



Full Length Article

S-type single alkali-atom on graphene

Evelina A. García^{a,*}, A. Iglesias-García^a, S.C. Gómez Carrillo^b, M.A. Romero^a^a Instituto de Física del Litoral (CONICET-UNL), Güemes 3450, S3000GLN Santa Fe, Argentina^b Departamento de Física, Facultad de Ingeniería Química (UNL), Santiago del Estero 2829, S3000AOM Santa Fe, Argentina

ARTICLE INFO

Article history:

Received 13 March 2018

Revised 25 April 2018

Accepted 1 May 2018

Available online 16 May 2018

Keywords:

Graphene

Electronic correlation

Adsorption

Adatom coverage

Quantum interferences

Alkali atom

ABSTRACT

We present a theoretical study of the localized aspects of the alkali-metal atoms (Li, Na, K) interacting with graphene. We use an *ab-initio* calculation of the Hamiltonian parameters where the chemical properties of the interacting atoms (alkali and C), and the extended features of the electronic band structure of the solid are considered. Adatoms with a *s*-type valence orbital where the electron repulsion (U) in the atom assumes a finite value are considered. Three possible configuration states are analyzed: zero, one (spin up or down), and two electrons in the valence state. We describe the surface-atom interaction by projecting the Anderson Hamiltonian on the subspace of these atomic configurations, and introduced the Green's functions required to calculate the magnitudes of interest. Physical quantities of interest such as hybridization function, the adatom spectral density and transferred charge are obtained. We find that the interaction of alkali-metal atoms with graphene involves several atoms of the solid due to the extension of the *s*-type alkali atomic state and C atomic states. Charge is mostly transferred from the adatom towards the graphene sheet.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Graphene and one-dimensional carbon nanotubes have been extensively studied both computationally and experimentally due to their wide range of applications in microelectronics, hydrogen storage, and chemical sensors [1–3]. Graphene was experimentally obtained for the first time in 2004 [4]. Among its remarkable properties we can mention the extraordinary high mechanical strength, thermal and electrical conductivities [5]. Thus, graphene became a promising material for numerous technological applications [6].

Alkali and alkaline adatom adsorption on graphene could be employed to improve graphene potential use as hydrogen storage device, field effect transistor, and superconducting material. Adsorbed alkali-metal adatoms have shown a substantial activity in gasification reactions (catalysis) [7–9], and alkali-metal monolayers exhibit interesting metallic properties as they appear as nearly ideal two-dimensional quantum wells, in which the metal valence electrons are confined and form discrete quantum well states [10–13]. In addition, most alkali-metal adatoms readily intercalate between graphene layers, and technological applications, for example, of lithium-graphite intercalation compounds

have been recently introduced as rechargeable solid-state Li-ion batteries [14,15].

Chan et al. [16] studied Li, Na, K and Ca on graphene monolayer using spin-polarized plane-wave periodic density functional theory (DFT) and reported migration energies, which are related to the stability of the adatom-graphene systems at room temperature. This value is the highest for Li on graphene, whereas are much smaller for adsorption of Na, K, and Ca. Also, the adsorption of the same alkalis on graphene monolayers is studied using DFT calculations by Dimakis et al. [17] under various adatom coverages. The charge transfer between the adatom and the graphene sheet and the almost unchanged densities of states spectra in the energy region near and below the Fermi level lead to an ionic bond pattern between the adatom and the graphene atoms. However, the presence of small orbital overlap between the metal and the nearest graphene atom is indicative of small covalent bonding. Liu et al. [18], based on DFT, studied the structural and electronic properties of different metal atoms (Li, Na, K, Ca, Fe, Cu and Ag) adsorbed on graphene. They calculated the geometries, adsorption energies, density of states, band structures, electronic dipole moment, magnetic moment and work function. They found that the hollow site at the center of a hexagon of C atoms had biggest adsorption energy, and they could predict that as the metals radius increases, the height (distance between metal atom and the layer of graphene) increases as well, and the bonding is reduced. Also, they found that the electronic dipole moment and magnetic moment

* Corresponding author.

E-mail address: evelina.garcia@santafe-conicet.gov.ar (E.A. García).

of each metal + graphene were very sensitive to the adsorbed metal atoms. Among the alkali atoms adsorbed graphene had the largest dipole moments and smallest magnetic moment. Metal + graphene obey the commonly accepted rule that electropositive (electronegative) adsorbates decrease (increase) the work function of the surface.

For adatoms from group I-III, the density of states (DOS) provides evidence for ionic bonding and charge transfer between the adsorbate and graphene [16]. Charge transferred is an ambiguous quantity and there is not a unique definition in DFT calculations. Charge values reported in the literature may vary due to the different methods for these calculations [17], and differ significantly depending on the definition, the method used to calculate it, and the surface work function. This last point is quite controversial, we found in the literature work function values of graphene varying from 4.26 eV [16] to 4.6 eV [18–20]. Some discussion of the concept of charge transfer in the context of adsorption to metal surfaces can be found in Ref. [21]. They found that, with increasing coverage the adsorbate becomes less charged, and that the adsorption distances are strongly dependent on the coverage [16,17].

In this work we study the interaction of alkali-atoms (Li, Na and K) with graphene within the Anderson model framework, by using the same formalism developed in [22] and later used in [23]. In the latter reference, the authors only consider the π band of graphene and make use of the *tight-binding* method to calculate the corresponding eigenstates and eigenenergies. However, using no more than the π band of graphene will be a proper approximation only if the adatom energy level is higher than -3.3 eV (relative to the graphene Fermi level). Otherwise, the adatom energy level would resonate with the σ band of graphene. Thus, to consider the complete band of graphene is crucial to have a good description, either to understand adsorption processes (where the distances involved are short), and to study atom-graphene collisions (where the turning points are small too [24]).

In this way, we use an *ab-initio* calculation of the Hamiltonian [25,26] that allows us to take into account the chemical properties of alkali-atoms and C atom, and the extended features of the electronic band structure of the solid. The complete density matrix for graphene was calculated by using the Fireball code [27,28] based on a density functional theory within a local density approximation that employs a localized numeric-like orbital basis set. Physical quantities of interest such as hybridization function, the adatom spectral density, and valence occupation (transferred charge) are calculated. We study the adatoms with a *s*-type valence orbital where the electron repulsion, U , assumes a finite value. Then, the atom has three possible configuration states, with zero, one (spin up or down), and two electrons in the valence state. We describe the surface-atom interaction by projecting the Anderson Hamiltonian on the subspace of these atomic configurations, and introduced the Green's functions required to calculate the magnitudes of interest [22].

The present manuscript is organized in the following way. In Section 2 the Anderson interaction model is presented. Afterward, the Green's functions required to calculate the magnitudes of interest are introduced. Section 3 is devoted to the discussion of the results concerning with the Hamiltonian terms, the hybridization width, the adatom valence occupation and charge transfer. Finally, Section 4 contains the conclusions.

2. Theory

2.1. Interaction model

The Anderson model Hamiltonian for *s*-type single adatom-surface interaction can be written as:

$$\hat{H} = \sum_{k\sigma} \varepsilon_k \hat{n}_{k\sigma} + \sum_{\sigma} \varepsilon_a \hat{n}_{a\sigma} + \sum_{\sigma} \frac{U}{2} \hat{n}_{a-\sigma} \hat{n}_{a\sigma} + \sum_{k\sigma} \left[V_{ka,\sigma} \hat{c}_{k\sigma}^{\dagger} \hat{c}_{a\sigma} + h.c. \right] \quad (1)$$

where k denotes the solid states with energy ε_k and a denotes the atom orbital state with energy ε_a . In the second quantization language, their respective occupation number operators are $\hat{n}_{k\sigma} = \hat{c}_{k\sigma}^{\dagger} \hat{c}_{k\sigma}$; $\hat{n}_{a\sigma} = \hat{c}_{a\sigma}^{\dagger} \hat{c}_{a\sigma}$, being σ the spin projection index. The U parameter represents the electronic intrasite Coulomb repulsion in the unique considered atomic orbital, and the hopping $V_{ka,\sigma}$ is the hybridization matrix element between the atomic state and the conduction states of the surface.

By taking into account only one *s*-type orbital state for the alkali-atom (Li, Na or K), we are limiting its electronic configurations to positive, neutral, and negative with zero, one (spin up or down), and two electrons, respectively. By using a projection operator technique [29], the electronic configurations of the atom are represented as follows: $|00\rangle$ zero electron; $|\uparrow 0\rangle$; $|0 \downarrow\rangle$ one electron with spin up or down respectively; and $|\uparrow \downarrow\rangle$ two electrons. Then, the Hamiltonian that describes the adatom can be written as:

$$\hat{H}_{at} = E_0 |0, 0\rangle \langle 0, 0| + E_1 [|\uparrow, 0\rangle \langle \uparrow, 0| + |0, \downarrow\rangle \langle 0, \downarrow| + E_2 |\uparrow, \downarrow\rangle \langle \uparrow, \downarrow| \quad (2)$$

where the total energies in Eq. (2) are related to ε_i (ionization energy), and U parameters in the following way (we have considered spin degeneration):

$$\begin{aligned} \varepsilon_1 &= E_1 - E_0 \\ \varepsilon_2 - E_0 &= 2\varepsilon_1 + U \end{aligned} \quad (3)$$

In this configuration subspace the correct normalization is:

$$|0, 0\rangle \langle 0, 0| + |\uparrow, 0\rangle \langle \uparrow, 0| + |0, \downarrow\rangle \langle 0, \downarrow| + |\uparrow, \downarrow\rangle \langle \uparrow, \downarrow| = 1 \quad (4)$$

In the same way, the interaction term of the Hamiltonian Eq. (1) can be written by using this electronic configurations. Finally, the Anderson Hamiltonian adopts the expression (see for more details Ref. [22]):

$$\begin{aligned} \hat{H} &= \sum_{k\sigma} \varepsilon_k \hat{n}_{k\sigma} + E_0 |0, 0\rangle \langle 0, 0| + E_1 \sum_{\sigma} |\sigma\rangle \langle \sigma| + E_2 |\uparrow, \downarrow\rangle \langle \uparrow, \downarrow| \\ &+ \sum_{k\sigma} \left[V_{ka,\sigma} \hat{c}_{k\sigma}^{\dagger} |0\rangle \langle \sigma| + V_{ka,\sigma}^* |\sigma\rangle \langle 0| \hat{c}_{k\sigma} \right] \\ &+ \sum_{k\sigma} (-1)^{p_{\sigma}} \left[V_{ka,\sigma} \hat{c}_{k\sigma}^{\dagger} |\sigma^{-}\rangle \langle \uparrow, \downarrow| + V_{ka,\sigma}^* |\uparrow, \downarrow\rangle \langle \sigma^{-} | \hat{c}_{k\sigma} \right] \end{aligned} \quad (5)$$

where we have introduced the following notation:

$$|\uparrow, 0\rangle; |0, \downarrow\rangle \equiv |\sigma\rangle, \quad |0, 0\rangle \equiv \langle 0|, \quad p_{\sigma} = \begin{cases} 0 & \text{if } \sigma = \uparrow \\ 1 & \text{if } \sigma = \downarrow \end{cases}$$

The Hamiltonian parameters are calculated by using the *bond-pair* model, previously developed in Ref. [26] to describe pairs of interacting atoms, and then generalized to atom-surface system. In this model, a proper calculation of the atom energy and the hopping term requires: a good atomic basis set for calculating the one and two electronic atomic integrals; and an appropriate description of the surface electronic structure based on a linear combination of atomic orbitals (LCAO) expansion of the band states. The one electron hopping term $V_{ka,\sigma}$ includes one and two electron contributions determined by performing a mean field approximation together with an overlap expansion of the many body Hamiltonian. $V_{ka,\sigma}$ finally is recovered as a superposition of the atomic (dimeric) hopping integrals [25,26]. We used atomic basis sets for C, Li, Na, and K atoms provided by Huzinaga et al. [30,31].

Download English Version:

<https://daneshyari.com/en/article/7833526>

Download Persian Version:

<https://daneshyari.com/article/7833526>

[Daneshyari.com](https://daneshyari.com)