# FULLERENE MOLECULE AS A NANOSIZE QUANTUM SYSTEM

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**Abstract.** It is shown that a strong Coulomb and exchange interactions between $\pi$ electrons in a fullerene molecule lead to the localization of these electrons, quantization of their energies, and a highly correlated state manifesting itself in the formation of electron crystals. In this approximation the fullerene molecule is a nanosize quantum system consisting of a positively charged rolled-up carbon backbone surrounded by three electron crystals: (i) two crystals formed by $\pi$ electrons in the 2 $p_z$ state that participate in the $\pi$ bond formation through the resonance of structures and are located on the convex and concave sides of the molecule, and (ii) the crystal formed by pairs of $\pi^*$ electrons excited into the $2p_z$ $3s$ state and participating in the formation of nonresonant $\pi^*$ bonds. The chemical activity and physical properties of such a system are determined by the crystal formed by electron pairs.

**Keywords:** fullerenes, highly correlated electron state, electron crystals, nanosize quantum system

## 1.Introduction

The $\pi$ electron state in the fullerene molecule is typically considered in the approximation of weakly interacting particles and is characterized by a set of molecular energy levels for $\pi$ electrons near $E_F$.

However, it is difficult to explain a number of rather unusual experimentally observed properties of the molecule in this approach. First of all, this concerns the molecule chemical activity. In contrast to benzene which consists of one carbon hexagon and is characterized by a negative electron affinity (-1.1eV), a fullerene molecule containing 20 hexagons shows a positive electron affinity (+2.7eV) [1]. As a consequence, the molecule is capable of accepting up to 12 additional electrons (without noticeably changing its icosahedral shape), but hardly loses electrons [2, 3].

In addition, the molecule demonstrates a pronounced selectivity of attachment sites [4], a high polarizability [5], and the ability to pass into an excited state [6]. The molecule is also characterized by a complex multistage ionization process when exposed to a laser radiation. This process is often accompanied by the formation of a short-lived triplet state [7], delayed ionization [8], and fragmentation of the molecule through the loss of neutral $C_2$ molecules [8, 9]. Besides, the absorption of one energy quantum often results in a simultaneous emission of two electrons [10].

It is also difficult to explain: (i) the rotation of molecules when they come closer to each other (a disordered rotation at high temperatures and a synchronous rotation at low temperatures) [11, 12]; (ii) excitation of Ridberg states [13]; (iii) a considerable scatter in the lengths of bonds between carbon atoms observed by neutron diffraction [14].

The attempts to explain these experimental facts led to the assumption that strong electron correlations can exist in the molecule [10]. The assumption of the presence of strong

intramolecular interactions resulted also from the observation of superconductivity in doped solid fullerenes [15]. However, the character of the interactions still remains unclear.

The hypothesis has recently been put forward [16] that the exchange and strong Coulomb interactions between $\pi$ electrons in an atomically flat carbon monolayer (graphene) can lead to their strongly correlated state which manifests itself in the formation of electron crystals.

Since the basis of the fullerene molecule is a carbon monolayer with $\pi$ electrons that perform the same function of resonant $\pi$ bonding as in a flat monolayer, it can be supposed that the state of $\pi$ electrons in the molecule must be similar to their state in the monolayer.

The goal of our study was to show that in the approximation of strongly interacting $\pi$ electrons the fullerene molecule, as well as the flat carbon monolayer, is a quantum system with $\pi$ electrons that form electron crystals.

## 2. Fullerene molecule in the approximation of strongly interacting $\pi$ electrons

It was shown in [16] that under the influence of exchange and strong Coulomb interactions between the $\pi$ electrons these electrons are localized on carbon atoms and form a spin-polarized electron crystal on each side of the carbon backbone. It would seem that exactly the same state of $\pi$ electrons and on the same terms as in [16] could also be expected in a fullerene molecule, since the molecule is formed by the rolled-up carbon monolayer. However, as also shown in [16], the process of rolling up of the carbon backbone under the condition of a strong interaction between electrons is accompanied by a change in the state of a part of $\pi$ electrons: they are pushed out from the $\pi$ electron crystal plane to the convex side of the curved carbon backbone and are excited from the $2p_z$ state into the hybrid $2p_z3s$ one. The $2p_z3s$ state is more extended in space and is higher in energy. The carbon atoms to which such excited electrons belong pass into a new hybridization state $sp^2 + 2p_z3s$ (see Fig. 1).
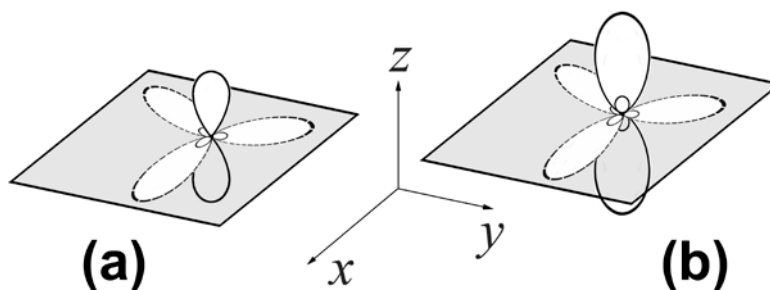


**Fig. 1.** Two states of hybridization of carbon atom in the fullerene molecule: $sp^2+2p_z$ (a) and $sp^2+2p_z3s$ (b)

According to [16], the ordering of such excited carbon atoms in the lattice can be accompanied by the formation of nonresonant $\pi$ bonds between neighboring atoms, i.e., the formation of pairs by the excited $\pi$ electrons, and also the formation of quasi-1D crystals from these pairs. By analogy, it can be expected that quasi-1D $\pi$-electron pair crystals will be formed on the convex side of the fullerene molecule whose carbon backbone is rolled-up to a truncated icosahedron.

As for the two spin-polarized $\pi$-electron crystals in the $2p_z$ state, mentioned above, they will have a quasi-spherical shape in the fullerene molecule since they will repeat the shape of the carbon backbone. Under a strong Coulomb interaction between $\pi$-electrons the ratio of squares of radii for these quasi-spherical crystals will be determined by the equality of electron densities on both sides of the rolled-up backbone. In order to achieve this equality of densities, a part of $\pi$ electrons of the internal electron crystal must pass to the convex side of

the molecule and must be excited into the hybrid $2p_z$ $3s$ state (Fig. 1). Thus, the number of $\pi$ electrons on two sides of the carbon backbone of the molecule will be different.

It is possible to find the number of such excited $\pi$ electrons and their location in the fullerene molecule by constructing resonant structures of the Kekule type. It is known that the number of such structures for the fullerene molecule is very high. However, if we take into account the spin ordering of $\pi$ electrons which arises due to the exchange interaction between them, the number of such resonant structures for the molecule decreases to nine. One of such structures is presented in Fig. 2a, where the projection diagram of the molecule is shown.
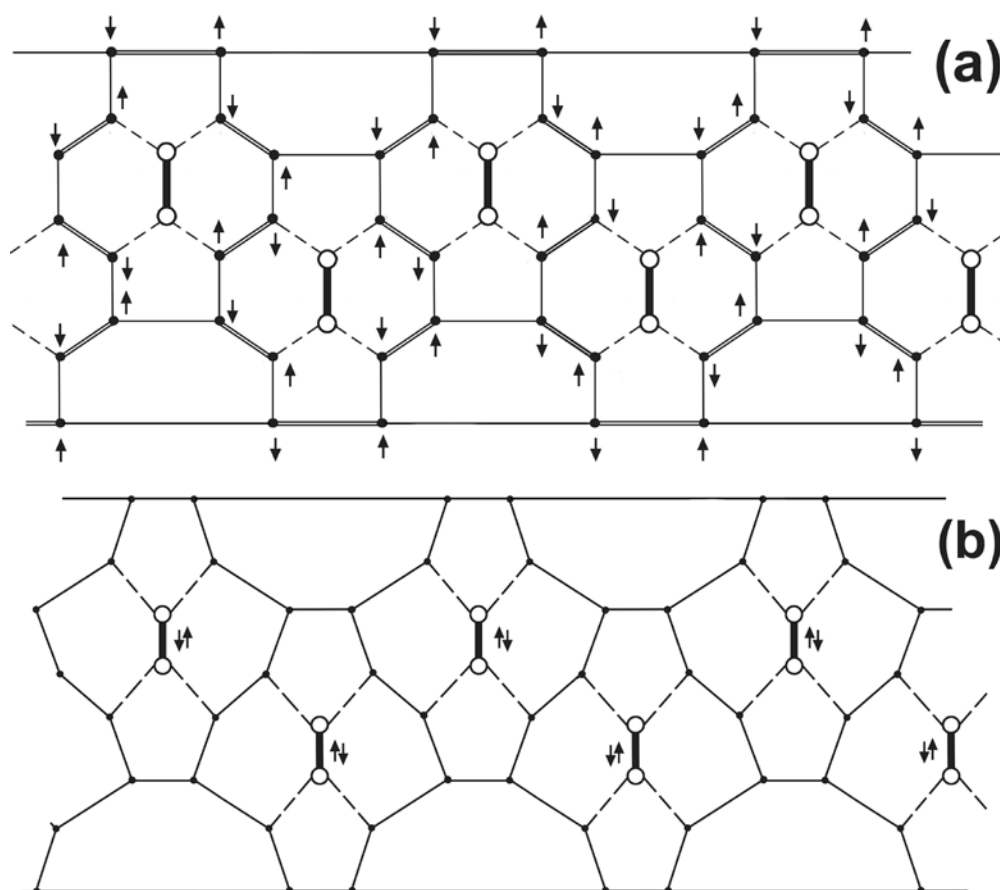


**Fig. 2.** Projection diagram of fullerene molecule: a) One of resonance structures of the molecule. Black circles show the carbon atoms the $\pi$ electrons of which participate in resonant $\pi$ bonding. Open circles are carbon atoms the $\pi^*$ electrons of which do not participate in resonant $\pi$ bonding. Double and single lines denote double ($\sigma + \pi$) and single bonds ($\sigma$) of the resonant bond state, respectively. Heavy lines correspond to double bonds between excited carbon atoms ($\sigma + \pi^*$). Dashed lines are single bonds between excited and unexcited atoms ($\sigma$). The arrows show the electron spin direction. b) Schematic representation of distortions of hexagons and pentagons, and the arrangement of quasi-1D crystal formed by $\pi^*$ electron pairs. Single lines correspond to resonant bonds, dashed lines are single $\sigma$ bonds, and heavy lines show double nonresonant bonds ($\sigma + \pi^*$)

The construction of such resonant structures which differ only in the arrangement of double and single bonds proved to be surprisingly informative. It allowed us to determine the multiplicity and, hence, the length of each of 90 bonds and their location in the molecule. The bond multiplicity was calculated from the frequency of occurrence of double and single bonds

in nine resonant structures.  The bond length was determined by extrapolating the known bond lengths in benzene and graphite under the assumption of a linear dependence of the length on multiplicity. Certainly, the accuracy of determining the bond length in this way is not high, but, as will be seen below, the accurate estimation of the bond lengths was not as important as revealing of the fact that there is a scatter in the bond lengths. The calculated scatter in the lengths and multiplicities is presented in Table 1.

Table 1. Scatter in lengths and multiplicities of bonds

| Bond multiplicity | Number of bonds | Bond length, Å |
|:---:|:---:|:---:|
| 1.0 | 24 | 1.52 |
| 1.14 | 18 | 1.48 |
| 1.29 | 12 | 1.43 |
| 1.50 | 12 | 1.41 |
| 1.57 | 12 | 1.37 |
| 1.85 | 6 | 1.35 |
| 2.00 | 6 | 1.33 |

It can be seen that most of the bonds (60 of 90) are characterized by different non-integral multiplicities, which points, in particular, to a non-equivalence of positions of carbon atoms in the fullerene molecule. The remaining 30 bonds proved to be either double bonds with a nonresonant $\pi$ bond (6) or single bonds (24). The scatter in the bond lengths also points to distortions of all hexagons and pentagons, except for two hexagons located at opposite points of the molecule. Their planes are parallel to each other and perpendicular to the same axis passing through their centers. These two undistorted hexagons with a bond multiplicity of ~1.30 and a bond length of ~1.43 Å form as if two poles of the fullerene molecule. In Fig. 2a, b these hexagons are developed on the plane and form the lines that limit the projection diagram of the molecule from above and below.

The presence of distorted hexagons and pentagons means that the fullerene molecule is not a regular truncated icosahedron. It can be seen from Fig. 2b that double and single bonds, i.e., the shortest and longest bonds, are located in the equatorial region relative to the molecule poles which are formed by two undistorted hexagons. It can also be seen that each distorted pentagon contains two single bonds belonging to one and the same carbon atom. This atom differs from the neighboring ones: the spin direction of its $\pi$ electron cannot be determined because the spin directions of the neighboring electrons are oppositely directed (Fig. 3). In other words, the $\pi$ electron of this atom cannot be spin-ordered relative to the $\pi$ electrons of neighboring atoms and, hence, cannot take part in resonant $\pi$ bonding.

It is this $\pi$ electron that will be pushed out by the Coulomb interaction with the remaining $\pi$ electrons of spin-polarized electron crystals and will be excited into the hybrid $2p_z3s$ state (Fig. 1). There will be 12 of such excited $\pi$ electrons. Under the influence of the same Coulomb repulsion, each excited $\pi$ electron will be forced to occupy only one of two hybrid $2p_z3s$ states located on the convex side of the molecule. As a result, the total number of electrons on the convex side of the molecule will exceed by 12 electrons their number on the concave side, i.e., there will be 36 electrons on the convex side and 24 electrons on the concave one. In all probability, this difference will ensure the equality of electron densities on both sides of the rolled-up carbon backbone under the conditions of a strong Coulomb interaction between electrons.
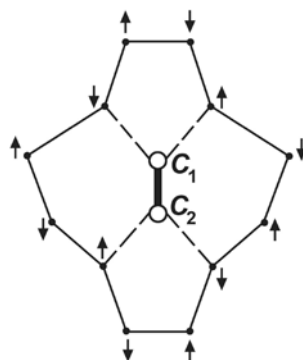
**Fig. 3.** Fragment of projection diagram of fullerene molecule. Impossibility of spin ordering of π electrons of carbon atoms ($C_1$ and $C_2$) at pentagon apexes is demonstrated. π* electrons can form only a π* bond between these atoms

In order to distinguish between the excited π electrons and the π electrons forming the resonant π bonds, we will denote them as π* electrons, and the bonds they form will be denoted as π* bonds.

The ordered arrangement of distorted pentagons and hexagons leads to an ordered arrangement of π* bonds between excited carbon atoms and, hence, an ordered arrangement of π* electron pairs. As a result, a quasi-1D crystal from π* electron pairs is formed in the equatorial region of the molecule. Such a crystal consists of six electron pairs and has a peculiar zigzag-like shape (Fig. 2b).

The π*-electron pairs of this quasi-1D crystal form negatively charged "protrusions" on the molecule surface that increase the diameter of the fullerene molecule in its equatorial region. This unscreened π*-electron pair crystal, along with the unscreened π-electron crystal and unscreened (in some places) carbon ions, make the electric field around the molecule highly inhomogeneous.

The crystallization of all π and π* electrons which are in definite quantum states ($2p_z$ and $2p_z3s$, respectively) makes the fullerene molecule a nanoscale quantum system of ~10 Å in diameter. The system consists of a positively charged rolled-up carbon backbone (including 12 excited carbon atoms) and the three electron crystals considered above. In contrast to the extremely unstable quantum system of a flat carbon monolayer [16], the quantum system of the fullerene molecule is stable. This stability is first of all due to the presence of the π* electron pair crystal on the convex surface of the fullerene molecule. This crystal (i) lowers the free energy of the system by the amount of energy of π* bonds, (ii) ensures the equality of electron densities on both sides of the rolled-up carbon backbone, (iii) partly screens the underlying π-electron crystal from external influences, (iv) converts the molecule from a radical to a non-radical (by pairing π* electrons).

## 3. On properties of a nanosize quantum fullerene system

The consideration of the quantum fullerene system structure described above and the state of π electrons in it leads to some conclusions on its chemical and physical properties. Below we compare the properties predicted by our model with the properties observed experimentally.

As shown above, the carbon backbone rolling up under the conditions of exchange and Coulomb interactions between π electrons is accompanied by distortions of hexagons and pentagons and, hence, a significant scatter in bond lengths. Neutron scattering experiments with crystalline fullerene at low temperatures [14] confirm the presence of a scatter in the bond lengths. It turns out that the lengths of the bonds shared by two hexagons and hexagon-pentagon lie in the ranges 1.366-1.412 Å and 1.420-1.487 Å, respectively. These values somewhat differ from the calculated ones (see Table 1). However, an exact coincidence in the

bond lengths cannot be expected because, on the one hand, the calculation of the bond length from its multiplicity is inaccurate and, on the other hand, the accuracy of the neutron scattering data can be affected by a permanent rotation of molecules relative to each other in the crystalline phase.

It is fairly obvious that the chemical activity of the quantum system should be determined by the electron crystal formed by pairs of $\pi^*$ electrons which are in the $2p_z3s$ state and are the farthest from the carbon backbone and less tightly bound to it than the $\pi$ electrons in the $2p_z$ state (the difference in bond energies depends on the energy of the 3s state for carbon atom and is likely to be several electron volts). Since the hybrid $2p_z3s$ states of excited atoms are occupied incompletely, the electron affinity of this system must be positive. Moreover, in accordance with the number of free hybrid states on the convex side of the molecule, the system can be capable of accepting at least 12 more electrons. This conclusion agrees well with the experimental observation of a positive electron affinity [1] and the attachment of 12 electrons not accompanied by noticeable changes in the molecule shape [2].

The presence of $\pi^*$ electrons must lead to a decrease in the work function of electron at the sites of their localization and also to a nonhomogeneity of the work function on the molecule surface. The location of $\pi^*$ electrons only in the equatorial region of the molecule must result in a highly nonhomogeneous polarizability of the molecule and also the selectivity of attachment sites for other atoms. All these features were observed experimentally [4, 5].

Because of the presence of $\pi^*$-electron pairs, simultaneous emission of two electrons of one pair can occur at absorption of one quantum of energy. In all probability, this was observed in [10] and is known as a double photoemission.

Since $\pi^*$ electrons belong to excited carbon atoms which are strongly coupled to each other via double bonds ($\sigma + \pi^*$) but are coupled much weaker to the carbon backbone (via single $\sigma$ bonds) (Fig. 3), the molecule ionization can result in a simultaneous loss of two excited atoms. Perhaps that is why a molecule fragmentation with a loss of $C_2$ was observed during its ionization [9].

In addition to the twelve $2p_z3s$ states on the convex side of the molecule, there are 12 completely unoccupied similar states on the concave side. Therefore, if an additional electron is accepted by the molecule, it can occupy one of free states, and then (in the case of $\pi^*$ bond rupture) triplet electron pair can appear in an excited carbon atom (in accordance with the Hund's rule for hybrid state filling). However, such a triplet state in the fullerene molecule will be extremely unstable due to a strong Coulomb repulsion of the accepted electron from the electron crystal formed by $\pi$ electrons on the concave side of the molecule. Such instability of the triplet state can apparently explain the observation of a short-lived highly reactive triplet state that appeared during electron bombardment of a fullerene molecule [7].

A strong nonhomogeneity of the electric field on the surface of the quantum fullerene system can result in a Coulomb interaction between molecules as they approach each other, i.e., the so-called configuration forces which depend on the mutual arrangement of charges in neighboring molecules arise. Possibly, these forces can cause clustering of molecules and their rotation when they come nearer to each other, which was observed in [11, 12]. Besides, the Coulomb interaction between molecules must also promote the crystallization of molecules in the structures which are more typical of ionic crystals, which is also observed experimentally (fcc at room temperature and sc at low temperatures) [14].

As for the magnetic properties of the quantum fullerene system in which there are no unpaired $\pi$ electrons, the system can show only the diamagnetism associated with the orbital rotation of $\pi$ electrons forming resonant bonds, like in a flat carbon monolayer [16]. However, the diamagnetic susceptibility of a fullerene molecule must be very weak because the curvature of the carbon backbone violates the parallelism of the planes of electron rotation

orbits which prevails in a flat monolayer [16]. A low diamagnetic susceptibility was observed experimentally in [17].

## 4. Conclusions

It has been shown that in the approximation of strongly interacting $\pi$ electrons the fullerene molecule $C_{60}$ proves to be a nanoscale quantum system consisting of a positively charged rolled-up carbon backbone and three electron crystals with quantized energies. Two of these crystals consist of spin-polarized $\pi$ electrons, have a quasi-spherical shape, and are located on opposite sides of the carbon backbone. The third crystal is quasi-1D, it consists of six pairs of $\pi^*$ electrons excited into the $2p_z3s$ state and is located on the convex side of the molecule (it encircles the molecule in the equatorial region). This crystal, which is the farthest from the carbon backbone, is responsible for the chemical activity of the fullerene molecule and its physical properties, including stability. It has been shown that the chemical activity and the physical properties of such a quantum system are in good agreement with the experimental data obtained.

The possibility to explain the set of available experimental data on the fullerene molecule properties demonstrated in this paper is a serious argument speaking in favor of the proposed approach.

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