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Electronic structure model for single B, C or N adatoms upon graphite

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Abstract. — An extra-orbital tight-binding scheme and a repulsive Born-Mayer model are used to determine the total adsorption energy of a 2p adatom (B, C or N) at the surface of graphite. The corresponding electronic structure of the adsorbed atom is deduced for the most stable (hollow) position. Our model allows us to exhibit an increase of the local density of states on the adatom and a decrease of charge transfer (from adatom to carbon) when going from boron to nitrogen.

1. Introduction.

Nitrogen adsorbed upon graphite is one of the adsorption systems for which various experimental and theoretical results exist [1-5]. Also graphite is one of the most commonly used materials in atomic-force-microscopy (AFM) [6] and scanning-tunnelling-microscopy [7] studies of surface morphology. Recently progress has been achieved in molecular-dynamics simulations of the metallic tip-substrate interaction in AFM [8]. Also the interaction energies between a sharp Pd tip with one apex atom and graphite were studied on the basis of first-principle calculations [9, 10]. Moreover there is a general interest in the study of the electronic structure of transition metal adatoms upon graphite since graphite is an ideal substrate for such adsorbates; for example open questions are the conditions of appearance of local magnetic moments at V adatoms [11] or also the general electronic structure trends along the 3d series of adatoms. Because carbon occupies a middle position in the order of electronegativity of the elements in the periodic table, graphite welcomes many chemicals (especially 2p or 3d) as adsorbates.

In the present paper we restrict our study to the electronic structure of light 2p atoms (B, C, N) adsorbed upon graphite, at the beginning of adsorption, i.e. when isolated adatoms predominate. More precisely we focus our attention on one (sixfold) hollow adsorbed atom and we
develop a simple extra-orbital tight-binding (EOTB) model. The simplicity of the model based on electron sharing between adsorbate and substrate, as well as its self-consistent screening in the sense of Friedel [12], permits us to describe the trends in chemisorption properties of the adatoms along the 2p series. It is also interesting from an electronic point of view to compare the present adsorption-situation to previously considered single-impurity intercalation-situation in bulk graphite [13-15]. As for an adatom, a total energy calculation, taking into account both band structure and repulsive contributions, is able to provide the most stable position of the adsorbed atom, in a given geometrical position, hollow for example in the present work. The actual adsorbate position is usually assumed to be the site with the largest coordination number (here six) available on the surface. This paper is organized as follows: in section 2 we first calculate the band structure of a basal-plane surface of graphite within the tight-binding (TB) method as well as the corresponding intersite Green functions. Next we present our EOTB adsorption model (Sect. 3) and our method to find out the most stable (hollow) position upon graphite from a total energy computation (Sect. 4). Finally (Sect. 5) we exhibit and discuss our numerical results for B, C, N adatoms.

2. Band structure of a graphite surface.

Recently the interlayer interactions within a bilayer of graphite have been studied using local density approximation [16]. It happens that the interlayer distance is only 0.7 % larger in a bilayer than in the bulk graphite; also the intercarbon distance within a graphite layer is practically the same for a bilayer and for bulk graphite. In the present study we assume that graphite surface is well represented by a bilayer of graphite within TB method. In this method the parameters corresponding to $\pi$ and $\sigma$ bands [13] are fitted [17]. The bilayer is obtained by disregarding the further hopping integrals $\gamma_2$ and $\gamma_5$ in a bulk-graphite model [18]. In our band structure calculation we use the following hybridized $sp^2$ atomic orbitals, $|1R\rangle$, $|2R\rangle$, $|3R\rangle$ built from linear combinations of $|sR\rangle$, $|xR\rangle$, $|yR\rangle$ and the nonhybridized $|4R\rangle$ orbital just given by:

$$|4R\rangle = |zR\rangle$$

(1)

Then, the density of states (DOS) per spin at a carbon site $R$ is given in terms of the bilayer graphite Green function $G^o(E)$ :

$$n^o_R(E) = -(1/\pi) \sum_\ell \text{Im} \ G^o_{\ell R R}(E); \quad G^o_{\ell R R}(E) = \left\langle \ell R \left| (E^+ - H^o)^{-1} \right| \ell R \right\rangle$$

(2)

In equation (2) $\ell = 1, \ldots , 4$ and $H^o$ is the bilayer graphite Hamiltonian. In order to determine the electronic structure of an adatom (next section) we also need to define and calculate intersite Green functions as [14]:

$$G^o_{\ell R R'}(E) = \left\langle \ell R \left| (E^+ - H^o)^{-1} \right| \ell' R' \right\rangle$$

(3)

In our numerical application we consider 10 000 $k$-points in the reduced Brillouin zone [15], keeping, the $k$-components parallel to the bilayer. Our results for the carbon DOS of a graphite bilayer is in fair agreement with reference [16]. It is interesting to decompose the carbon DOS (Fig. 1) into (i) a $\pi$-contribution (arising from $|4R\rangle$ orbitals) which is unique in the vicinity
of the Fermi level \( E_F = -0.05 \text{ eV} \), and (ii) a \( \sigma \)-contribution which is also unique at higher energies. At intermediate energies both \( \sigma \) and \( \pi \) symmetries contribute.

3. Electronic adsorption model.

The EOTB Hamiltonian for an adatom \( A \) on graphite is then written as \( H = H^0 + \) the following terms:

\[
\sum_{m} |m_A\rangle \ E_{m_A}^m \langle m_A| + \sum_{R \ell m} \left( |m_A\rangle \beta_{A R}^{m \ell} \langle \ell_R| + \text{h.c.} \right) + \sum_{R \ell} |\ell_R \rangle \ V_{R R}^{\ell \ell} (A) \langle \ell_R|
\]  

(4)

in equation (4), \( E_{m_A}^m \) is the energy level introduced by the adsorbed orbital \( |m_A\rangle \) at site \( A \) at a distance \( h \) above the graphite surface with the atomic orbital symmetry \( m = s, x, y, z \) for adatoms belonging to the 2p series; \( \beta_{A R}^{m \ell} \) is the hopping integral between the adsorbed atomic orbital \( |m_A\rangle \) and a surrounding carbon molecular orbital \( |\ell_R\rangle \) \( (\ell = 1, ... 4) \) : it is expressed in terms of Slater-Koster atomic hopping integrals [19]. In the last term of equation (4) \( V_{R R}^{\ell \ell} (A) \) designates the additional perturbation potential at carbon site \( R \) due to the adsorption phenomenon. From a numerical point of view (see Sect. 5) \( E_{m_A}^m \) and \( V_{R R}^{\ell \ell} (A) \) will be determined for a given \( h \) from:

(i) the Friedel sum rule which is expressed in terms of \( G_h(E) \), the perturbed Green function associated to \( H \):

\[
2 \ Z_h(E_F) = N_A^0; \\
Z_h(E) = -(1/\pi) \text{Im} \int \int E' \ Tr \left( G_h(E') - G^\ast(E') \right) dE' 
\]  

(5)  

(6)
with \( N_\mathrm{A}^\circ = 3, 4, 5 \) corresponding respectively to the number of external s and p electrons brought by A = B, C, N, and with \( Z_h(E) \) defining the total number of displayed states per spin, up to the energy \( E \), after the adsorption of an A atom at a distance \( h \) above the graphite surface.

ii) the local neutrality on the cluster AC\(_6\) when A occupies a hollow position upon a carbon hexagon of graphite:

\[
2 \int_{E_F}^{E_F} \left( N_A(E) + \sum_{R=1}^{6} \Delta N_R(E) \right) \mathrm{d}E = N_\mathrm{A}^\circ
\]  

(7)

In equations (5) and (7) the factor 2 stands for the spin degeneracy and the local DOS (LDOS) per spin at site A is defined by:

\[
N_A(E) = (-1/\pi) \Im \sum_m G_{\mathrm{AA}}^m(E),
\]

(8)

whereas the variation of the LDOS at a carbon site \( R \) due to the adsorption is:

\[
\Delta N_R(E) = (-1/\pi) \Im \sum_{\ell} \left( G_{\ell R}^{\ell R}(E) - G_{\ell R}^{\ell R}(E) \right)
\]

(9)

Actually within a first order expansion in terms of \( V_{\mathrm{R R}}^{\ell R}(A) \), it is quite easy to explicit the perturbed Green functions of equation (8): it is a straightforward extension of equations (2.2), (2.3) and (2.4) in reference [15]. A similar expression has been derived for \( \Delta N_R(E) \) in equation (9) [20].

4. Total adsorption energy.

There is an interesting point in the adsorption problem: the exact height \( h \) of the adatom A above the graphite surface is determined through a total energy calculation corresponding to the adsorption process of atom A. The general definition [21] of the total adsorption energy \( E_{\text{ad}}(h) \) of an A atom at a distance \( h \) above graphite is given by a sum of (i) an attractive (band contribution) \( E_{\text{bs}}(h) \) term, (ii) an electronic Coulomb term \( E_{\text{cc}}(h) \) which has to be subtracted because it has been counted twice in \( E_{\text{bs}}(h) \) and (iii) a repulsive (Born-Mayer contribution) \( E_r(h) \) term:

\[
E_{\text{ad}}(h) = E_{\text{bs}}(h) - E_{\text{cc}}(h) + E_r(h)
\]

(10)

The band structure term can be written as follows with an evident notation:

\[
E_{\text{bs}}(h) = E(A/\text{graphite}) - E(A) - E(\text{graphite})
\]

(11)

After a bit of manipulation, \( E_{\text{bs}} \) can be cast into the following form:

\[
E_{\text{bs}}(h) = 2 E_F Z_h(E_F) - 2 \int_{E_F}^{E_F} Z_h(E) \mathrm{d}E - \sum_m N_A^m E_{\text{at}}^m
\]

(12)

where \( N_A^m \) is the electron number of symmetry \( m \) brought by the adatom A and \( E_{\text{at}}^m \) is the corresponding atomic level. The electronic Coulomb term is given by the following expression
\[ E_{ee}(h) = \sum_{\lambda n} U_{\lambda}^n \delta N_{\lambda}^n(h) \left( N_{\lambda}^{n0} + \frac{1}{2} \delta N_{\lambda}^n(h) \right) \]  

(13)

\[ \delta N_{\lambda}^n(h) = N_{\lambda}^n(h) - N_{\lambda}^{n0} ; \ \lambda = \{ A, R \} ; \ n = \{ s, p \} \]  

(14)

where \( \delta N_{\lambda}^n(h) \) is the variation of the local electron number at site \( \lambda \) and of symmetry \( n \) due to the adsorption, whereas \( N_{\lambda}^n(h) \) is the local electron number after adsorption of \( A \) within a distance \( h \). Also \( U_{\lambda}^n \) is the intrasite Coulomb energy between two \( n \) electrons at site \( \lambda \). The repulsive term \( E_r(h) \) can be phenomenologically represented by a Born-Mayer potential: it describes at short distances the ion-ion repulsive interaction between the \( A \) atom and the neighbouring carbon atoms of the graphite surface. The general phenomenological form of \( E_r \) is written as follows [24] in terms of the height \( h \) of the adatom above graphite:

\[ E_r(h) = a \exp(-\alpha h) \]  

(15)

where \( a \) and \( \alpha \) are the parameters of the Born-Mayer potential which characterize each type of adsorption. For example in the case of an adsorbed carbon atom upon graphite \( a = 208 \) eV and \( \alpha = 3.3 \) (\( \text{Å} \))\(^{-1} \) according to reference [25]. For simplicity and due to a lack of data, in the following section, we will keep the above carbon parameters also for boron and nitrogen adatoms, since these elements are close by in the classification table. Of course the equilibrium position \( h_o \) of the adatom corresponds to the energy minimum of \( E_{\text{ad}}(h) \) as we will see in the next section.

5. Numerical results and discussion.

The hopping integrals \( \left\{ \beta_{A,R}^{n,f} \right\} \) appearing in equation (4) are calculated according to references [15, 20]. They are reduced to four two-center integrals \( \beta_i(i = 1, \ldots 4) \) corresponding to \( ss\sigma, \ ssp\sigma, \ pp\sigma \) and \( pp\pi \) [19]. We also scaled the integrals in order to be able to recover their values in pure graphite [20]. The difference of energy levels \( E_A^p - E_A^s \) (see Eq. (4)) which characterizes the adatom \( A \) is taken from Clementi [26]. The value of \( U_A^p (= U_A^s) \) for nitrogen is taken to be 2.39 eV according to reference [21]. The corresponding values for boron and carbon are deduced from that for nitrogen, proportionally to the atomic values [27]. The ratio of the corresponding perturbation potentials \( \frac{V_R^p(A)}{V_R^s(A)} \) (see Eq. (4) with \( V_R^{SI}(A) \equiv V_R^p(A) \) on a neighbouring graphite site) is assumed to be given by the ratio of the crystal field integrals which are calculated similarly to the hopping integrals. Finally we end up with two unknown variables \( E_A^s \) and \( V_R^s(A) \) : they are self-consistently determined through equations (5) and (7) as explained in section 3. This is true for a given height \( h \) of \( A \) right upon a hexagon of graphite carbon atoms. The last step of our computation is to find out the most stable height corresponding to a minimum of the total adsorption energy. To do this the zero of energy is assumed to be the vacuum level. Next the graphite band is located so as to satisfy the experimental work function value for graphite [28]; in this case the Fermi level is at \(-5 \) eV. Then the atomic energy levels \( E_{\text{at}}^{n,f}(h) \) of equation (12) are also taken from Clementi [26]. Figure 2 summarizes our results of the total adsorption energy for B, C and N adatoms. The most stable heights \( h_o \) are 1.02 Å, 0.85 Å and 1.06 Å (see also Fig. 3a) which correspond to distances between the adatom and the graphite carbon neighbours of 1.74 Å, 1.65 Å and 1.77 Å respectively. (Notice that the C-C shortest distance within a hexagon in graphite is 1.42 Å whereas in the intercalation case...
Distance above graphite surface (Å)

Fig. 2. — Total adsorption energy for a boron (a), carbon (b) or nitrogen (c) adatom (hollow position) with respect to its distance above graphite surface.

of Refs. [14, 15] the two first carbon neighbours of an interstitial atom are at 1.83 Å and the four next nearest at 2.09 Å). Moreover the charge transfer from A toward the graphite carbon neighbours is decreasing along B, C and N (Fig. 3b). This suggests a change in chemisorption from a rather strong coupling situation in the case of boron to a rather weak coupling situation
In the case of nitrogen. For the most stable hollow positions, it is interesting to exhibit the corresponding LDOS for boron, carbon and nitrogen adatoms (Fig. 4). In all three cases as in the intercalation case [15], there is a strong virtual bound state (vbs) at the Fermi level, the origin of which is essentially $2p_x$ and $2p_y$. Note that these two contributions are not strictly identical from symmetry reasons between $x$ and $y$ within a hexagon of carbon atoms. However since the difference between $x$ and $y$ is small, we exhibit $x + y$ on one hand and $z$ in the other (Fig. 5). The vbs at $E_F$ is less filled for boron (Fig. 4a) and rather filled for nitrogen (Fig. 4c).

Also in the three cases of figure 4 due to a corresponding strong adsorbate-substrate hopping integral there is an extended s bound state below the graphite band [20] the filling of which increases from boron to nitrogen. Our main numerical results are summarized in table I.

In this paper we have studied the most stable (hollow) position of a 2p light adatom (B, C, N) upon graphite surface by using a total adsorption energy calculation. Although our EOTB approach for the band structure contribution is quite crude, we are sure to satisfy the Friedel sum rule as well as a local neutrality condition on the adatom and its first graphite carbon neighbours. Our model allows us to exhibit an increase of the local density of states on the adatom and a decrease of charge transfer (from adatom to carbon) when going from boron to

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Fig. 3. — Distance above graphite (a) and charge transfer ratio $M_G/N_A^0$ from the adatom to the graphite carbon atoms (b) with respect to the considered adsorbate (B, C, N).
Fig. 4. — Local density of states (LDOS) of a boron (a), carbon (b) and nitrogen (c) adatom upon graphite at the most stable (hollow) height. The Fermi level ($E_F = -0.05$ eV) is visualised by a dashed line. The s bound state below the graphite band is represented by a thin straight line.

The present calculation will be extended to the case of transition metal adatoms upon graphite for which there is a number of interesting experimental data. Another interesting
Fig. 5. — Contributions of \((p_x + p_y)\) and \(p_z\) orbitals to the local density of states (LDOS) of a boron (a), carbon (b) and nitrogen (c) adatom upon graphite at the most stable (hollow) position.

Extension of the present model would be to describe the evolution of the electronic adsorption of one given element when going from one single adatom (as is the case in the present paper) to one single overlayer with possible metallization upon graphite. These investigations are now under progress.
Table I. — The most stable height $h_o$ of adatom A, corresponding distance $d_o$ (bond length) to each of the carbon atoms of the considered substrate hexagon, perturbation potentials $V^*_R$ on the six graphite carbon neighbours of A, final charge $M_A$ upon A, final charge transfer $M_G$ onto the six graphite neighbours of A after adsorption, charge $N^*_A$ initially brought by A with A = B, C, N, s energy level introduced by the adsorbed $|sA|$ orbital, intrasite Coulomb energy $U^*_A$ between two p electrons at site A.

<table>
<thead>
<tr>
<th>A</th>
<th>Boron</th>
<th>Carbon</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h_o$ (Å)</td>
<td>1.02</td>
<td>0.85</td>
<td>1.06</td>
</tr>
<tr>
<td>$d_o$ (Å)</td>
<td>1.74</td>
<td>1.65</td>
<td>1.77</td>
</tr>
<tr>
<td>$V^*_R(A)$ (eV)</td>
<td>0.22</td>
<td>0.05</td>
<td>-0.01</td>
</tr>
<tr>
<td>$M_A = 2 \int_{E_F}^{E_F} N_A(E) , dE$</td>
<td>1.14</td>
<td>2.69</td>
<td>3.63</td>
</tr>
<tr>
<td>$M_G = 2 \int \sum_{R=1}^{6} \Delta N_R(E) , dE$</td>
<td>1.86</td>
<td>1.31</td>
<td>1.37</td>
</tr>
<tr>
<td>$N^*_A$</td>
<td>3.00</td>
<td>4.00</td>
<td>5.00</td>
</tr>
<tr>
<td>$E^*_A$ (eV)</td>
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<td>-4.32</td>
<td>-11.38</td>
</tr>
<tr>
<td>$U^<em>_A (= U^</em>_A)$ (eV)</td>
<td>1.42</td>
<td>1.89</td>
<td>2.39</td>
</tr>
</tbody>
</table>

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References