NANOCARBONS THROUGH COMPUTATIONS: FULEERENES, NANOTUBES, AND GRAPHENE

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Summary

Fullerenes, carbon nanotubes, and graphene belong to a particular class of nanomaterials for which a non-completed covalent coupling of odd electrons is a distinguished feature. The odd electrons, whose number is determined by the difference between the numbers related to valence electrons and to bonds formed by atoms, provide an enhanced chemical activity of the molecular body due to appearing effectively unpaired electrons by a total number N_D. Their partitioning over atoms N_{DA} exhibits individual atom chemical reactivity and/or susceptibility.

Both quantities can be transparently calculated within unresricted single-determinant Hartree-Fock approximation (broken spin-symmetry approach) thus providing grounds for a highly controlled computational synthesis based on the N_{DA} distribution (N_{DA} map).

Governing by the map one can convincingly perform a computational chemical modification or, by other words, computational synthesis of derivatives that are the products of the considered addition reaction. A choice of target atoms by the highest

N_{DA} value is the leading point of the procedure. The procedure is equally applicable to fullerenes, carbon nanotubes, and graphene.

1. Introduction

One important area of research in the modern material nanoscience concerns carbon-based materials, particularly benzenoid-structured species such as fullerenes, nanotubes, graphite, and graphene. Nanochemistry of the 21st century, new light nanomagnets, new optical devices, new drugs, new mechanic devices – these and other excitedly sounded promises implying carbon-based material can be heard through over the world. What makes them so exclusive for the properties of the materials to be outstanding indeed? We shall try to answer this question from the viewpoint of computational nanoscience. This consideration is based on the electronic properties of the materials. Two corner stones lay the foundation of the electronic nanocarbon computational building. The first concerns *odd-electron* nature of their atomic system and is an internal property by nature. The other is provided with extremely high donor and acceptor characteristics of the species and is intimately connected with interaction between them that is smoothly transformed into peculiar internal property of composites. It turns out that the two concepts make allowance for interconnecting the nanocarbon building constructions via tight interrelations between nanochemistry and nanomedicine; nanomagnetism and nanophotonics; nanomechanics and nanoinformatics. In its turn, the intrinsic concordance of the above building departments forms the ground for unified theoretical approach. Before entering the building, let us look at the stones that form the construction fundament.

1.1. Why Odd Electrons and Not Aromatic π Electrons?

The term "odd electrons" has come from organic chemistry where it was introduced to describe the electronic structure of diradicals. It naturally covers terming π electrons, "magnetic electrons", and "open-shell molecule electrons". With respect to benzenoid nanocarbons it manifests that the number of valence electrons of each carbon atom is larger by one than that of interatomic bonds it forms.

Aromaticity has been the first and the oldest concept applied to the odd-electron problem, which started in 1825 when Sir Michael Faraday discovered benzene. The 185-year development of the concept has followed and reflected in the best way the build-up of the molecular physics and chemistry in general and organic chemistry in particular. The term π electrons was suggested by Hückel in 1931 for planar {4n+2} aromatic molecules. From that time π electrons have become a peculiar qualitative characteristic of a molecule possessing two distinctive features, namely, (1) odd electron delocalization over molecule atoms and (2) a complete covalent bonding of the odd electrons so that the corresponding π orbitals are occupied by the electrons in pairs. These characteristics of the electrons are well coherent with four criteria of aromaticity, often referred to as classic criteria, which have been originated in due course of long-time development of the aromaticity concept. Those are concerned with the following characteristics:

(1) Chemical behavior – electrophilic aromatic substitution;

(2) Structural feature – bond length equalization due to cyclic delocalization;
(3) Energetic conditions – enhanced stability (large resonance energy);
(4) Magnetic behavior – "ring current" effects:
      (a) anomalous chemical shift disclosed by nuclear magnetic resonance (NMR).
      (b) large magnetic anisotropies.
      (c) diamagnetic susceptibility exaltation.

Initially, the criteria were suggested empirically. The development of electronic theory of molecules allowed for obtaining electronic conceptual view on the phenomenon (started by Hückel) and for proving the criteria computationally. By the time of fullerene discovering in 1985, which marked the start of a sharp growing interest to nanocarbons, the main theoretical concept of aromaticity has been constructed. According to the latter, π electrons can be considered in the first approximation as an electron gas incasing the σ framework in a double skin. The wave functions of this electron gas are characterized by the angular momentum quantum numbers $l = 0, 1, 2, 3, \ldots$ corresponding to s, p, d, and f π shells; π electrons are subordinated to the Pauli principle and are accommodated on the orbitals by pairs, which has given rise to the *restricted* formalism of the electron consideration.

When fullerene C_{60} was discovered, Harold Kroto, who later was awarded by the Nobel Prize for the discovery, suggested that it could be "the first example of a spherical aromatic molecule". This suggestion was supported by a large discussion of its extremely stable aromatic character. However, the hypothesis was soon rejected in the light of numerous chemical reactions undergone by fullerenes. Nowadays, it is generally assumed that fullerenes have an ambiguous aromatic character, with some properties that support the aromaticity of these systems in view of the above criteria while the others do not. Thus, there is broad evidence that fullerenes experience substantial ring currents. This fact, together with rather considerable stability, seems to stress their aromatic character. Oppositely, evidence from chemical reactivity is against the aromaticity, since fullerenes are very reactive and easily undergo a large variety of chemical transformations that unlike with most aromatic compounds, are in most cases addition reactions to the conjugated π system. The enthalpy of formation of fullerenes does not support the energetic criterion of the aromatic character either. In addition, the existence of two types of C-C bonds in C_{60} ([6,6] and [5,6]-bonds) violates the criterion on the bond length equalization and indicate that π electrons of the fullerene are partially localized. Therefore, only magnetic and NMR properties seem to evidence delocalization by ring currents. Basing on these findings it was concluded that the scope of aromaticity is much broader for Hückel-type aromatic molecules than for fullerenes where it is essentially limited to a single criterion (4). At the same time, the 185-year history of the aromaticity has convincingly highlighted that aromatic compounds cannot be characterized by a single property so that the concept has a multidimensional character. This stimulated looking for additional criteria that might prove the fullerene aromaticity. Since neither new empirical yardstick for the fullerene aromaticity could be offered, researches have been concentrated on computational chemistry relying on a sharp progress of the latter. A restricted formalism of the electrons approach therewith has been kept unchanged. Later on a similar story has happened with carbon nanotubes.

Two main streams of the modern computational chemistry are based on either Hartree-Fock (HF) or density functional theory (DFT). Both computational schemes were applied to prove the classic aromaticity criteria to fullerenes, nanotubes, and graphene. A few computational characteristics that are outside the above classic criteria have been suggested. There are the following among the latter.

(1) The topology of the DFT electron density as well as properties derived from the density such as the electron localization function and local ionization potential.
(2) Weighted HOMO-LUMO gap as an index of kinetic stability (T), as well as absolute and relative hardness (η).
(3) Delocalization index $(\delta(A,B))$.

Additionally to the ring-current criterion (4), the issues tend to assist in the description of the delocalization-aromatic behavior of fullerenes in the framework of restricted computational schemes. However, they are too yang to get the status similar to that of classic criteria.

Since odd electrons exist not only in benzenoid-structured compounds, and since their manifestation in various compounds has become clear for many researches, the aromaticity approach was tried to be expanded over these species, both 2D- and 3D-dimensional, among which there are conjugated heterocycles, [n]trannulenes, Möbius and metallacycles, transition-metal(half-) sandwiches such as ferrocenes, carbon free sandwich complexes like$[(P_5)_2 Ti\}^{2-}$, boron-based clusters, bimetallic and metallic clusters, and many others. However, as turned out, the approach was able to catch only some traces of the odd electrons delocalization while the electronic behavior of the species does not fit in the framework based on the classic aromaticity criteria. An unavoidable requirement either to significantly develop the aromaticity concept or to suggest an alternative one has been widely anticipated.

An alternative approach to the odd electron problem has come from molecular magnetism of molecular complexes in which transition metal ions form net of spins caused by magnetic electrons that interact weak. The scheme in Figure 1 explains main points of the odd electron problem. Initially doubly degenerated atomic levels Ψ_A and Ψ_B are split due to electron interaction with the energy difference ΔE. Two spins of the relevant electrons can be distributed over the levels by five different ways. Configurations I, II, III, and IV are related to singlet state while the only configuration V describes the triplet one. As a result, the triplet state is spin-pure at any ΔE, while the singlet state is either completely covalent that is in consonance with the aromaticity concept (configuration I) and, consequently, spin-pure at large ΔE, or is a mixture of configurations I-IV and becomes spin-mixed when the interaction is weak. The energy difference ΔE turns out to be the main criterion for attributing the species to either covalently bound or diradical species. A deep understanding of the underlying physics followed from the work of Löwdin, Nesbet, Anderson, Hay and co-workers, and others has resulted in a necessity of the configuration interaction (CI) to be applied in the case. Moreover, the unrestricted formalism with respect to wave function construction, which oppositely to restricted aromaticity takes the electrons spin into account, should be taken as starting point for a further CI consideration.
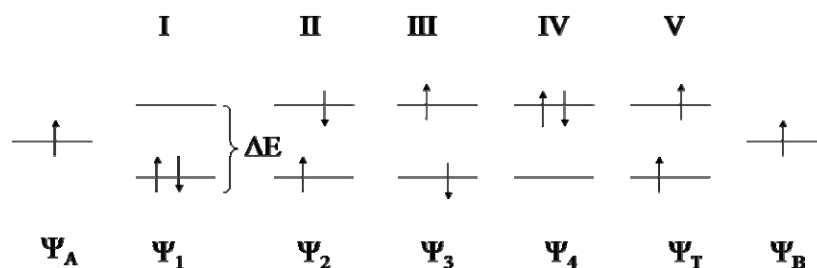
Figure. 1. Scheme of the distribution of two electrons over split orbitals

Thus, if a number of electron pairs are weakly coupled, the CI expansion will be slowly convergent and high-order excitation from the reference configuration (see ψ_2, ψ_3, and ψ_4 in Figure 1) will contribute significantly to the wave function. Benard found that the unrestricted Hartree-Fock (UHF) energy is much lower than the restricted one (RHF). Therefore, coming back to species, aromatic character of which is under question, one can suggest a decisive computational criterion by misalignment of their energies $\Delta E^{RU} = E^{R} - E^{U}$ calculated following conceptually identical restricted (E^{R}) and unrestricted (E^{U}) schemes. Obviously, the aromaticity concept in its classical formulation should be applied to the species if only $\Delta E^{RU} = 0$.

First attempts of a direct CI approach based on unrestricted wave functions and applied to the odd electron interaction was performed for metal dimers. However, until now the application of CI computational scheme is restrained by a severe complication of the computational procedure. Thus, the traditional complete-active-space-self-consistent-field (CASSCF) methods that deal correctly with diradicals and some dinuclear magnetic complexes, cannot handle systems with larger number of odd electrons due to a huge number of configurations generated in the active space of the system. To imagine arising technical difficulties it is worthwhile to cite E.Davidson, "If there are 'm' singly occupied orbitals on each of 'n' identical centers, then 2^{mn} Slater determinants can be formed by assigning spins up or down each of the 'nm' orbitals". So that no CASSCF type approach, including a simplified embedded-cluster CASSCF supplemented by the complete active space second-order perturbation theory (CASPT2), seems feasible for many-odd electron systems such as fullerenes and other nanocarbons. That is why addressing single-determinant approaches seems to be the only alternative.

The open-shell *unrestricted broken symmetry* (UBS) approach suggested by Noodleman is the most widely known among the latter. Since the early remark of Slater and the "symmetry dilemma" later formulated by Löwdin, the term "broken symmetry" has implied that the energetically best HF solution is not necessarily symmetry-adapted. Noodleman showed that when the magnetic orbitals (singly occupied orbitals) of two dimer subunits were allowed to interact by overlapping in a self-consistent field (SCF) procedure, a state of mixed spin symmetry and lowered space symmetry was obtained. This spin-mixed or broken symmetry state is considered within the framework of the UBS approach.

A general view of the broken symmetry wave function $|\psi_B\rangle$ for n pairs of magnetic electrons is the following

$$|\psi_B\rangle = (N!)^{-1/2} M^{-1/2} \det\left[(a_1 + cb_1)\alpha, a_2\alpha \ldots a_n\alpha \big| (b_1 + ca_1)\beta, b_2\beta \ldots b_n\beta\right]$$
$$\approx M^{-1/2}\left(\phi_1 + c\phi_2 + c\phi_3\right). \tag{1}$$

The function describes the singlet state; doubly occupied canonical molecular orbitals that describe paired electrons are omitted. Here a_i represent singly occupied magnetic orbitals centered on atom A, all magnetic electrons of which have spin α, while b_i do the same for atom B with spin β attributed to its magnetic electrons. Mixing parameter c implies a slight nonortogonality of orbitals $\bar{a}_1 = (a_1 + cb_1)$ and $\bar{b}_1 = (b_1 + ca_1)$. The principal determinant ϕ_1 describes pure covalent coupling of n odd electrons while small amounts of the charge transfer determinants ϕ_2 and ϕ_3, corresponding to $A^- - B^+$ and $A^+ - B^-$ configurations (see configurations II and III in Figure1) are mixed in due to nonorthogonality of atomic orbitals $\bar{a}_1$ and $\bar{b}_1$. Configuration IV is usually omitted since the relevant state energy is high. The open-shell manner for the function $|\psi_B\rangle$ is just appropriate to distinguish electron spins of atoms A and B. The weaker interaction between the electrons, the bigger is contribution of ϕ_2 and ϕ_3 constituents into $|\psi_B\rangle$ and, consequently, the bigger difference in the energy of restricted (ϕ_1) and unrestricted $|\psi_B\rangle$ configuration. The aromaticity concept corresponds to the first term in (1) and should be attributed to strong interaction between odd electrons.

The UBS approach is not reduced to routine UHF or unrestricted DFT (UDFT) calculations but consists in determining energy of pure spin states on the basis of calculations using $|\psi_B\rangle$ within either UHF or UDFT computational schemes. This determination is possible at the level of the second-order perturbation theory with respect to parameter c supplemented by variationally determined $S_{\bar{a}\bar{b}}$, that is, meeting the requirements

$$\frac{\partial E_B}{\partial S_{\bar{a}\bar{b}}} = 0 \ \text{ and } \ \frac{\partial E(S)}{\partial S_{\bar{a}\bar{b}}} = 0 \tag{2}$$

for the spin-mixed and pure spin state, respectively. Here $S_{\bar{a}\bar{b}}$ presents the magnetic orbitals overlap. This level of theory is equivalent to explicit CI calculations.

Everybody can easily convince oneself that a complete coincidence of E^R and E^U energies takes place for benzene, the energies slightly deviate for naphthalene, but the difference ΔE^{RU} grows when the number of benzenoid cycles increases. As for fullerenes, carbon nanotubes, and graphene, first attempts to compare the application of RHF and UHF computational schemes to fullerene C_{60} were undertaken seven years ago. Later on this was found to happen with fullerene C_{70}, carbon nanotubes, and

graphene. It turned out that the ΔE^{RU} constituted about 2-4, 12-15, and ~20% from the total energy of fullerenes, carbon nanotubes, and graphene, respectively. The finding has highlighted a considerable weakening of odd electron interaction in the species in comparison with benzene. It became obvious that difficulties of fitting these nanocarbons in the aromaticity concept were connected with this finding. On the other hand, the application of the UBS approach has opened new possibilities to quantitatively describe all features of the species making nanocarbon science quite understandable and predictable.

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Prof. Elena F. Sheka was born in Kiev (USSR). She was graduated from the Kiev State University on physics and spectroscopy; then post-graduated at the Institute of Physics of the Academy of Sciences of the Ukrainian Republic of the USSR; Kiev and defended Ph. D. Thesis on "Exciton Spectra of Naphthalene Crystals" in Lebedev's Physical Institute of the Ac.Sci of the USSR. Her Doctor Sci. dissertation on "Exciton Spectra of Molecular Crystals" was later defended in Lebedev's Physical Institute of the Ac.Sci. of the USSR as well. She has been assistant professor of solid state physics spectroscopy since 1978 and full professor since 1985. Affiliations: Institute of Physics of the Ac.Sci. of the Ukrainian SSR (Kiev) 1958-1966; Institute of Solid State Physics of the Ac.Sci of the USSR (Chernogolovka, Mosc. distr.) 1966-1986; Moscow Physical-Technical Institute (professorship) 1978-1986; Peoples' Friendship University of Russia (Moscow) since 1986 till now. Currently she is a

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