Computational Strategy for Graphene: Insight from Odd Electrons Correlation

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The correlation of odd electrons in graphene turns out to be significant so that the species should be attributed to correlated ones. This finding profoundly influences the computational strategy addressing it to configuration-interaction computational schemes. Owing to serious problems related to the schemes realization, a compromise can be suggested by using single-determinant approaches based on either Hartree-Fock or Density-Functional Theory in the form of unrestricted open-shell presentation. Both computational schemes enable to fix the electron correlation, while only the Hartree-Fock theory suggests a set of quantities to be calculated that can quantitatively characterize the electron correlation and can be used for a quantitative description of such graphene properties as magnetism, chemical reactivity, and mechanical response. The paper presents concepts and algorithms of the unrestricted Hartree-Fock theory applied for the consideration of magnetic properties of nanographenes, their chemical modification by the example of stepwise hydrogenation, as well as a possible governing the electron correlation by the carbon skeleton deformation.

Keywords: Odd Electrons, Electron Correlation, Effectively Unpaired Electrons, Graphene, Magnetism, Chemical Modification, Deformation.

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1. INTRODUCTION

According to Wikipedia, 'Graphene is an allotrope of carbon, whose structure is one-atom-thick planar sheets of sp^2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice' [1]. The definition clearly exhibits a molecular-crystal duality of this extraordinary substance. The peculiar duality is embodied in the computational strategy of graphene, as well. On one hand, the solid state microscopic theory of quasiparticles in 2D space forms the ground for the description of graphene crystal. On the other hand, quantum molecular theory creates the image of the graphene molecule. However, as earlier, the two seemingly different concepts are tightly interconnected at computational level. Thus, the solid state quasiparticles are usually described in the approach based on a unit cell and/or supercell followed with periodic boundary conditions; besides, the unit cell is described at the molecular theory level. Therefore, the latter lays the foundation of both approaches, whilst rather differently. It is connected with the different origin of the molecular object under study. In the case of solid state approach, the cell and/or supercell should be chosen as a known crystalline motive. When graphene is considered as a molecule, no structural restrictions are introduced in advance. In both cases, it becomes necessary to understand which molecular theory is applicable for the graphene to be studied in the best way. The current paper concerns peculiarities of the molecular theory of graphene. The latter are obviously connected with both the odd-electron origin of the graphene electron system and these electrons correlation that turns out to play the governing role.

2. ODD ELECTRONS CORRELATION

In spite of formally monatomic crystalline structure of graphene, its properties are evidently governed by the behaviour of odd electrons of hexagonal benzenoid units. The only thing that we know about the behaviour for sure is that the interaction between odd electrons is weak; nevertheless, how weak is it? Is it enough to provide a tight covalent pairing when two electrons with different spins occupy the same place in space or, oppositely, is it too weak for this and the two electrons are located in different spaces thus becoming spin correlated? This supremely influential molecular aspect of graphene can be visualized on the platform of molecular quantum theory.

When speaking about electron correlation, one must address the problem to the configuration interaction (CI). However, neither full CI nor any its truncated versions, clear and transparent conceptually, can be applied for computations valuable for graphene nanoscience that requires a vast number of computations to be performed as well as a great number of atoms to be considered [2, 3]. Owing to this, techniques based on single unrestricted open-shell determinants becomes the only alternative. Unrestricted Hartree-Fock (UHF) and unrestricted DFT (spin polarized, UDFT) approaches form the techniques ground and are both sensitive to the electron correlation, but differently due to different dependence of their algorithms on electron spins [4, 5]. Application of the approaches raises two questions: 1) what are criteria that show the electron correlation in the studied system and 2) how much are the solutions of single-determinant approaches informative for a system of correlated electrons.

Answering the first question, three criteria, which highlight the electron correlation at the single-determinant level of theory, can be suggested. Those concern the following characteristic parameters:

Criterion 1:

$$\Delta E^{RU} \geq 0 \, ,$$

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where $\Delta E^{RU} = E^R - E^U$ presents a misalignment of energy. Here, E^R and E^U are total energies calculated by using restricted and unrestricted versions of the program in use.

Criterion 2:

$$N_D \neq \mathbf{0} ,$$

where N_D is the total number of effectively unpaired electrons and is determined as

$$N_D = trD\left(r\middle|r'\right) \neq \mathbf{0} \text{ and } N_D = \sum_A D_A .$$

Here, $D\left(r\middle|r'\right)$ [6] and D_A [7] present the total and atom-fractioned spin density caused by the spin asymmetry due to the location of electrons with different spins in different spaces.

Criterion 3:

$$\Delta S^2 \geq \mathbf{0} ,$$

where $\Delta S^2 = S_U^2 - S(S+1)$ presents the misalignment of squared spin. Here, S_U^2 is the squared spin calculated within the applied unrestricted technique while $S(S+1)$ presents the exact value of S^2.

Criterion 1 follows from a well known fact that the electron correlation, if available, lowers the total energy. Criterion 2 highlights the fact that the electron correlation is accompanied with the appearance of effectively unpaired electrons that provide the molecule

radicalization [6-8]. These electrons total number depends on interatomic distance: when the latter is under a critical value R_{cov}^{crit}, two adjacent electrons are covalently bound and $N_D = 0$. However, when the distance exceeds R_{cov}^{crit}, the two electrons become unpaired, $N_D \geq 0$, the more, the larger is the interatomic spacing. In the case of the sp^2 C-C bonds, $R_{cov}^{crit} = 1.395$ Å. Criterion 3 is the manifestation of the spin contamination of unrestricted single-determinant solutions [6-8]; the stronger electron correlation, the bigger spin contamination of the studied spin state.

Table 1 presents sets of the three parameters evaluated for a number of right-angled (n_a, n_z) fragments of graphene (n_a and n_z count the numbers of benzenoid units along armchair and zigzag edges of the fragment), nanographenes, NGrs below, by using AM1 version of semiempirical UHF approach implemented in the CLUSTER-Z1 codes. To our knowledge, only these codes allow for computing all the above three parameters simultaneously.

The data convincingly evidence that the electron correlation in graphene is significant. In view of the correlation, one can answer the second question put above suggesting quantitative explanation of peculiarities of the graphene magnetism, chemistry, and mechanics, much as this has been done for fullerenes [3].

Table 1 – Identifying parameters of the odd electron correlation in right-angle nanographenes

Fragment $\left(n_a, n_z\right)$	Odd electrons N_{odd}	ΔE^{RU} [1] $kcal/mol$	δE^{RU} % [2]	N_D , e⁻	δN_D , % [2]	ΔS_U^2
(5, 5)	88	307	17	31	35	15.5
(7, 7)	150	376	15	52.6	35	26.3
(9, 9)	228	641	19	76.2	35	38.1
(11, 10)	296	760	19	94.5	32	47.24
(11, 12)	346	901	20	107.4	31	53.7
(15, 12)	456	1038	19	139	31	69.5

[1] Presented energy values are rounded off to an integer

[2] The percentage values are related to $\delta E^{RU} = \Delta E^{RU} / E^R(\mathbf{0})$ and $\delta N_D = N_D / N_{odd}$, respectively

3. CONCLUSIVE REMARKS

Data presented in the current paper have shown that the correlation of odd electrons in graphene is significant so that the species should be attributed to correlated ones. This finding considerably complicates the computational strategy addressing it to CI computational schemes. Owing to serious problems related to the realization of such schemes in practice, a compromise can be suggested by using single-determinant approaches based on either Hartree-Fock or density-functional theory in the form of unrestricted open-shell presentation. Both computational schemes can fix the electron correlation, while only the Hartree-Fock theory suggests a set of quantities to be calculated that can quantitatively characterize the electron correlation and be used for a quantitative description of

such graphene properties as magnetism, chemical reactivity, and mechanical response.

Magnetic constant J, the inverse value of which directly characterizes the strength of the electron correlation [9], lays the foundation of the description of magnetic properties of graphene. As shown, the constant is ~-16 $kcal/mol$ for a graphene regular crystal, which is too much for the magnetism to be observable. In contrast to crystalline graphene, nondeformed and nondestructured nanographenes can be magnetic, since the magnetic constant rough-inversely depends on the NGr size. The latter determines the correlation zone and provides a recordable magnetization if J is from a few units to tens nanometers. Small enough J values can be provided as well by magnetic nanostructuring of rather large graphene pieces caused by the introduction of

half-spin impurities or defects into the graphene body. Additionally, the odd number of the latter may change the singlet spin multiplicity of the ground state. Both scenarios find their verification in practice.

The correlated-electron algorithm-in-action has been applied in the current paper to the chemical modification of (5, 5) NGr by the example of its algorithmic stepwise hydrogenation [10]. As shown, both the hydrogenation of NGr itself and the final hydrides depend on several external factors, namely: 1) the state of the fixation of graphene substrate; 2) the accessibility of the substrate sides to hydrogen; and 3) molecular or atomic composition of the hydrogen vapor. These circumstances make both computational consideration and technology of the graphene hydrogenation multimode with the number of variants not less than eight if only molecular and atomic adsorption does not occur simultaneously. Thus, in full agreement with experimental evidence, a regular chair-like cyclohexanoid structure known as graphane can be obtained only for fixed membranes accessible to hydrogen atoms from both sides. Oppositely, one-side hydrogenation of the membrane results in irregular quasi-amorphous structure. A detailed consideration of all variants should be mandatory included in any serious project aimed at application of the hydrogen-graphene-based nanomaterials in general and for hydrogen-stored fuel cells, in particular.

The electron correlation is highly sensitive to the graphene deformation since the interatomic spacing is the main regulator of the former. Both static and dynamic deformation may influence the action. Static deformation, considered in the paper, is caused by one-side hydrogenation of the pristine sample [9]. When hydrogen atoms are removed, the carbon skeleton keeps its concave, either a canopy-like or basket-like, shape supported by stretched C-C bonds. The stretching stimulates both a significant increasing of the number of effectively unpaired electrons and a remarkable decreasing the magnetic constant absolute value. The former changes the electron-density image of the sample and evidence the enhancement of its chemical reactivity. The latter may result in the deformation-stimulated magnetization of the sample.

In view of these findings, an alternative, correlated-electron explanation of peculiarities related to the density images of the graphene bubbles found on different substrates [11] has been suggested [9].

The dynamic deformation is illustrated by the example of the (5, 5) NGr uniaxial tension. As shown, the strengthening of the electron correlation accompanies each step of the deformation [12]. This is followed by both enhancement of chemical reactivity and magnetic ability. In spite of predominantly plastic character of the graphene deformation, the latter can be applied to regulate both abilities of the sample.

The odd electron correlation is not a prerogative of graphene only. Similar phenomenon is characteristic for all sp^2 nanocarbons, including both fullerenes and nanotubes [3]. The only preference of graphene consists in much larger variety of cases when this inherent characteristic of the class can be visualized.

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