

Correlation of odd electrons in graphene: Effect on chemistry, magnetism, and mechanics

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In the imagination of the majority of quantum computationists, involved in the graphene nanoscience, the motion of weakly bound odd electrons of graphene with different spins is not correlated. Only this fact can justify them using computational techniques based on single restricted closed-shell determinants such as widely used DFT schemes. Sometimes, the schemes have even been heralded as indisputable standard of the computations in the field. However, the electron behavior in graphene is much richer and does not fit a Procrustean bed of the electron correlation neglect just revealing peculiarities related to graphene edges, structurally inhomogeneous chemical reactivity, size-dependent magnetism, enhancement of the electron density of graphene bubbles, and so forth.

When speaking about electron correlation, one must address the problem to the configuration interaction (CI). However, neither full CI nor any its truncated version, clear and transparent conceptually, can be applied for computations, valuable in graphene nanoscience, so that techniques based on single unrestricted open shell determinants become the only alternative. UDFT and unrestricted Hartree-Fock (UHF) approaches form the techniques ground and are both sensitive to the electron correlation, but differently due to different dependence on electron spins. Nevertheless, one can suggest three characteristic parameters that may characterize the extent of the electron correlation and that can be evaluated within the framework of both techniques. Among the parameters there are the following:

1. Misalignment of energy

$$\Delta E^{RU} = E^R - E^U. \quad (1)$$

Here E^R and E^U present total energies calculated by using restricted and unrestricted versions of the same program;

2. The number of effectively unpaired electrons

$$N_D = \text{tr}D(\mathbf{r}') \text{ and } N_D = \sum_A D_A, \quad (2)$$

where $D(\mathbf{r}')$ and D_A present the total and atom-fractioned spin density caused by the spin asymmetry due to location of electrons with different spins in different spaces;

3. Misalignment of squared spin

$$\Delta \hat{S}^2 = \hat{S}_U^2 - S(S+1). \quad (3)$$

Here \hat{S}_U^2 presents the squared spin value calculated within the applied unrestricted technique.

Table 1 presents a set of the three parameters evaluated for a number of right-angled fragments (n_a, n_z) of graphene (n_a and n_z count the numbers of benzenoid units along armchair and zigzag edges of the fragment, respectively) by using AM1 version of semiempirical UHF approach. The first two

parameters are definitely not zero by absolute value, besides greatly dependent of the fragment size. At the same time, their relative values are constant within ~10% accuracy pointing to a stable and size independent effect caused by the electron correlation. Additionally, the relation $N_D = 2\hat{S}_U^2$, which is characteristic for correlated electrons in the singlet state, is rigidly kept over all fragments.

Table 1.

| Fragment (n_a, n_z) | Odd electrons N_{odd} | ΔE^{RU} | | N_D | | \hat{S}^2 |
|--------------------------|----------------------------|-----------------|--|-------|-----------------------------------|-------------|
| | | Kcal/mol | $\delta E^{RU} = \Delta E^{RU} / E^R$ % | e^- | $\delta N_D = N_D / N_{odd}$ % | |
| (5, 5) | 88 | 307.6 | 17 | 31 | 35 | 15.5 |
| (7, 7) | 150 | 376.2 | 15 | 52.6 | 35 | 26.3 |
| (9, 9) | 228 | 641.6 | 19 | 76.2 | 35 | 38.1 |
| (11, 10) | 296 | 760.1 | 19 | 94.5 | 32 | 47.2 |
| (11, 12) | 346 | 900.6 | 20 | 107.4 | 31 | 53.4 |
| (15, 12) | 456 | 1038.1 | 19 | 139 | 31 | 69.5 |

The data convincingly evidence that the electron correlation in graphene is significant. In view of the correlation, peculiarities of the graphene chemistry, magnetism, and mechanics can be explained at the quantitative level.

Chemical reactivity of graphene is atomically mapped due to difference in values D_A in (2). The value, whose expression should be properly adapted to the computational scheme in use, serves a quantitative indicator of the target atom at any step of the chemical addition and lays the foundation of computational synthesis of the graphene polyderivatives of any kind [1].

The electron correlation is the main reason for the species magnetism. In the case of graphene the magnetism is molecular by origin and size dependent since the values of the magnetic constant J , small enough for the magnetic behavior of the singlet-ground-state species to become recordable, is achieved at the average linear size of the graphene fragment of a few nm. The magnetism obviously disappears when the size exceeds the electron mean free path [2].

Stretching graphene sheets results in strengthening the electron correlation thus providing increase in their unpairing, which leads to lifting the electron density in general, and atomic chemical reactivity, in particular [3], so that not a virtual magnetic field is responsible for a peculiar behavior of graphene bubbles, but a predictable change in the electron density of a stretched object lays the feature foundation.

General aspects of the odd electrons correlation related to sp^2 nanocarbons and its manifestation in the electronic properties of the species are presented in [4].

References

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