties of AGNR is included in the calculations. Under the assumption that the gas molecules adsorb on the ribbon sites with uniform probability distribution, the applicability of the method is examined for finite concentrations of adsorption of several simple gas molecules (CO, NO, CO₂, NH₃) on 10-AGNR. We show that the states contributed by the adsorbed CO and NO molecules are quite localized near the center of original band gap and suggest that the charge transport in such systems cannot be enhanced considerably, while CO₂ and NH₃ molecules adsorption acts as acceptor and donor, respectively. The results of this theory at low gas concentration are in good agreement with those obtained by density-functional theory calculations.

I. INTRODUCTION

In the past two decades carbon nanostructures, such as carbon nanotubes (CNTs) and graphene, have attracted much attention due to their novel fundamental properties and possible applications in future carbon-based nanoelectronics [1]. An important feature of these materials is their sensing property and on this basis, gas sensors [2, 3], pH sensors [4], and biosensors [5] have been proposed.

Among various types of sensors, most of the experimental [6–13] and theoretical [14–22] studies have been focused on the gas sensors characteristics of the carbon nanostructures due to their promising applications in various fields such as electronics, agriculture and medicine [2, 3].

It has been demonstrated that the CNTs can be used as chemical sensors for detecting very small concentration of NO₂, NH₃ and other gases with high sensitivity at room temperature [2, 3]. The interaction of graphene with chemical environments and the possibility of detecting individual molecules have also been reported [10, 12]. The results indicate that the sensing mechanism is based on changes in the charge carrier concentration induced by gas molecules adsorbed on the graphene surface and acting as donors or acceptors. For instance, Leenaerts et al [21], based on the first-principle calculations, showed that H₂O and NO₂ behave as acceptors while NH₃, CO and NO act as donors. They found that, molecular doping, i.e. charge transfer between the adsorbates and the graphene surface, is almost independent of the adsorption site, which can be attributed to the translational symmetry of the system. In fact, due to the flat structure and thus larger accessible surface area, graphene as well as graphene nanoribbons (GNRs) may act better than any other carbon-based materials as gas sensors.

The special electronic behavior of GNRs corresponds to the two typical topological shapes of the carbon atoms on their edges, namely armchair and zigzag. These ribbons can be either semiconducting with a size dependent gap or metallic [23]. The first-principles calculations and the results of simple tight-binding approximation show that all AGNRs with edge deformation are semiconducting with a finite band gap [24, 25]. Due to the semiconducting feature of the AGNRs, their sensing properties were investigated recently, based on the tight-binding approximation [26, 27] and the ab initio calculations [28]. By changing the values of hopping integrals and atomic on-site energies for simulating the gas adsorption on the edges of an AGNR and using the coherent potential approximation for studying the effect of finite concentration of gas molecules, the sensing properties of the AGNR were discussed in Ref. [27]. Based on density functional theory (DFT) calculations, Huang and co-workers [28] studied the adsorption of CO, NO, NO₂, O₂, N₂, CO₂, and NH₃ on the edges of an AGNR in the presence of dangling bond defects. The gas adsorption only around the defect sites, centered at the edges, was considered. They found that the adsorption of CO₂ and O₂ molecules changes the AGNR to p-type semiconductors, while NH₃ adsorption changes the system to an n-type semiconductor.

We should note that although the ab initio techniques based on DFT obtain a good degree of accuracy to describe the electronic properties of pristine materials, it is somewhat restricted when we consider disordered systems such as gas sensors. The reason is that, in a real disordered system such as gas adsorption on GNR, one should consider all of the configurations and obtain a physical quantity by averaging over all possible adsorption configurations, while in the DFT calculations only one configuration is usually considered.

In order to fully understand the effects of adsorbed molecules on the electronic properties of AGNRs, we should consider all possible configurations of gas adsorption, i.e. the variation of the position of the gas molecule
The width, as shown in Fig. 1(a), and following conventional notation [30], the ribbon is referred as 10-AGNR. We assume that the dangling $σ$ bonds at the edges have been passivated by hydrogen atoms (not shown), hence we expect the bond lengths between carbon atoms at the edges differ from those in the interior of the ribbon (see the blue bonds in Fig. 1(a)). In addition, the gas molecules can be diatomic, triatomic or quadratomic and we assume that each gas molecule adsorbs to only one carbon atom (i.e., single contact) as shown in Fig. 1(b)-1(d). In such a device, the electronic structure of entire system can be described by a single-electron Hamiltonian in a basis of localized atomic orbitals for the atoms in the molecule and $π$-orbitals in the 10-AGNR. We use the tight-binding approximation for both the ribbon and the gas molecules. The Hamiltonian of the system can be expressed as

$$
\hat{H} = \hat{H}_R + \hat{H}_M + \hat{V},
$$

where $\hat{H}_R$ corresponds to the pristine 10-AGNR (before gas adsorption) and can be written as

$$
\hat{H}_R = \sum_i \hat{\epsilon}_i \hat{c}_i^\dagger \hat{c}_i - \sum_{\langle i,j \rangle} \hat{t}_{ij} \hat{c}_i^\dagger \hat{c}_j,
$$

where the operator $\hat{c}_i^\dagger$ ($\hat{c}_i$) creates (annihilates) an electron at site $i$ of the ribbon, $\hat{\epsilon}_i$ is the on-site energy and $\hat{t}_{ij}$ is the hopping integral. Since there is no spin effect, we have suppressed the spin indices here.

Because of the hydrogen passivation of the edge carbon atoms, both $\hat{\epsilon}_i$ and $\hat{t}_{ij}$ of the edges can change. Here, we only consider the variation in the hopping integrals and we set $\hat{\epsilon}_i = 0$ as an origin of the energy. It is reported that the hopping integral between $π$-orbitals at the edges of AGNRs increases about $\delta t_{ij} = 12\% t_R$ [23]. Therefore, we set $\hat{t}_{ij} = 1.12 t_R$ for the edges and $\hat{t}_{ij} = t_R$ with $t_R = 2.66$ eV for the interior carbon atoms [31]. Also, the Hamiltonian of the adsorbed molecules, $\hat{H}_M$, is obtained by summation over the Hamiltonian of the isolated molecules ($\hat{h}_\ell$ for molecule $\ell$) as:

$$
\hat{H}_M = \sum_\ell \hat{h}_\ell,
$$

with

$$
\hat{h}_\ell = \sum_n \epsilon_n \hat{d}_n^\dagger \hat{d}_n - \sum_{\langle n, \ell \rangle} t_{n, \ell} \hat{d}_n^\dagger \hat{c}_\ell,
$$

where $\hat{d}_n^\dagger$ ($\hat{d}_n$) creates (annihilates) an electron on atomic orbital $n$ of the molecule $\ell$ and for simplicity, the atomic basis orbitals are taken to be orthonormal. Extension to the non-orthogonal bases is straightforward in principle. The quantities $\epsilon_n$ and $t_{n, \ell}$ are the on-site energy and hopping integral parameters for the atoms in the gas molecule. These parameters depend on the type and the geometrical arrangements of atoms in the molecule. For instance, CO$_2$ molecule consists of two type atoms,
molecule $\ell$ with gas molecules is written as a sum over each molecule:

$$V = \sum_{\ell} \hat{v}_{\ell} ,$$

with

$$\hat{v}_{\ell} = - \sum_{i=1}^{N_s} \sum_{n=1}^{N_m} t_{in} (\hat{c}_i^\dagger \hat{d}_n + \hat{d}_n^\dagger \hat{c}_i) \delta_{i,i'} \delta_{n,n_{\ell}} ,$$

where the indice $n_{\ell}$ labels the atomic site $n$ of the molecule $\ell$ that is adsorbed on site $i = i_{\ell}$ of the ribbon, and $t_{in} = \tau$ is the hopping integral between the ribbon and the molecule. $N_m$ is the number of atoms at each molecule.

Now we can calculate the Green’s function of the whole system to obtain the average LDOS. For this purpose, as mentioned above, we divide the system into an infinite series of supercells. The supercells are labeled by $\ell = 0, \pm 1, \pm 2, \cdots$ and we focus on one of them, say $\ell = 0$, and consider the supercells $\ell = -1, -2, \cdots$ and $\ell = +1, +2, \cdots$ as neighboring supercells at the left and right, respectively. Based on the iterative procedure introduced by López Sancho et al. [29], the Green’s function of each supercell (in the presence of the gas molecules), due to the periodicity of the system, can be expressed as

$$\hat{G}(E) = (\hat{\epsilon} - \hat{H}_{00} - \hat{H}_{01} \hat{T} - \hat{T}^\dagger \hat{H}_{01}^\dagger)^{-1} ,$$

where $\hat{\epsilon} = (E + i\eta) \hat{I}$ with $\eta$ being a positive infinitesimal number and $\hat{I}$ is the identity matrix. $\hat{H}_{00}$ represents the

coupling between atoms within each supercell and $\hat{H}_{01}$ stands for the interaction between two nearest-neighbor supercells. We note that, both are matrices of dimension $(N_m + N_s) \times (N_m + N_s)$. If we designate the Hamiltonian of a single supercell (say, $\ell = 0$) of the pristine 10-AGNR by $\hat{\mathcal{H}}_{R}^{(00)}$, then $\hat{H}_{00}$ can be written in matrix form as

$$\hat{H}_{00} = \begin{pmatrix} \hat{h}_0 & \hat{v}_0 \\ \hat{v}_0^\dagger & \hat{\mathcal{H}}_{R}^{(00)} \end{pmatrix} ,$$

and

$$\hat{H}_{01} = \begin{pmatrix} \hat{0} & \hat{0} \\ \hat{0} & \hat{\mathcal{G}}_{R}^{(01)} \end{pmatrix} ,$$

where $\hat{0}$ is a $(N_m + N_s - 10) \times (N_m + N_s - 10)$ zero matrix and $\hat{\mathcal{G}}_{R}^{(01)}$ corresponds to the interaction between nearest-neighbor zigzag lines (perpendicular to the periodic direction) in the $\ell = 0$ and $\ell = 1$ supercells. Also, $\hat{T}$ and $\hat{\bar{T}}$ are the transfer matrices which can be easily computed using the matrices $\hat{H}_{00}$ and $\hat{H}_{01}$ through the iterative procedure [29],

$$\hat{T} = \hat{P}_0 + \hat{P}_0 \hat{P}_1 + \hat{P}_0 \hat{P}_1 \hat{P}_2 + \cdots + \hat{P}_0 \cdots \hat{P}_{q-1} \hat{P}_q ,$$

$$\hat{\bar{T}} = \hat{P}_0 + \hat{P}_0 \hat{P}_1 + \hat{P}_0 \hat{P}_1 \hat{P}_2 + \cdots + \hat{P}_0 \cdots \hat{P}_{q-1} \hat{P}_q ,$$

where $\hat{P}_k$ and $\hat{\bar{P}}_k$ can be determined from the following recursion relations:

$$\hat{P}_k = (\hat{\bar{\hat{I}}} - \hat{P}_{k-1} \hat{P}_{k-1} - \hat{P}_{k-1} \hat{P}_{k-1})^{-1} \hat{P}_{k-1}^2 \hat{P}_{k-1} ,$$

$$\hat{\bar{P}}_k = (\hat{\bar{\hat{I}}} - \hat{\hat{P}}_{k-1} \hat{P}_{k-1} - \hat{\hat{P}}_{k-1} \hat{P}_{k-1})^{-1} \hat{\bar{P}}_{k-1}^2 \hat{\hat{P}}_{k-1} ,$$

and

$$\hat{P}_0 = (\hat{\epsilon} - \hat{H}_{00})^{-1} \hat{\bar{H}}_{01}^\dagger ,$$

$$\hat{\bar{P}}_0 = (\hat{\epsilon} - \hat{H}_{00})^{-1} \hat{H}_{01} .$$

The process can be performed until the desired precision is achieved, that is, until $\hat{P}_q, \hat{\bar{P}}_q \leq \delta$ with $\delta$ arbitrarily small.

To study the electronic properties of the system, we obtain the diagonal matrix elements of the supercell Green’s function at the ribbon sites and average over all configurations. Therefore, the the average LDOS per carbon atom can be expressed as

$$\langle D(E) \rangle = -\frac{1}{\pi N_s^2} \sum_{i=1}^{N_s} \sum_{i=1}^{N_s} \text{Im} G_{ii}(i; i; E) ,$$

where $G_{ii}(i; i; E)$ corresponds to the diagonal matrix elements of $\hat{G}(E)$ at the ribbon sites, when the gas molecule is contacted to the ribbon at site $i = i_0$.

III. RESULTS AND DISCUSSION

We now use the model described above to study gas sensing properties of the system. The results of numerical computations will be presented for CO, NO, CO$_2$, NO$_2$, O$_2$, and NH$_3$. In all cases, we find that the average LDOS per carbon atom is strongly sensitive to the gas molecule, with a peak sensitivity occurring at the Fermi level ($\epsilon = 0$). The peak sensitivity is observed for CO, NO, and CO$_2$, while NO$_2$, O$_2$, and NH$_3$ show a weaker sensitivity. The sensitivity is also affected by the adsorption site, with the peak sensitivity occurring at the carbons adjacent to the adsorbed molecule.

In summary, the results of this study provide a detailed understanding of the electronic properties of 10-AGNRs before and after adsorption of different gas molecules.
and NH₃ gas molecules adsorbed on the 10-AGNR. These simple molecules have been chosen due to their different electronic properties in the adsorption process on the ribbon. In order to obtain the hopping parameters related to the adsorbates, we use of the scaling form of the tight-binding hopping integrals as

\[ t_{\alpha\beta} \simeq t_R \left( \frac{d_R}{d_{\alpha\beta}} \right)^2, \tag{13} \]

where \( d_R = 1.42 \) Å is the bond length between carbon atoms in graphene [1], while \( d_{\alpha\beta} \) can be the bond length between the ribbon and the molecule, i.e. \( \alpha \in \text{ribbon} \) and \( \beta \in \text{molecule} \), or between the atoms in the molecule, i.e. \( \alpha \) and \( \beta \in \text{molecule} \). We should note that, this formula is a valid approximation for the variation of the hopping parameter for a bond between two specific atoms when the distance between the atoms is slightly varied. In spite of this, we believe that, by scaling all the hopping parameters with \( t_R \), this formula is able to qualitatively reproduce the electronic states of adsorbates similar to the \textit{ab initio} results. To calculate the exact values for \( t_{\alpha\beta} \), we need \( d_{\alpha\beta} \) parameters. Accordingly, we use the DFT results for these bond lengths to investigate the adsorption effects of the above-mentioned molecules [28]. Moreover, the exact values for \( \epsilon_n \) are found with varying the on-site energies to obtain the desired LDOS which is consistent with the reported DFT results [28]. Below we present the values of these parameters and discuss the adsorption effects of each adsorbate on the ribbon separately. Note that, we can also use the results of Ref. [21] for comparison, in addition to Ref. [28], because in this study the gas molecules can be adsorbed by each carbon atom across the ribbon width, contrary to Ref. [28].

### A. CO on 10-AGNR

We first emphasize that, according to the DFT calculations [21], the size of charge transfer between the molecules and the ribbon depends on the orientation of the molecules with respect to the ribbon surface. Moreover, the highest occupied molecular orbital in CO molecule is located on the C atom. Therefore, CO molecule is attached to a single atom of the ribbon via its carbon atom with the bond distance \( d_{C-C} = 1.35 \) Å,
while the bond length of the adsorbed CO is $d_{C-O} = 1.18$ Å [28]. Inserting these values into Eq. 13, we obtain $\tau = 1.114 t_R$ and $t_{C-O} = 1.45 t_R$. Also, the appropriate on-site energies are given by $\epsilon_C = -1.40 t_R$ and $\epsilon_O = -1.40 t_R$. Hence, the effect of this adsorbed molecule on the electronic structure of the system can be calculated numerically.

The band structure and the average LDOS of 10-AGNR with CO adsorption are shown in Figs. 2(b) and 3, respectively. The band structure, which corresponds to gas concentration $x = 0.05$, has been calculated for a configuration in which the molecule is connected to one of the ribbon edges. In comparison with Fig. 2(a) for the pristine 10-AGNR, it induces an impurity state in the band gap, slightly above the Fermi energy of the clean system. To see the effects of all configurations in the presence of finite concentrations of gas molecule, we have plotted the average LDOS for two concentrations; $x = 0.05$ which indicates that each supercell with one unit cell contains a single CO molecule, as shown in Fig. 3(a), and $x = 0.0083$ which indicates that each supercell with six unit cells contains a single CO molecule as shown in Fig. 3(b).

B. NO on 10-AGNR

In adsorption of NO molecules on the 10-AGNR, only N atoms are attached to the ribbon [28], with the bond distance $d_{C-N} = 1.43$ Å, while the bond length of the adsorbed NO is $d_{N-O} = 1.24$ Å. Accordingly, using Eq. 13 the hopping energies are given as $\tau = 0.98 t_R$ and $t_{N-O} = 1.31 t_R$. In addition, the appropriate values for the on-site energies are $\epsilon_{N} = -1.42 t_R$ and $\epsilon_{O} = -1.35 t_R$. In this case, a single NO molecule on one of the ribbon edges induces an impurity state in the band gap, slightly below the Fermi energy of the pure system [see Fig. 2(c)].

The results of LDOS clearly indicate that the values of charge density of the pristine 10-AGNR are modulated by averaging over all adsorption configurations. This type of adsorbate, similar to CO molecule, does not change the position of the bottom (top) of the conduction (valence) band.

From the average LDOS in Figs. 3 and 4, we notice that the adsorption of both CO and NO molecules by the AGNR decreases the original band gap, especially at high $x$, and may affect the optical properties of the system. At low gas concentration, such as $x = 0.0083$, the density of states of gas molecules consists of a $\delta$-function peak near the center of band gap, while at high $x$, such as $x = 0.05$, a narrow band appears instead of a level. However, this narrow band is far from the bottom (top) of the conduction (valence) band and one expects that such a gas adsorption does not enhance the charge transport of the system.

In the case of CO and NO adsorption, we expect that the Fermi level does not change considerably due to the position of molecular level inside the band gap with respect to the edges of valence and conduction bands. As we know, in a non-degenerate $n$-type ($p$-type) semiconductor, the Fermi energy is rather far from the edge of the conduction (valence) band. This feature indicates that the 10-AGNR with adsorbed molecules like CO and NO behaves as a non-degenerate semiconductor.

C. CO$_2$ on 10-AGNR

The DFT results of CO$_2$ adsorbed on the ribbon show that the molecule sits 1.51 Å away from the edge carbon atoms and the length of C-O bonds is 1.26 Å [28]. Accordingly, the calculated hopping energies are given as $\tau = 0.89 t_R$ and $t_{C-O} = 1.27 t_R$. Moreover, we choose $\epsilon_{C} = 1.75 t_R$ and $\epsilon_{O} = 1.40 t_R$ as the suitable values for the on-site energies. Using these parameters, the band structure for the configuration where the molecule sits on one of the edges is given by Fig. 2(d). An interesting feature of this figure is that the molecular states form an impurity band in the original band gap with width 0.3 eV. We see that, due to the type of charge exchange between the gas molecule and the ribbon, the energy levels of the molecule are close to the edge of the valence band.
Also, the average LDOS analysis clearly show that, at \( x = 0.05 \) (Fig. 5(a)) the impurity band overlaps with the valence band and consequently the band gap reduces significantly. On the other hand, for low enough doping, such as \( x = 0.0083 \), the impurity states become more localized on the gas molecules, the adsorbate bandwidth decreases and a gap opens between impurity and the top of the valence bands [see the arrow in Fig. 5(b)]. This type of molecular doping can enhance the charge transport in this system and hence the CO\(_2\) molecule will act as an acceptor at finite \( x \) and temperature.

### D. NH\(_3\) on 10-AGNR

The ab initio studies of gas adsorption on graphene \[21\] and 10-AGNR \[28\] indicate that in the ammonia molecule, the N atom is closer to the surface than the H atoms. The bond lengths of the adsorbed NH\(_3\) are given as \( d_{C-N} = 1.49 \) Å and \( d_{N-H} = 1.03 \) Å \[28\]. Therefore, the hopping parameters are \( \tau = 0.9t_R \) and \( t_{N-H} = 1.9t_R \), and the on-site energies are chosen to be \( \epsilon_N = -3.45t_R \) and \( \epsilon_H = -2.65t_R \). Fig. 2(c) shows the electronic band structure of the system where the molecule sits on one of the ribbon edges. In this case the impurity band is close to the bottom of the conduction band with width 0.38 eV.

We see in Fig. 6(a) that in the case of \( x=0.05 \), by averaging over all gas adsorption configurations, the impurity band overlaps with the conduction band and the band gap decreases considerably. In addition, at \( x=0.0083 \) as shown in Fig. 6(b), the impurity bandwidth decreases and at low enough \( x \) the impurity band is separated from the conduction band and a gap gradually opens [see the arrow in Fig. 6(b)]. This indicates that NH\(_3\) molecule acts as a donor, which is in good agreement with experimental \[10\] and theoretical studies of NH\(_3\) adsorption on graphene surface \[21\] and 10-AGNR \[28\].

From the above discussions we conclude that, CO\(_2\) or NH\(_3\) molecules adsorption shifts the Fermi energy towards and even into the original valence or conduction band, and the system exhibits \( p \)-type or \( n \)-type semiconducting behavior. On the other hand, when the Fermi energy is close to or even higher (lower) than the bottom (top) of the conduction (valence) band, we have a so called degenerate semiconductor. Therefore, by looking at the Figs. 5 and 6, one can conclude that the adsorption of CO\(_2\) or NH\(_3\) molecules converts the electronic structure of 10-AGNR as a degenerate semiconductor. We should note that, this feature which strongly depends on the gas concentration has not been investigated in the reported DFT calculations.

By comparing Figs. 2(b)-2(e) which correspond to the gas adsorption configuration on one of the ribbon edges with Figs. 3-6 which correspond to the average of LDOS over all configurations, we conclude that the interaction between gas molecules and the carbon atoms at the ribbon edges is much stronger than that of the interior carbon atoms, which is consistent with the DFT results \[28\].

### IV. CONCLUSION

In this research, using the parameters obtained from DFT results, we have modeled the adsorption of gas molecules CO, NO, CO\(_2\), and NH\(_3\) on the 10-AGNR. Under the assumption that the variation of bond lengths between carbon atoms is only localized on the edges of ribbon, and including this effect in our calculations, we studied the influence of finite concentrations of the adsorbates on the average LDOS. In addition, we assumed that only one molecule can occupy the ribbon sites and there is no interaction among the adsorbed molecules.

The results show that, although all types of gas molecules can influence the electronic properties of the system, the average LDOS varies from one type to other. In the cases of CO and NO molecules adsorption, the impurity states are very localized at the center of original band gap. Therefore, adsorption of these gas molecules on 10-AGNR cannot notably affect the charge transport through such systems. In the cases of CO\(_2\) and NH\(_3\) adsorption, however, the system exhibits \( p \)-type and \( n \)-
type semiconducting behavior, respectively. Despite the simplicity of the model, reasonable agreement with DFT results is demonstrated. The results can be useful in designing future gas sensors and $p$-type or $n$-type semiconductors.

Acknowledgement

The author thanks F.M. Peeters for valuable comments and M. Farjam for useful discussions. This work was supported by Payame Noor University grant.

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