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Energy Spectrum and Optical Properties of Bromide Fullerene $C_{70}Br_{10}$ within the Hubbard Model

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The energy spectrum of molecule $C_{70}Br_{10}$ of symmetry group Cs were obtained within the Hubbard model in the mean-field approximation. Using group theory methods, the classification of energy states was carried out, and the allowed transitions in the energy spectrum of bromide fullerene $C_{70}Br_{10}$ of symmetry group Cs were determined. On the basis of this spectrum, an interpretation of experimentally observed optical absorption bands of molecule $C_{70}Br_{10}$ is proposed.

Keywords: Hubbard model, Green's functions, energy spectrum, nanosystems, C_{70}, $C_{70}Br_{10}$.

Introduction

The fullerene C_{70} shown in Fig. 1 [1] was discovered in 1985 simultaneously with fullerene C_{60} [2]. Nuclear magnetic resonance (NMR) [3] studies of fullerene C_{70} showed that the ^{13}C NMR spectrum of this fullerene consists of five peaks, the presence of which indicates the existence of five groups of atoms that are not equivalent to each other. Meanwhile, the peak intensities in the NMR spectrum are in the ratio $10:20:10:20:10$, which indicates the number of carbon atoms in each group. Thus, these studies have shown that the C_{70} fullerene molecule has the D_{5h} symmetry. It can be seen from the Schlegel diagram in Fig. 2 [1] that fullerene C_{70} with symmetry group D_{5h} has eight non-equivalent bonds, denoted by letters a, b, c, d, e, f, g, h, and five groups of non-equivalent carbon atoms: $G_1 = \{1, 2, 3, 4, 5, 62, 63, 66, 67, 70\}$, $G_2 = \{6, 9, 12, 15, 18, 61, 64, 65, 68, 69\}$, $G_3 = \{7, 8, 10, 11, 13, 14, 16, 17, 19, 20, 43, 44, 47, 48, 51, 52, 55, 56, 59, 60\}$, $G_4 = \{21, 22, 25, 26, 29, 30, 33, 34, 37, 38, 41, 42, 45, 46, 49, 50, 53, 54, 57, 58\}$, $G_5 = \{23, 24, 27, 28, 31, 32, 35, 36, 39, 40\}$.

The G_1 set includes atoms, which are at vertices of junction of the two hexagons and one pentagon and, furthermore, each of these atoms has one adjacent neighbor of the same G_1 set. The G_2 set includes atoms that are located at the vertices of the junction of two hexagons and one pentagon, and each of them has no nearest neighbors from the same G_2 set. The set G_3 set includes atoms that are located at the vertices of the junction of two hexagons and one pentagon, and each of them has one nearest neighbor from the same G_3 set. In this case, the edge to which both atoms belong is the boundary between two hexagons. The G_4 set includes the atoms that are located at the vertices of the junction of two hexagons and one pentagon, and each

of them has one nearest neighbor from the same G_4 set, and the edge to which both atoms belong is the boundary between the hexagon and the pentagon. The G_5 set includes atoms, which are at vertices of junction of one hexagon and two pentagons, and each of these atoms has one adjacent neighbor of the same G_5 set.

Almost immediately, as soon as they learned how to synthesize C_{60} and C_{70} fullerenes in macroscopic quantities, intensive studies of their chemical properties began. One of the first chemical compounds of these fullerenes were compounds with halogens [4,5]. In particular, quite a lot of research was devoted to the study of the properties of fluorides, chlorides and bromides of fullerene C_{70} [6–8]. The increased interest in fullerene halides is due to the fact that they have a number of properties that are valuable for practical purposes. For example, $C_{50}Cl_{10}$ is a promising material for nonlinear optics, since this compound has a fairly high static polarizability and a second hyperpolarizability [9]. It should also be noted that halogenated fullerenes are promising as multifunctional additives to petroleum products that can simultaneously improve their antioxidant and anti-wear performance characteristics [10]. In addition, fullerene halides are important compounds that are used to produce a wide variety of materials. To design new materials based on fullerene halides, knowledge of the chemical and physical properties of these compounds is necessary.

It should be noted that fullerene C_{70} halides are the easiest to obtain bromides of this fullerene. For instance, the interaction of fullerene C_{70} with liquid bromine, which occurs at room temperature, produces monosolvated bromide $C_{70}Br_{10}*Br_2$, heating of which to $70°C$ leads to the formation of fullerene bromide $C_{70}Br_{10}$, the yield of which is approximately 91% [11].
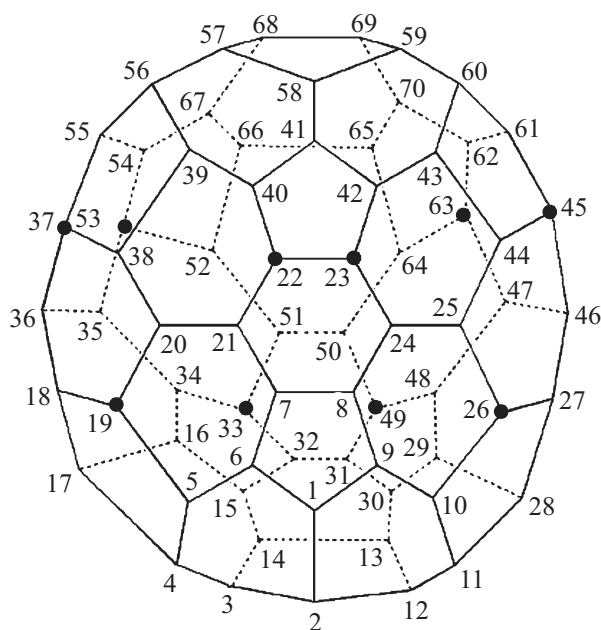
Figure 1. Molecule C$_{70}$Br$_{10}$ with symmetry group C_s indicating carbon atoms, as well as carbon atoms to which bromine atoms are bonded [1].
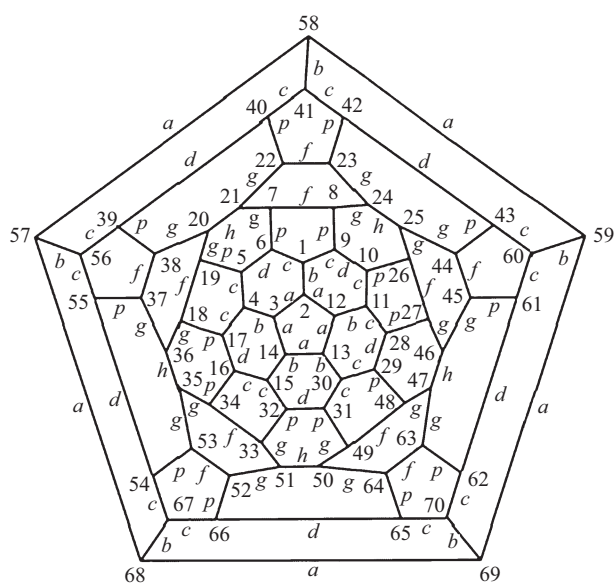

Figure 2. Schlegel Fullerene diagram of C$_{70}$ indicating the position of the carbon atoms and the bonds between the carbon atoms[1].

The conducted studies [12] have shown that the molecule C$_{70}$Br$_{10}$ has a symmetry of Cs, and the bromine atoms are associated with those carbon atoms that, as can be seen from Fig. 1, they are located in the equatorial area of fullerene C$_{70}$. From the Schlegel diagram for the molecule C$_{70}$Br$_{10}$, shown in Fig. 3 [1], it can be seen that bromine atoms are bound to carbon atoms that belong to the G$_4$ set, and in each hexagon, which consists of four atoms

belonging to the G$_4$ set and two atoms belonging to the G$_5$ set, contains two carbon atoms bound to bromine atoms.

The Hubbard model [13] is widely used to describe the electronic properties of nanosystems consisting of carbon atoms. As part of this model, in the mean field approximation, the energy and optical absorption spectra of fullerene C$_{80}$ with symmetry group I_h [14], fullerene C$_{70}$ [15], fullerene C$_{60}$ [16], fullerene C$_{50}$ [15] and fullerene chloride C$_{50}$Cl$_{10}$ with symmetry group D_{5h} [17], fullerene C$_{36}$ with symmetry group D_{6h} [18], fullerene C$_{28}$ with symmetry groupT_d [19], fullerene C$_{26}$ with symmetry group D_{3h} [20], fullerene C$_{24}$ with symmetry groups O_h, D_6 and D_{6d} [21] and fullerene C$_{20}$ with symmetry groups I_h, D_{5d} and D_{3d} [22], while the paper [23] studied the electronic properties of carbon nanotubes. The results obtained in [15–17] agree fairly well with experimental data.

The objective of this paper is to study the energy spectrum of fullerene bromide C$_{70}$Br$_{10}$ as part of the Hubbard model in the mean field approximation.

Energy spectrum of fullerene bromide C$_{70}$Br$_{10}$

As is known, the electronic properties of fullerenes and nanotubes consisting of carbon atoms depend mainly on the behavior of π electrons in these nanosystems. To describe the behavior of π electrons in fullerene bromide C$_{70}$Br$_{10}$, we use the Hubbard model [13], the Hamiltonian of which has the following form:

$$H = \sum_{\sigma, i} \varepsilon_i n_{i\sigma} + \sum_{\sigma, i \neq j} t_{ij} c_{i\sigma}^+ c_{j\sigma} + \frac{1}{2} \sum_{\sigma, i} U_i n_{i\sigma} n_{i\bar{\sigma}}, \quad (1)$$

where $c_{i\sigma}^+$, $c_{i\sigma}$ — operators for the creation and annihilation of electrons with spin σ at the i site; $n_{i\sigma}$ — number operator for particles with spin σ at i site; ε_i — energy of one-electron atomic state at the i site; t_{ij} — transfer integral describing electron jumps from the i site to the j site; U_i — Coulomb repulsion energy of two electrons located at the i-th site; $\bar{\sigma} = -\sigma$.

As it is known, the exact solution for the Hubbard model has been obtained for a limited number of systems, for example, for the one-dimensional model [24], for the dimer [25], for the dimer in the extended Hubbard model [26]. In studying the electronic properties of various physical systems as part of the Hubbard model, various approximate methods are used [27]. Among the approximate methods used in the study of physical systems in the framework of the Hubbard model, the mean field approximation is widely used. As part of this approximation, as it is well known [27], the following change should be made in the Hamiltonian (1):

$$n_{i\sigma} n_{i\bar{\sigma}} \rightarrow n_{i\sigma} \langle n_{i\bar{\sigma}} \rangle + n_{i\bar{\sigma}} \langle n_{i\sigma} \rangle, \quad (2)$$

where $\langle n_{i\sigma} \rangle$ — average number of electrons with spin σ located at the i site.

Substituting (2) into Hamiltonian (1), we will obtain the Hamiltonian of the Hubbard model in the mean field approximation:

$$H = \sum_{\sigma,i} \varepsilon'_{i\sigma} n_{i\sigma} + \sum_{\sigma,i\neq j} t_{ij} c^+_{i\sigma} c_{j\sigma}, \qquad (3)$$

where

$$\varepsilon'_{i\sigma} = \varepsilon_i + U\langle n_{\bar{\sigma}}\rangle. \qquad (4)$$

In order to find the energy spectrum of fullerene bromide $C_{70}Br_{10}$, we use the method of anticommutator Green's functions [28], which have the following form:

$$G_{f\sigma}(\tau) = \langle\langle c^+_{f\sigma} | c_{f\sigma}\rangle\rangle = \theta(\tau)\langle[c^+_{f\sigma}(\tau), c_{f\sigma}(0)]_+\rangle. \quad (5)$$

As known, the energy spectrum of the quantum system is determined by Fourier transforms of anticommutator Green functions, which, in the mean-field approximation, refer to the following [15,16]:

$$\langle\langle c^+_{f\sigma} | c_{f\sigma}\rangle\rangle_E = \frac{i}{2\pi}\sum_{m=1}^p \frac{Q_{j,m}}{E - E_m + ih}, \quad E_m = \varepsilon' + e_m, \tag{6}$$

where p — number of energy states of the quantum system, E_m — energy of the m-th state of the quantum system, e_m — energy of the m-th state of the quantum system relative to ε', $Q_{j,m}$ — spectral density of the m-th energy state, knowing which the degree of degeneracy of each energy level [15,16] can be found:

$$g_i = \sum_{j=1}^N Q_{j,i}, \qquad (7)$$

where g_i — degree of degeneracy of the i-th energy level, N — number of nanosystem sites.

Let us find the creation operators $c^+_{f\sigma}(\tau)$, which are included in the Green's functions (5). To do this, for all creation operators $c^+_{f\sigma}(\tau)$, which are given in the Heisenberg representation, we write down the equations of motion:

$$\frac{dc^+_{f\sigma}(\tau)}{d\tau} = [H, c^+_{f\sigma}(\tau)], \qquad (8)$$

where $f = 1, \ldots, N$; $\tau = it$; t — time; i — imaginary unit.

Substituting the Hamiltonian (3) into the equations of motion (8) and using the Schlegel diagram in Fig. 3, we will obtain a closed system of differential equations:

$$\begin{cases} \frac{dc^+_{1\sigma}}{d\tau} = \varepsilon'_\sigma c^+_{1\sigma} + t_c c^+_{2\sigma} + t_g(c^+_{6\sigma} + c^+_{9\sigma}), \\ \cdots \\ \frac{dc^+_{70\sigma}}{d\tau} = \varepsilon'_\sigma c^+_{70\sigma} + t_j c^+_{65\sigma} + t_i c^+_{62\sigma} + t_b c^+_{69\sigma}). \end{cases} \tag{9}$$

Before solving the system of equations (9), we find the numerical values of all the parameters that are included in it. In order to find the numerical values of the transfer integrals that enter into (9) and correspond to the molecule $C_{70}Br_{10}$, we use the following relation [14,15]:

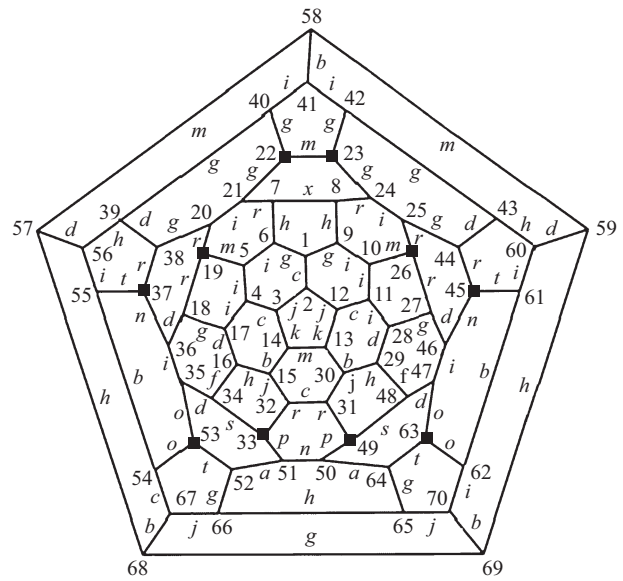$$t_s = -8957.33\exp(-6.0207 x_s). \qquad (10)$$

Figure 3. Schlegel diagram of fullerene bromide $C_{70}Br_{10}$ showing the positions of carbon atoms, bonds between carbon atoms and carbon atoms to which bromine atoms are bonded [1].

The conducted x-ray diffraction studies have shown [12] that in fullerene bromide $C_{70}Br_{10}$ the distances between carbon atoms have the following values:

$$x_a = 1.37(2)\,\text{Å}, \quad x_b = 1.38(2)\,\text{Å}, \quad x_c = 1.39(2)\,\text{Å},$$

$$x_d = 1.40(2)\,\text{Å}, \quad x_f = 1.41(2)\,\text{Å},$$

$$x_g = 1.42(2)\,\text{Å}, \quad x_h = 1.43(2)\,\text{Å}, \quad x_i = 1.44(2)\,\text{Å},$$

$$x_j = 1.45(2)\,\text{Å}, \quad x_k = 1.46(2)\,\text{Å},$$

$$x_m = 1.48(2)\,\text{Å}, \quad x_n = 1.49(2)\,\text{Å}, \quad x_o = 1.50(2)\,\text{Å},$$

$$x_p = 1.51(2)\,\text{Å}, \quad x_r = 1.52(2)\,\text{Å},$$

$$x_s = 1.53(2)\,\text{Å}, \quad x_t = 1.54(2)\,\text{Å}, \quad x_x = 1.59(2)\,\text{Å}, \quad (11)$$

Thus, from relations (10) and (11) it follows that for fullerene bromide $C_{70}Br_{10}$ with symmetry group C_s the transfer integrals have the following values:

$$t_a = -2.20714\,\text{eV}, \quad t_b = -2.07817\,\text{eV}, \quad t_c = -1.95675\,\text{eV},$$

$$t_d = -1.84241\,\text{eV}, \quad t_f = -1.73476\,\text{eV},$$

$$t_g = -1.63340\,\text{eV}, \quad t_h = -1.53796\,\text{eV}, \quad t_i = -1.44810\,\text{eV},$$

$$t_j = -1.36348\,\text{eV}, \quad t_k = -1.28381\,\text{eV},$$

$$t_m = -1.13817\,\text{eV}, \quad t_n = -1.07167\,\text{eV}, \quad t_o = -1.00905\,\text{eV},$$

$$t_p = -0.95009\,\text{eV}, \quad t_r = -0.89458\,\text{eV},$$

$$t_s = -0.84231\,\text{eV}, \quad t_t = -0.79309\,\text{eV}, \quad t_x = -0.58693\,\text{eV}. \tag{12}$$

In order to find the numerical value of the energy ε', we note that the process of formation of this molecule can be described as follows. When a molecule $C_{70}Br_{10}$ is formed, ten valence electrons of the fullerene C_{70} and one valence

electron each at bromine atoms pair and form strong bonds between carbon and bromine atoms. Then, as follows from relation (4), the energy ε' is defined as follows:

$$\varepsilon' = \begin{cases} \varepsilon'_{C_n}, & \text{for } C_n, \\ \varepsilon'_{C_n} - qU/n, & \text{for } C_n^{+q}X_k^{(-q)}, \end{cases} \quad (13)$$

where ε'_{C_n} — this ε' corresponds to the fullerene C_n; q — number of electrons transferred from fullerene C_n to k atoms X.

It follows from relation (13) that

$$\varepsilon'_{C_{70}Br_{10}} = \varepsilon'_{C_{70}} - \frac{qU}{n} = -4.979 - \frac{10 \cdot 5.662}{70} = -6.111 \, \text{eV},$$
$$(14)$$

where $U = 5.662$ eV [29], $\varepsilon' = -4.979$ eV [15].

Substituting the numerical values for the transfer integrals (12) and the energy ε' (14) into the system of differential equations (9) and solving the resulting system of equations, we obtain expressions for the creation operators $c_{f\sigma}^{+}(\tau)$. Since the expressions for creation operators are rather cumbersome (each birth operator contains $70 \times 70 = 4900$ terms), we do not present them here. As can be seen from Fig. 1, the structural elements of the considered fullerene are pentagons (pentagons) and hexagons (hexagons). The appendix contains a detailed solution for the pentagon. Now, using the expressions for the creation operators and relations (5) − (7), we obtain its energy spectrum for the molecule C$_{70}$Br$_{10}$. The calculation results are given in Table 1, as well as in Fig. 4. As can be seen from relation (6) and Fig.4, the energy levels of fullerene bromide C$_{70}$Br$_{10}$ with symmetry group C_s are concentrated near the energy $\varepsilon' = \varepsilon'_{C_{70}Br_{10}}$.

The energy states of the C$_{70}$Br$_{10}$ fullerene with the C_s symmetry group can be classified in accordance with the irreducible representations of this group, which has the following irreducible representations: a', a'' [30]. Table 1 and Fig. 4 show which irreducible representations of the C_s group are related to the energy states of fullerene bromide C$_{70}$Br$_{10}$. Note that in Fig. 4 the index $'$ corresponds to the irreducible representation a', and the index $''$ corresponds to the irreducible representation a''.

Thus, the results of these calculations showed that the energy spectrum of fullerene bromide C$_{70}$Br$_{10}$ with symmetry group C_s consists of 70 non-degenerate energy states. In the paper [15] the energy spectrum of fullerene C$_{70}$ with symmetry group D_{5h} was obtained, which is shown in Fig. 5. Comparing the energy spectra of fullerene C$_{70}$Br$_{10}$ bromide with symmetry group C_s and fullerene C$_{70}$ with symmetry group D_{5h}, which are presented in Fig. 4 and 5, we see that the symmetry reduction caused by the addition of bromine atoms to fullerene C$_{70}$, led to splitting of doubly degenerate energy states.

The optical absorption spectrum is an important characteristic of any molecule. Using the energy spectrum of fullerene bromide C$_{70}$Br$_{10}$ obtained above with the symmetry group C_s, it is possible, using group theory, to
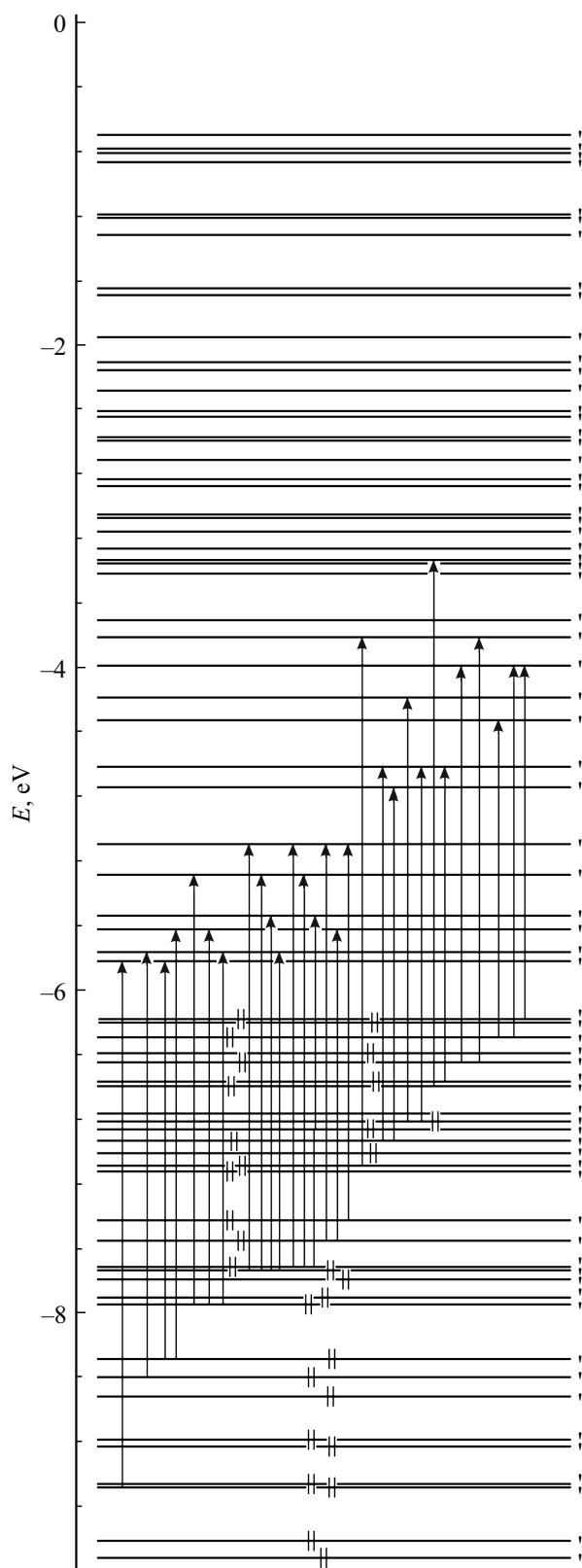

Figure 4. Energy spectrum of the molecule C$_{70}$Br$_{10}$.

find the transitions that determine the optical spectrum of this molecule. It can be shown that all transitions [30]

Table 1. Energy spectrum of the $C_{70}Br_{10}$ molecule with the C_s symmetry group: values of levels energy, multiplicity of their degeneration and irreducible representations of the C_s group, to which they belong

№	e_j, eV	E_j, eV	g_j	$E(\Gamma_j)$	№	e_j, eV	E_j, eV	g_j	$E(\Gamma_j)$
1	−4.535	−9.514	1	$E_1(a')$	36	−0.100	−5.080	1	$E_{36}(a'')$
2	−4.425	−9.405	1	$E_2(a')$	37	0.254	−4.725	1	$E_{37}(a'')$
3	−4.097	−9.077	1	$E_3(a'')$	38	0.381	−4.599	1	$E_{38}(a')$
4	−4.072	−9.052	1	$E_4(a')$	39	0.670	−4.309	1	$E_{39}(a')$
5	−3.837	−8.816	1	$E_5(a'')$	40	0.810	−4.169	1	$E_{40}(a'')$
6	−3.797	−8.776	1	$E_6(a')$	41	1.008	−3.972	1	$E_{41}(a')$
7	−3.529	−8.508	1	$E_7(a')$	42	1.183	−3.797	1	$E_{42}(a'')$
8	−3.407	−8.386	1	$E_8(a')$	43	1.289	−3.690	1	$E_{43}(a')$
9	−3.298	−8.277	1	$E_9(a'')$	44	1.580	−3.399	1	$E_{44}(a'')$
10	−2.956	−7.936	1	$E_{10}(a'')$	45	1.642	−3.337	1	$E_{45}(a'')$
11	−2.915	−7.895	1	$E_{11}(a')$	46	1.662	−3.317	1	$E_{46}(a')$
12	−2.802	−7.781	1	$E_{12}(a')$	47	1.736	−3.243	1	$E_{47}(a')$
13	−2.744	−7.723	1	$E_{13}(a')$	48	1.837	−3.143	1	$E_{48}(a'')$
14	−2.743	−7.722	1	$E_{14}(a'')$	49	1.923	−3.057	1	$E_{49}(a')$
15	−2.563	−7.543	1	$E_{15}(a'')$	50	1.948	−3.032	1	$E_{50}(a'')$
16	−2.433	−7.412	1	$E_{16}(a')$	51	2.124	2.855	1	$E_{51}(a')$
17	−2.134	−7.114	1	$E_{17}(a')$	52	2.163	−2.817	1	$E_{52}(a')$
18	−2.100	−7.080	1	$E_{18}(a'')$	53	2.281	−2.699	1	$E_{53}(a'')$
19	−2.020	−6.999	1	$E_{19}(a')$	54	2.405	−2.574	1	$E_{54}(a'')$
20	−1.940	−6.920	1	$E_{20}(a'')$	55	2.426	−2.553	1	$E_{55}(a')$
21	−1.874	−6.853	1	$E_{21}(a')$	56	2.552	−2.427	1	$E_{56}(a)$
22	−1.826	−6.805	1	$E_{22}(a'')$	57	2.584	−2.396	1	$E_{57}(a'')$
23	−1.771	−6.750	1	$E_{23}(a')$	58	2.714	−2.266	1	$E_{58}(a'')$
24	−1.603	−6.583	1	$E_{24}(a'')$	59	2.840	−2.139	1	$E_{59}(a'')$
25	−1.573	−6.552	1	$E_{25}(a')$	60	2.888	−2.091	1	$E_{60}(a')$
26	−1.459	−6.438	1	$E_{26}(a'')$	61	3.047	−1.932	1	$E_{61}(a'')$
27	−1.401	−6.381	1	$E_{27}(a'')$	62	3.308	−1.671	1	$E_{62}(a'')$
28	−1.297	−6.277	1	$E_{28}(a')$	63	3.351	−1.628	1	$E_{63}(a')$
29	−1.210	−6.190	1	$E_{29}(a'')$	64	3.683	−1.297	1	$E_{64}(a'')$
30	−1.202	−6.181	1	$E_{30}(a')$	65	3.789	−1.190	1	$E_{65}(a')$
31	−0.827	−5.807	1	$E_{31}(a')$	66	3.810	−1.169	1	$E_{66}(a'')$
32	−0.773	−5.753	1	$E_{32}(a'')$	67	4.132	−0.8472	1	$E_{67}(a')$
33	−0.632	−5.612	1	$E_{33}(a'')$	68	4.192	−0.788	1	$E_{68}(a')$
34	−0.544	−5.523	1	$E_{34}(a')$	69	4.217	−0.763	1	$E_{69}(a'')$
35	−0.289	−5.269	1	$E_{35}(a')$	70	4.300	−0.680	1	$E_{70}(a'')$

Table 2. Experimental and theoretical values of the wave lengths and energies which correspond to the absorption bands within the optical spectrum of the molecule $C_{70}Br_{10}$

Absorption bands	[31] λ, nm	[31] E, eV	Calculation E, eV
a	380	3.269	3.270
b	470	2.643	2.643
c	505	2.460	2.463
d	535	2.322	2.324
f	565	2.199	2.200
g	635	1.956	1.954

are allowed in the energy spectrum of a molecule with symmetry group C_s.

In the paper [31], experimental studies were carried out on the optical absorption spectrum of fullerene bromide $C_{70}Br_{10}$ in benzene, 1,2-dichlorobenzene, and 1,2-dimethylbenzene. The conducted studies have shown that in the optical absorption spectrum of fullerene bromide $C_{70}Br_{10}$, six absorption bands can be distinguished, as can be seen from Fig. 6 [1,31]: a, b, c, d, f, g, which are presented in Table 2. Knowing the energy spectrum of the $C_{70}Br_{10}$, molecule, its experimentally observed spectrum of optical absorption can be interpreted as follows. The bands of the optical absorption spectrum that correspond to the experimentally observed energies E_a, E_b, E_c, E_d, E_f, E_g presented in Table 2 can be interpreted as bands formed by transitions presented in Table 3. These transitions are also shown in Fig. 4. As can be seen from Table 4, the energies of these transitions are close to the experimental values [31].
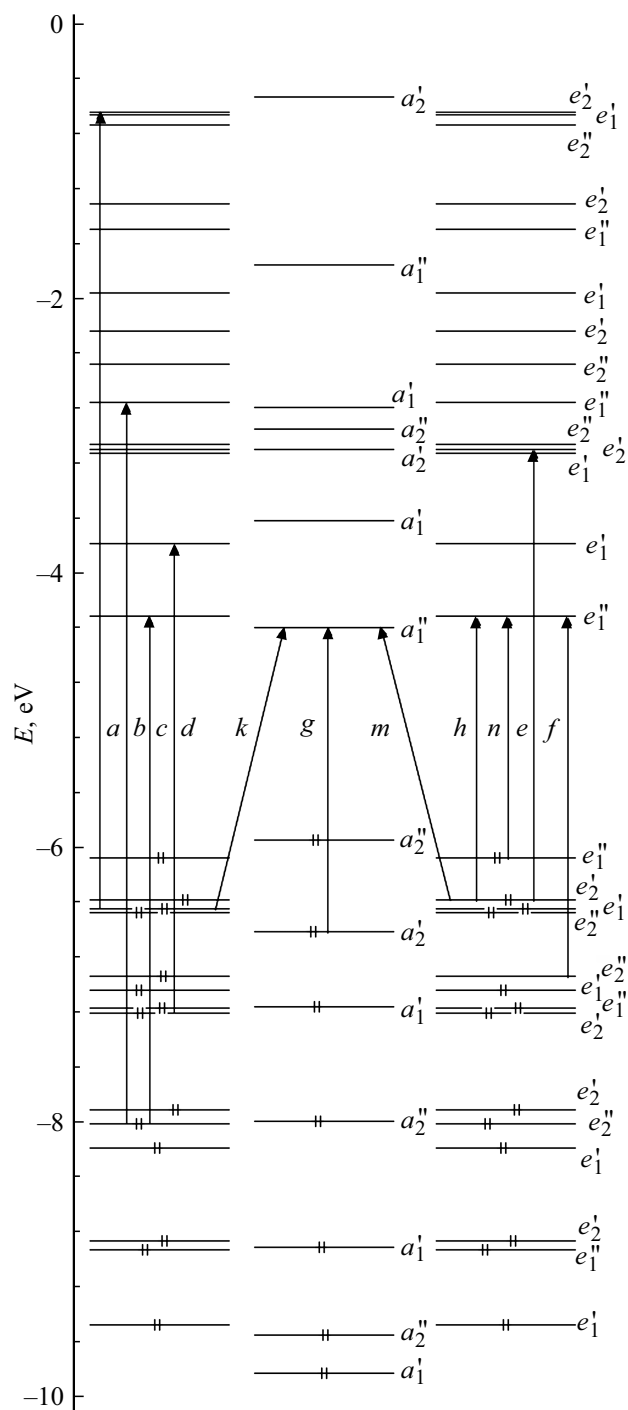
Figure 5. Energy spectrum of the molecule C_{70} [15].

Figure 6. Absorption spectrum of fullerene bromide $C_{70}Br_{10}$ in benzene (*1*), in 1,2-dichlorobenzene (*2*), in 1,2-dimethylbenzene (*3*) [1,31].

Table 3. Transitions forming absorption bands *a*, *b*, *c*, *d*, *f*, *g*

ΔE	ΔE, eV	ΔE	ΔE, eV	ΔE	ΔE, eV
a		*c*		*f*	
$E_{46}-E_{24}$	3.2653	$E_{35}-E_{14}$	2.4542	$E_{32}-E_{10}$ 2.1832	
$E_{31}-E_3$	3.2699	$E_{35}-E_{13}$	2.4546	$E_{37}-E_{20}$	2.1947
$E_{42}-E_{18}$	3.2829	$E_{36}-E_{15}$	2.4629	$E_{34}-E_{14}$	2.2000
b		$E_{41}-E_{26}$	2.4667	$E_{34}-E_{13}$	2.2004
$E_{32}-E_8$	2.6337	$E_{31}-E_9$	2.4703	$E_{38}-E_{22}$	2.2066
$E_{40}-E_{22}$	2.6361	*d*		$E_{41}-E_{30}$	2.2095
$E_{42}-E_{26}$	2.6417	$E_{41}-E_{28}$	2.3052	*g*	
$E_{36}-E_{14}$	2.6431	$E_{38}-E_{20}$	2.3209	$E_{33}-E_{15}$	1.9311
$E_{36}-E_{13}$	2.6435	$E_{33}-E_{10}$	2.3241	$E_{38}-E_{25}$	1.9536
$E_{33}-E_9$	2.6653	$E_{36}-E_{16}$	2.3326	$E_{39}-E_{28}$	1.9675
$E_{35}-E_{10}$	2.6670			$E_{32}-E_{14}$	1.9704
				$E_{32}-E_{13}$	1.9708

$Y_3N@C_{80}$ and fullerene chloride $C_{50}Cl_{10}$, carried out as part of the Hubbard model in the mean field approximation [20,19,18,14] showed good agreement between experimental data and theoretical results. This allows one to state that the Hubbard model in the mean field approximation field approximation characterizes fairly well the electron properties of carbon nanosystems.

Conclusions

Conducted research also demonstrated that optical absorption spectrum of the $C_{70}Br_{10}$ molecule, which is observed experimentally [31] is rather well agreed with the optical absorption spectrum obtained within the Hubbard model in the mean-field approximation.

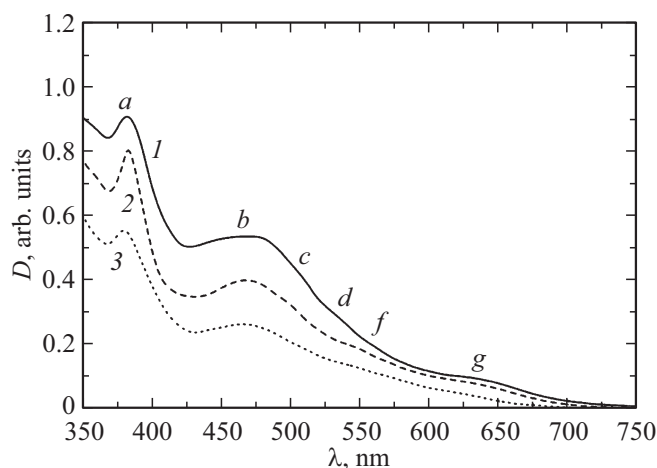We also note that studies of the optical properties of fullerenes C_{60} and C_{70}, as well as endofullerene

Appendix

Let us find, as part of the Hubbard model in the mean field approximation, the energy spectra of the pentagon and hexagon, which are shown in Fig. 7. Let us find the creation operators $c_{f\sigma}^{+}(\tau)$, which are included in the Green's functions (5). Substituting the Hamiltonian (3) into the equations of motion (8) and using Fig. 7, in the case of a pentagon, we obtain a closed system of differential
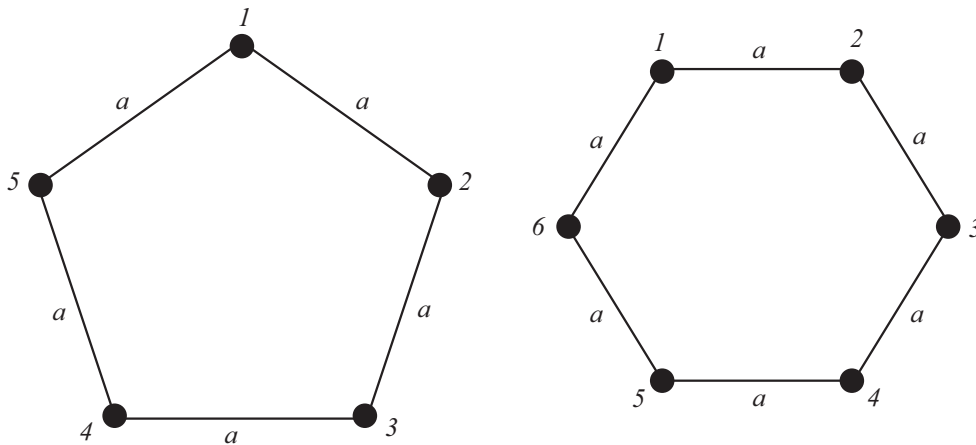
Figure 7. Pentagon and hexagon — structural elements of fullerene.

equations

$$\frac{dc_{1\sigma}^+(\tau)}{d\tau} = \varepsilon' c_{1\sigma}^+(\tau) + t_a(c_{2\sigma}^+(\tau) + c_{5\sigma}^+(\tau)),$$

$$\frac{dc_{2\sigma}^+(\tau)}{d\tau} = \varepsilon' c_{2\sigma}^+(\tau) + t_a(c_{1\sigma}^+(\tau) + c_{3\sigma}^+(\tau)),$$

$$\frac{dc_{3\sigma}^+(\tau)}{d\tau} = \varepsilon' c_{3\sigma}^+(\tau) + t_a(c_{2\sigma}^+(\tau) + c_{4\sigma}^+(\tau)), \qquad \text{(A1)}$$

$$\frac{dc_{4\sigma}^+(\tau)}{d\tau} = \varepsilon' c_{4\sigma}^+(\tau) + t_a(c_{3\sigma}^+(\tau) + c_{5\sigma}^+(\tau)),$$

$$\frac{dc_{5\sigma}^+(\tau)}{d\tau} = \varepsilon' c_{5\sigma}^+(\tau) + t_a(c_{1\sigma}^+(\tau) + c_{4\sigma}^+(\tau)).$$

Using the methods of operational calculus [32,33], we will solve the system of differential equations (A1). To do this, in the system of equations (A1) we will make the following replacement:

$$\frac{d}{d\tau} \to p,$$
$$x(\tau) \to x(p), \qquad \text{(A2)}$$
$$y(\tau) \to y(p),$$

where p — parameter.

Substituting (A2) into (A1), we obtain a system of algebraic equations:

$$pc_{1\sigma}^+(p) - c_{1\sigma}^+(0) = \varepsilon' c_{1\sigma}^+(p) + t_a(c_{2\sigma}^+(p) + c_{5\sigma}^+(p)),$$

$$pc_{2\sigma}^+(p) - c_{2\sigma}^+(0) = \varepsilon' c_{2\sigma}^+(p) + t_a(c_{1\sigma}^+(p) + c_{3\sigma}^+(p)),$$

$$pc_{3\sigma}^+(p) - c_{3\sigma}^+(0) = \varepsilon' c_{3\sigma}^+(p) + t_a(c_{2\sigma}^+(p) + c_{4\sigma}^+(p)),$$

$$pc_{4\sigma}^+(p) - c_{4\sigma}^+(0) = \varepsilon' c_{4\sigma}^+(p) + t_a(c_{3\tau}^+(p) + c_{5\sigma}^+(p)),$$

$$pc_{5\sigma}^+(p) - c_{5\sigma}^+(0) = \varepsilon' c_{5\sigma}^+(p) + t_a(c_{1\tau}^+(p) + c_{4\sigma}^+(p)).$$
$$\text{(A3)}$$

Using Cramer's method [34], we find the solution of the system of equations (A3), which is a system of algebraic

equations for the unknowns $c_{1\sigma}^+(p)$, $c_{2\sigma}^+(p)$, $c_{3\sigma}^+(p)$, $c_{4\sigma}^+(p)$, $c_{5\sigma}^+(p)$:

$$c_{1\sigma}^+(p) = [((p-\varepsilon')^2 + t_a(\varepsilon' - t_a - p))c_{1\sigma}(p)$$
$$+ t_a(p - t_a - \varepsilon')(c_{2\sigma}^+(p) + c_{5\sigma}^+(p))$$
$$+ t_a^2(c_{3\sigma}'(p) + c_{4\sigma}^+(p))] : [(p - 2t_a - \varepsilon')$$
$$\times ((p-\varepsilon')^2 + t_a(p - \varepsilon' - t_a))]. \qquad \text{(A4)}$$

Making a cyclic permutation of indices $1 \to 2 \to 3 \to 4 \to 5 \to 1$ in equation (A4), we obtain the remaining operators $c_{2\sigma}^+(p)$, $c_{3\sigma}^+(p)$, $c_{4\sigma}^+(p)$, $c_{5\sigma}^+(p)$. Knowing these operators and using the inverse Laplace transform [35], we obtain expressions for the creation operators:

$$c_{1\sigma}^+(\tau) = \frac{1}{5}(c_{1\sigma}^+(0) + c_{2\sigma}^+(0) + c_{3\sigma}^+(0) + c_{5\sigma}^+(0))$$

$$\times \exp(E_1\tau) + \frac{1}{10}(4c_{1\sigma}^+(0) + (\sqrt{5}-1)(c_{2\tau}^+(0) + c_{5\sigma}^+(0))$$

$$- (\sqrt{5}+1)(c_{3\sigma}^+(0) + c_{4\sigma}^+(0))) \exp(E_2\tau)$$

$$+ \frac{1}{10}(4c_{1\sigma}^+(0) + (\sqrt{5}+1)(c_{3\tau}^+(0) + c_{5\sigma}^+(0))$$

$$+ (\sqrt{5}-1)(c_{2\sigma}^+(0) + c_{4\sigma}^+(0))) \exp(E_3\tau),$$
$$\text{(A5)}$$

where

$$E_1 = \varepsilon + 2t_a, \quad E_2 = \varepsilon + t_a(\sqrt{5}-1)/2,$$

$$E_3 = \varepsilon - t_c(1 + \sqrt{5})/2. \qquad \text{(A6)}$$

Making a cyclic permutation of indices $1 \to 2 \to 3 \to 4 \to 5 \to 1$ in equation (A5), we obtain the remaining operators $c_{2\sigma}^+(\tau)$, $c_{3\sigma}^+(\tau)$, $c_{4\sigma}^+(\tau)$, $c_{5\sigma}^+(\tau)$.

Substituting the creation operator (A5) into formula (5) and performing the Fourier transform, we obtain the Fourier

transform of the anticommutator Green's function:

$$\langle\langle c_{j\sigma}^{+}|c_{j\sigma}\rangle\rangle_{E} = \frac{i}{2\pi}\frac{1}{5}\left\{\frac{1}{E-E_{1}+ih}+\frac{2}{E-E_{2}+ih}\right.$$

$$\left.+\frac{2}{E-E_{3}+ih}\right\}, \quad j=1\ldots 5, \qquad (A7)$$

where expressions (A6) represent the energy spectrum of the pentagon, the energy states of which, according to relations (7), (6) and (A7), have the following degrees of degeneracy:

$$g_{1}=1, \quad g_{2}=g_{3}=2. \qquad (A8)$$

Similarly, the Fourier transform of the anticommutator Green's function and the energy spectrum for the hexagon can be obtained:

$$\langle\langle c_{j\sigma}^{+}|c_{j\sigma}\rangle\rangle_{E} = \frac{i}{2\pi}\frac{1}{6}\left\{\frac{1}{E-E_{1}+ih}+\frac{2}{E-E_{2}+ih}\right.$$

$$\left.+\frac{2}{E-E_{3}+ih}+\frac{1}{E-E_{4}+ih}\right\}, \qquad (A9)$$

$$E_{1}=\varepsilon+2t_{a}, \quad E_{2}=\varepsilon+t_{a},$$

$$E_{3}=\varepsilon-t_{a}, \quad E_{4}=\varepsilon-2t_{a}, \qquad (A10)$$

$$g_{1}=g_{4}=1. \quad g_{2}=g_{3}=2. \qquad (A11)$$

Let us note that (A5) shows that in case of a pentagon, each creation operator contains $5\times 3=15$ terms. Similarly, it can be shown that the production operators for fullerene bromide $C_{70}Br_{10}$ with the symmetry group C_{s} each contain $70\times 70=4900$ terms.

Conflict of interest

The author declares that he has no conflict of interest.

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