Electron energy loss spectrum of graphene from first-principles calculations

H. Nejati, M. Dadsetani *
Department of Physics, University of Lorestan, Khorrramabad, Iran

**Abstract**

In this study, the energy loss near edge structure (ELNES) of carbon atoms in chair and tricycle conformers of hydrogenated graphene, namely 'graphane', has been calculated in the density functional theory using FP-LAPW method, and then, it has been compared with that of graphite and graphene. Using ELNES from chair conformer, the carbon K-edge was found to have a few main features including electron transition from 1s orbital of carbon atom to \( \pi^* \), \( \sigma^* \), and a hybridization of these two states. The first feature in tricycle conformer, however, has contributions of both \( \pi^* \) and \( \sigma^* \) states. The comparison of ELNES and the unoccupied density of states in each structure also justifies this. The energy difference between \( \pi^* \) and \( \sigma^* \) features of graphene conformers was decreased relative to it in graphite and graphene. Since the inclusion of core-holes and super-cells is essential for accurate reproduction of features in graphite and graphene, it may be essential as well for the ELNES spectra of graphene conformers.

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**1. Introduction**

Graphene (Novoselov et al., 2004), a single sheet of graphite, is a two-dimensional carbon material consisting of a monolayer of carbon atoms in a honeycomb lattice. This material exhibits many unusual properties in relevant areas of physics, chemistry and material science (Geim and Novoselov, 2007; Katsnelson, 2007; Castro Neto et al., 2009) such as the high electrical conductivity, the optical transparency and the half quantized quantum Hall effect, etc.

Graphene, a fully hydrogenated graphene sheet, which is a covalently bonded hydrocarbon, was theoretically proposed by Sofo et al. (2007), and it was synthesized in the laboratory by Elias et al. (2009). Some various interesting properties of graphene including insulting wide band gap (Sofo et al., 2007; Boukhvalov et al., 2008) and magnetization by partial dehydrogenation of the sheet (Neek-Amal and Peeters, 2011) were reported. Experimentally, adsorption of hydrogen on graphene was indeed observed to result in a gap opening in the electron states (Elias et al., 2009). Therefore, the adsorption of hydrogen turns the highly conductive graphene into insulting graphene, as theoretical predictions show (Sofo et al., 2007; Boukhvalov et al., 2008). However, the exact value of the band gap is still unknown. The thermal contraction effect and the heat capacity of graphene are larger than those of graphene (Neek-Amal and Peeters, 2011). Six possible conformers of this hydrocarbon were reported, known as 'chair', 'boat-1', 'boat-2', 'stirrup', 'twist-boat', and 'tricycle', for the connection of the hydrogen atoms to up-and-down-side of carbon atoms in a honeycomb lattice (Sofo et al., 2007; Samarakoon and Wang, 2009; Flores et al., 2009; Chaoyu et al., 2012; Wen et al., 2011). The chair conformer is the most stable, and the tricycle conformer is the second one (Chaoyu et al., 2012). Other physical properties of graphene conformers are under study.

Energy loss near edge structure (ELNES) spectroscopy, which is often performed within a TEM (Egeron, 1996), is a routine technique to detect and measure the electronic structure of materials. Since ELNES originates from the electron transition from a core orbital to unoccupied bands, spectral features of the ELNES reflect the partial density of states of unoccupied bands, and it can provide information on the atomic arrangements, electronic structures, and the chemical bonding of an objective atom in the materials (Botton et al., 1996; Mizoguchi et al., 2003, 2004). Despite the fact that DFT is not intended for the calculation of electronically excited states, the calculation of ELNES and the low-loss spectra with the DFT works pretty well (Rez et al., 1995). Among a variety of codes available for DFT calculations, in addition to the pseudopotential CASTEP code (Segall et al., 2002), the FP-LAPW+lo code WIEN2k (Blaha et al., 2001) has been successfully applied to EELS calculations of many different materials (Holec et al., 2008; Keast et al.,...
2. Computational details

2.1. Calculation parameters

The calculations presented in this work are based on the FP-LAPW method in which no shape approximation on potential or the electronic charge density is made. The calculations of structural and electronic properties have been done relativistically. We used the WIEN2k (Blaha et al., 2001) implementation of the method, which allows inclusion of local orbitals in the basis, improving upon linearization and enabling consistent treatment of the semicore and valence states in an energy window, hence ensuring proper orthogonality. In independent particle Kohn–Sham DFT, the exchange-correlation potential within the GGA was calculated by means of the scheme of Perdew et al. (1996) for all spectra. The interstitial plane wave vector cut off \( k_{\text{Max}} \) was chosen in a way that converging \( R_{\text{MT}} K_{\text{Max}} \) of total energy, charge density and atomic forces equals 8 for the ground state. Since the use of super-cell increases the volume of calculations, and given the presence of very light materials like hydrogen, a smaller value of \( R_{\text{MT}} K_{\text{Max}} \) for core-hole super-cell calculations is sufficient (http://www.wien2k.at/reg_user/faq/rmt.html).

The maximum Quantum number for the wavefunction expansion inside the atomic sphere was confined to \( l_{\text{max}} = 12 \). The \( G_{\text{max}} \) parameter was taken to be 18 Bohr\(^{-1}\). Brillouin zone (BZ) integrations within self-consistency cycles were performed via a tetrahedron method containing 24 k-points in the irreducible BZ of all structures. It corresponds to a mesh with dimensions \( 9 \times 9 \times 2 \) for graphite, \( 14 \times 14 \times 1 \) for graphene and chair, and \( 1 \times 5 \times 15 \) for tricycle structures, respectively. Crystal lattices and atomic positions of chair and tricycle conformers of graphene are fully optimized up to the residual force on every atom less than 1 mRyd/de\( \text{a} \). In order to neglect any interlayer interactions, we set the distance 15 Å between hydrocarbon layers.

Although there are different studies on the energy gap of chair, there is no experimental report of it. Moreover, the lack of an exact calculation of energy gap of tricycle reveals the need for knowledge of energy gap values of graphene conformers through a precise method. Therefore, the many body \( G_0W_0 \) approximation (Hedin, 1965) implemented in Exciting-code was used to calculate the exact values of chair and tricycle band gaps. It should be noted that \( G_0W_0 \) changes the band structures, these changes do not in general improve the calculation of spectra and \( G_0W_0 \) data are not typically used for XANES or ELNES modeling.

2.2. The spectra method

In a band structure, the ELNES is calculated within the first Born approximation with the assumption that the incoming and outgoing fast electrons are plane waves with wave vectors \( \vec{k}_i \) and \( \vec{k}_f \). The double differential scattering cross section (DDSCS) for the inelastic electron scattering is given by (Bethe, 1930):

\[
\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} (E, \mathbf{q}) = \frac{4 \pi^2}{\alpha^2 q^4} \sum_{ijk} \left| \langle f | e^{i \vec{q} \cdot \vec{r}} | i \rangle \right|^2 \delta(E - E_f + E_i)
\]

(1)

where \( \vec{q} = \vec{k}_f - \vec{k}_i \) is the momentum transfer, \( \alpha_0 \) is the Bohr radius, \( E \) is the energy loss, and \( \gamma = \sqrt{1 - \frac{\vec{q}^2}{\alpha_0^2}} \) is the relativistic factor. The summation is done over all occupied initial and unoccupied final one-electron states. The initial state is the ground state of the target electron and the final state is the state occupied by the target electron in the conduction band after interaction. Eq. (1) can be recast in terms of the unoccupied density of states, \( \chi(E) \). With some approximation (Neliebel et al., 1999), we can write:

\[
\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} (E, \mathbf{q}) = \sum_{l_f} \left| M_{lf}(E, \mathbf{q}) \right|^2 \chi_{l_f}(E)
\]

(2)

which is a sum of transitions to final states of \( l_f \)-character (s, p, d, ...). \( M_{lf}(q, E) \) is a smooth and slowly decaying function of energy loss, representing the overall shape of the edge, in a way that variations in DDSCS represent the energy dependence of the densities of states (DOS) above the Fermi level. To simulate the energy loss near the edge structure, we used the TELNES3 program (Blaha et al., 2001), a modified version of TELNES (Neliebel et al., 1999), which involves the fully relativistic effects, and which is a part of the WIEN2k program.

Since the core-hole left by the excited electron locally changes the potential, and therefore, influencing the electron density, it serves as a perturbation, so the valence and conduction states can be contracted and shifted. The projected density of states is changed, and the overall shape of the spectrum can be strongly modified, in a way that it may even lead to excitonic peaks in the ELNES. The core-hole calculations have been carried out by the reduction of the occupancy of the core level corresponding to the observed edge. In order to avoid renormalization problems, the missing charge is added to the unit cell as a uniform background charge. In order to avoid the interaction among neighboring core-holes, we used super-cell structures. This approach including the DFT, the super-cell, and the core-hole, namely, “Final State Rule” (FSR) (Jorissen, 2007), was used for all spectra. This rule states that the calculation is done via Fermi’s golden rule with final states being
calculated with a final state Hamiltonian including an appropriately screened core-hole, while the initial states should be those for the ground state.

We used 108 \((3 \times 3 \times 3)\), 50 \((5 \times 5 \times 1)\), 64 \((4 \times 4 \times 1)\) and 128 \((1 \times 2 \times 4)\) atoms (dimensions of super-cells) for graphite, graphene, chair- and tricycle-graphane super-cell structures, respectively, to avoid the interaction among neighboring core-holes. These sizes of super-cells have been optimized up to the results of the spectra without changes.

The calculated ELNES must be broadened before being compared to the experiments. Thus, we performed an energy-dependent broadening on the spectra with a linear Lorentzian function \(I' = 0.1E\), originating from the excited states lifetime.

3. Results and discussion

Fig. 1 represents lattice structures of the chair and tricycle graphene. We fully optimized lattice parameters, and we also relaxed atomic positions of both structures. Our calculations for structural properties of chair and tricycle conformers have been listed in Table 1. Unlike a graphene layer, chair- and tricycle-graphane structures are not flat materials. Hydrogen (H) atoms are chemically bound to the carbon (C) atoms on alternating sides of the membrane, causing a local buckling of the membrane. In other words, carbon atoms are displayed from planar geometries by hydrogen atoms in both structures as represented in the side view of Fig. 1.

Chair conformer, with H atoms alternating on both sides of the sheet (UDUDUD hydrogenation in each hexagonal carbon ring, with U and D denoting up and down, respectively), is the most stable structure proposed so far the graphene (Chaoyu et al., 2012). In chair graphene conformer, carbon atoms are connected with hydrogen attached to the opposite sides of the plane via C–C bonds. The calculated C–C and C–H bond lengths are 1.534 and 1.109 Å, respectively, and in good agreement with Sofo’s reports (Sofo et al., 2007), confirming the precision of our calculations. The C–C bond length in a graphite plane and in a graphene is 1.42 Å, that is, less than that of the chair structure. Tricycle graphene (with the UUUDUD hydrogenation) is the second stable material among the graphene allotrope groups (Chaoyu et al., 2012). The first five allotropes of graphene have one inequivalent C–H bond in their crystal cells, whereas the tricycle graphene allotrope contains two pairs of inequivalent C–H bonds.

Band structures of chair and tricycle conformers are shown in Fig. 2. We used PBE exchange correlation functional and \(G_0W_0\) approximation to calculate band gaps of the chair and the tricycle. Our results based on PBE functional showed that chair is an insulator with a direct band gap of 3.23 eV at \(\Gamma\) point. This property in \(G_0W_0\) approximation was calculated as 5.85 eV which is near to 5.4–6.05 eV obtained from other \(GW_0\) and \(G_0W_0\) approximations (Karlicky et al., 2012; Lebégue et al., 2009; Leenaerts et al., 2010;

![Fig. 1. The structure of graphene (extended and side view) in (a) chair and (b) tricycle conformations. The carbon atoms are shown in yellow and the hydrogen atoms in blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image)

![Fig. 2. Band structures of chair (left) and tricycle (right) from GGA-PBE in Kohn–Sham DFT (blue) and many body \(G_0W_0\) (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image)
Pulci et al., 2010). Moreover, the calculation of the tricycle band gap by means of G0W0 approximation and PBE showed that the tricycle is an insulator with a large direct band gap equaling 5.45 eV in the former, while it was 3.1 eV in the latter. As it can be seen in Fig. 2, GW approximation not only shifts the conduction bands to higher energies, but also it modifies the valence bands, although insignificantly.

However, these two conformers of graphane are insulators with large energy gaps. Hydrogenation clearly changes the hybridization of carbon atoms in graphene from sp² to sp³ (Samarakoon and Wang, 2009; Flores et al., 2009; Chaoyu et al., 2012; Wen et al., 2011), which causes separation between the valence and the conduction band. Therefore, the hydrogenated graphene exhibits very different electronic properties, as compared with graphane.

Afterwards, using a beam of electrons with energy 300 keV, we have calculated energy loss near carbon K-edge in chair and tricycle structures within the GGA approximation. The results presented here were obtained by the setting of the fast electron beam convergence semi-angle of 1.87 mrad, and the collection semi-angle was set to the magic value of 3.06 mrad. This microscope setting is to get orientation independent ELNES spectra. For a better analysis, the calculated ELNES of graphite and graphene spectra are also shown in Fig. 3. Various approaches were used to calculate the spectra, corresponding to the ground state and the full core-hole with different sizes of super-cells (FSR) up to the convergence of the results.

In Fig. 3, the threshold energy for C K-edge has been set to zero by a shift equal to 285 eV (the required energy to remove 1s electron of carbon atom), so that a suitable comparison can be made. When a core-hole is created due to the excitation of a core electron, valence electrons move, and they screen the core-hole potential. In metals, the valence electrons can move easily, so the core-hole effect would be less significant, whereas in insulators, the electrons cannot move easily because of the filled valence band, and therefore, the core-hole effect would contribute significantly to the unoccupied DOS. Since both chair and tricycle structures have large energy gaps in our results, the screening effect on the core-hole by the valence electrons is weak. Due to the selection of large size super-cells in order to neglect the interaction between neighboring core-holes, and due to the large energy gaps, ELNES spectra are very different in the ground state cells and super-cells. Similarly, this effect seems to be significant in graphite and graphene structures. In order to check it, Fig. 4 shows the C K-edge in graphite and graphene calculated without and with the core-hole for the cell and different sizes of the super-cells. Differences between the ELNES of graphene obtained for a super-cell containing 18 (3 × 3 × 1) atoms and 50 (5 × 5 × 1) atoms are faint but still visible. The 50-atoms super-cell seems to be a good compromise (Suenaga and Koshino, 2010). In the case of graphite, super-cell sizes with 108 (3 × 3 × 3) atoms and 216 (3 × 3 × 6) match together. Thus, the selective super-cell is 3 × 3 × 3. It should be mentioned that the K-edges spectra of all carbon atoms in each structure were the same.

We also used the core-hole approach for all structures in Fig. 3. It was found that for the C K-edge of graphite, a super-cell with 3 × 3 × 3 dimensions had a close match with the experiment displayed in the left hand side of Fig. 5 (Hamon et al., 2004). Increasing the super-cell further than 3 × 3 × 3 for graphite does not produce any changes anymore (see Fig. 4). The two main peaks ‘a’ and ‘b’ in the C K-edge of graphite have been reproduced in 0.4 and 7.1 eV, which are equivalent to purely π* and σ* features, respectively. The difference 6.7 eV between the two features is in good

<table>
<thead>
<tr>
<th>System</th>
<th>Lattice constant (Å)</th>
<th>Positions</th>
<th>Bond lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chair P3m1 (164)</td>
<td>a=b=2.53</td>
<td>C: (1/3,2/3,0.5151)</td>
<td>C–C: 1.534</td>
</tr>
<tr>
<td></td>
<td>c=15.0</td>
<td>H: (1/3,2/3,0.5881)</td>
<td>C–H: 1.109</td>
</tr>
<tr>
<td>TricyclePbcm (57)</td>
<td>a=15, b=7.681</td>
<td>C1: (0.4981,0.0563,0.25)</td>
<td>C1–C1: 1.539</td>
</tr>
<tr>
<td></td>
<td>c=2.544</td>
<td>C2: (0.5731,0.1934,0.25)</td>
<td>C2–C2: 1.541</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H1: (0.4328,0.1235,0.25)</td>
<td>C1–H1: 1.108</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H2: (0.6364,0.1190,0.25)</td>
<td>C2–H2: 1.109</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C2–C1: 1.540</td>
</tr>
</tbody>
</table>

![Fig. 3. ELNES spectra of the C K-edges of chair- and tricycle-graphane, graphite and graphene structures.](image-url)
agreement with previous theoretical and experimental reports (Hamon et al., 2004; Titantah and Lamoen, 2004). The equivalent peaks exist in the graphene ELNES structure but with a 6.2 eV difference between them. The reproduced features of graphene are in agreement with Suenaga et al.’s experimental work (Suenaga and Koshino, 2010) as it has been presented in the right hand side of Fig. 5.

The first feature in the ELNES of chair (tricycle), i.e. ‘a’, is at 2.55 (3.1) eV and the second feature, i.e. ‘b’, is at 6.25 (6.05) eV. Therefore, the difference between two main peaks, $\pi^+$ and $\sigma^*$, considerably decreases in the hydrogenated graphite structure to 3.7 (2.95) eV. This difference indicates that the bindings are changed in the presence of hydrogen atoms. In a graphene layer, each carbon atom is connected to others with $sp^2$ hybridization. When hydrogen atoms are added to a carbon layer, hybridization must apparently be changed from $sp^2$ to $sp^3$. Moreover, $C-C$ lengths in both graphite structures are larger than those in graphite and graphene (see Table 1). It can justify the decreased energy difference between $\pi^+$ and $\sigma^*$ features of graphene conformers relative to it in graphite and graphene. This effect has been observed in the studies on the changes of ELNES with respect to the bond length in carbon systems by Titantah and Lamoen (2005). They showed that when the C–C bond length is changed to larger values in graphite and the amorphous carbon, the $\sigma^*$ edge shifts to lower energy, while the $\pi^*$ edge is less sensitive to it. It is found that when carbon is bonded to a foreign atom like hydrogen or nitrogen the shift to lower energies can be drastic, resulting in an entirely different energy loss near edge structure, or near-edge X-ray absorption fine structure, at energies intermediate between the main $\pi^*$ and $\sigma^*$ features. In all structures, the intensity of the first peak is less than the second one.

Fig. 6 shows the site and symmetry-projected DOS above the Fermi energy of chair, tricycle, graphene and graphene structures, which directly interprets the ELNES of C K-edges. Since the matrix elements in Eq. (1) smoothly vary with respect to the energy, DDSCS is correlated with the unoccupied density of states of the excited atom, projected on the proper symmetries allowed by the dipole selection rules (Eq. (2)).

C p-DOS in chair graphene has a significant intensity at 2.55 eV, so peak ‘a’ observed in the same energy loss of C K-edge of chair graphene could be considered as a transition to antibinding $\pi^+$ ($p_z$) of the carbon atom. Similarly, peak ‘b’ in chair structure can be due to transition to the antibinding $\sigma^*$ (more $p_x + p_y$), because of the most intense peak in the partial DOS of 6.2 eV.

The symmetry-projected density of states in tricycle conformer has a rather different behavior in comparison with the other three structures, in a way that, in this structure, the first peak in C p-DOS at 3.1 eV is composed of not only $\pi^*$($p_z$) orbitals, but also the contribution of the $\sigma^*$($p_x + p_y$) is not zero. It has a significant DOS value, as compared to $\pi^*$. Peak ‘a’ in the ELNES of tricycle conformer is due to the transition to both unoccupied $\pi^*$ and $\sigma^*$ orbital, because of the common coincidence of ELNES and unoccupied DOS. Thus, peak ‘a’ in the tricycle structure can be attributed to a composition of $sp^2$ and $sp^3$ hybridizations of bonds between each carbon atom with three carbons and one hydrogen atom in the nearest neighborhoods, whereas the first peak observed in the ELNES of graphite and graphene and chair-graphene, is the $\pi^*$ orbital because of $sp^2$ hybridization of carbon atoms. Like the other three structures, peak ‘b’ is composed of more $\sigma^*$ and less $\pi^*$ orbitals.

When we look at Fig. 3, we can see that there is a feature at 4.95 (3.8) eV between $\pi^*$ and $\sigma^*$ peaks in the C K-edge of chair (tricycle) graphene, which was not observed in the C K-edge of graphite and graphene. The origin of this feature as a rather broad shoulder in chair (a small peak in tricycle) at the lower energy part of $\sigma^*$, that is ‘c’, is explained by a careful study of the unoccupied C p-DOS of chair and tricycle graphene (see Fig. 6). The unoccupied C p-DOS of chair (tricycle) shows a similar peak around 5 (3.8) eV, corresponding to the position of feature ‘c’ in the C K-edge. At this energy in the unoccupied DOS of the chair (tricycle) conformer, the contribution of local DOS is composed of $p_z$ and $p_x + p_y$ states of carbon atoms equal to 0.027 (0.02) and 0.03 (0.016) states/eV.
Fig. 6. Calculated unoccupied p-DOS of chair- and tricycle-graphane, graphite and graphene structures.

respectively. Since these partial densities of states have significant intensities, it could be a sign of the $\pi-\sigma$ hybridization in both chair and tricycle conformers of graphene. Furthermore, there is a C–H feature in the ELNES spectrum of benzene solid structure between the $\pi^*$ and $\sigma^*$ features (Stöhr, 1992). Also, in NEXAFS spectra of the tetrahedral amorphous carbon, a peak between $\pi^*$ and $\sigma^*$ features has been observed which corresponds to the $\sigma_{2p}$ transition of the C–H bonds that would originate from the absorption of hydrocarbon to the surface dangling bonds (Lee et al., 2004). By attention to this point that the unoccupied DOS of hydrogenated graphene, in both chair and tricycle conformers, introduce a hybridization of $\pi^*$ and $\sigma^*$ between these two main peaks, at the peak positions of ‘c’, and further this trait is not observed in graphite and graphene, therefore peak ‘c’ can be assigned to the presence of hydrogen.

4. Conclusions

The energy loss near edge structure of the hydrogenated graphene, namely ‘graphane’, was calculated in the framework of the density functional theory by means of the FP-LAPW method and it was compared with that of graphite and graphene. Since the inclusion of core-holes was found to be essential for the accurate reproduction of features in graphite and graphene, it can be deduced that a full core-hole leads to the more reasonable ELNES spectra of graphene conformers than a ground state. In other words, a full core-hole with different sizes of super-cells (FSR) was required in order to reproduce features close to the carbon K-edges. We found that there were three features in the ELNES spectrum of chair and tricycle conformers of graphene. The ELNES spectrum of chair conformer included transition from 1s carbon orbital to $\pi^*$ and $\sigma^*$, and a shoulder between the two main features. In tricycle conformer, the first feature had contributions of both $\pi^*$ and $\sigma^*$ orbitals. Moreover, the energy difference between $\pi^*$ and $\sigma^*$ features of graphene conformers was decreased relative to it in graphite and graphene. The unoccupied DOS of hydrogenated graphene, in both chair and tricycle conformers, introduced a hybridization of $\pi^*$ and $\sigma^*$ between these two main peaks, at the peak positions of ‘c’, that this trait was not observed in graphite and graphene. Therefore peak ‘c’ can be assigned in the hydrogenated graphene to the presence of hydrogen. Moreover, according to this prediction, ELNES will be able to distinguish between different types of graphene structures. This is evidenced by the finding of distinctive features in the ELNES spectra of chair- and tricycle-graphane.

References

A density-functional theory (DFT) and excited states package based on the linearized augmented plane-wave (LAPW) method, http://exciting-code.org


