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Electronic Structure of Dimers Based on C₅₈ Fullerene Isomers as Structural Elements of Films on the Au Surface

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Within the framework of the Hubbard model, the energy spectra of the C_s and C_{3v} isomers of C₅₈ fullerene and dimers based on them are calculated. The obtained curves of the density of electronic states of these systems are compared with the experimental curves of the films, which were obtained by deposition of the C_s and C_{3v} isomers of C₅₈ fullerene on the (1,1,1) gold surface. A comparative analysis of the curves of the density of electronic states shows that in those sites through which a bond is formed between fullerenes, carbon is not in the *sp*², but in the *sp*³ hybridized state.

Keywords: fullerene, dimer, energy spectrum, Hubbard model, Hubbard subband, density of electronic states.

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1. Introduction

Carbon nanosystems, carbon nanotubes (CNT), and fullerenes, despite the fact that a quarter-century has passed from the time of their discovery, are still under the spotlight of researchers. The interest in them is connected with wide prospects of their application in various fields of science and technology. Surely this is a consequence of their unique electron structure. In these systems carbon is in *sp*² hybridized state. Three of four valence electrons of carbon in these systems are hybridized forming rigid σ -bonds. These bonds form a core, a frame of the system, while the fourth non-hybridized electron, remaining partly localized, forms π -bands. The boundary between unoccupied and occupied electron states in these compounds is in the region of π -band energies. Therefore, electronic and optical properties of fullerenes and CNTs are formed by states of exactly these electrons.

As shown in our studies of electron structure of fullerenes and CNTs [1–5], all these systems should be semiconductors by the type of their conductivity, with a gap that is the energy gap between the Hubbard subbands. As a consequence, depending on the doping in them or external environment, these systems may exhibit semiconductor or metal properties.

Carbon nanosystems, for example fullerenes, most commonly can be used not as separate objects, but as compounds bonded to each other, that, in particular, is observed in films formed on their basis on different substrates. It is evident that in this case different kinds of bonds arise between the fullerenes, that can significantly change the electron structure of the system. In this context, it is of interest to consider how the electron properties of fullerenes change depending on their bonds to each other.

Bearing this in mind, the goal of this work is to study the electron structure of isomers of the C₅₈ fullerene, not as separate objects, but as interconnected systems.

2. Model and method

In [1–5] we have shown, that the electron structure and optical properties of fullerenes and CNTs can be described correctly within the idea that in these compounds the parameter of effective Coulomb interaction of π -electrons is $U \sim 6\text{--}8\text{ eV}$ [6], and the transition integral of these electrons between neighboring sites is $B \sim 1\text{ eV}$. It is evident, that these systems with strong intrasite Coulomb interaction can be described correctly within the Hubbard model [7]:

$$H = \varepsilon \sum_{i,\sigma} \hat{n}_{i\sigma} + B \sum_{i,j,\sigma} (a_{i\sigma}^+ a_{j\sigma} + a_{j\sigma}^+ a_{i\sigma}) + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}. \quad (1)$$

Here $a_{i\sigma}^+, a_{i\sigma}$ — operators of creation and annihilation of π -electrons with spin σ in sites i , $\hat{n}_{i\sigma} = a_{i\sigma}^+ a_{i\sigma}$ — operator of particle number in site i with spin σ , ε — parameter that plays a role of electron energy in site i , B — transition integral, U — Coulomb integral. In (1) summation over i is performed over all sites of the system, and summation over j in the second term is performed over the sites that are neighboring to the site i . The second term in (1) describes electron transitions from one site to another, and the third term describes their Coulomb interaction on one site.

The Hubbard model is extremely complex in terms of obtaining calculation results, therefore, one or another approximation is used when working within this model. If we neglect the Kondo anomalies and other multiparticle effects, which is reasonable at room temperatures, then we

can use the so-called static fluctuation approximation (SFA) suggested in [8]. Within this approximation the Coulomb interaction of electrons on one site and their transition from one site to another is taken into account precisely. The processes of interference of these interactions are neglected.

In [9,10] we have shown within the framework of SFA, that in carbon nanosystems, CNTs, and fullerenes, due to the intrasite Coulomb interaction, the band of π -electrons is split into two „Hubbard“ subbands with a width of $W \approx 6$ V, and a distance of $\Delta \approx U - W$ between them.

3. The energy spectra of C_s and C_{3v} isomers of C₅₈ fullerene and dimers based on them. Comparison with experimental data

Recently a number of experimental studies were published devoted to the creation and studying of films made of fullerenes on the surface of precious metals. It is evident that the interest in these systems is caused by the prospects of creation of nanoelectronics hardware components on their basis. In [11], films were formed by depositing isomers of C₅₈ fullerenes on the surface of Au(111). The authors of [11] state that according to results of numerical simulation [12], films of C₅₈ fullerenes are formed on the surface of gold by C_{3v} and C_s isomers. The Schlegel diagrams of these isomers are shown in Fig. 1 and 2, according to [12] the isomers are deposited in such a way that these isomers contact the surface of Au(111) with the sites that are shown as unfilled circles, and are interconnected to each other via the sites shown black.

Topographic and electron characteristic of films in [11] were checked and measured using scanning tunnel microscopy (STM) at a temperature of ~ 4.2 K. Densities of electron states (DES) measured between different points of the obtained films are shown in Fig. 3. This figure shows DES curves for thick films with several (~ 5) layers composed by fullerenes.

According to our results reported in [1–5], the Coulomb interaction plays a significant role in forming electron properties of carbon nanosystems. In this work, within the Hubbard model in SFA, we calculated the energy spectra and DES values of C_{3v} and C_s isomers of C₅₈ fullerene as separate objects, not connected to each other. We carried out our calculations within the framework of (SFA) (see [9] for the detailed description of the calculation method). The energy spectra of C_s and C_{3v} isomers of C₅₈ fullerene at the Hubbard model parameters of $B = -1.0$ and $U = 7.0$ eV are presented in Tables 1 and 2. In these tables energy levels with negative energies correspond to occupied states, and positive energies correspond to unoccupied states. It can be seen from Table 1 that the energy spectrum of the C_s isomer of C₅₈ fullerene is composed of 106 levels, two of which have degeneracy order equal to six, other levels are nondegenerated. The width of the occupied band is equal to $W \approx 5.62$ eV. The unoccupied band has the

Table 1. The energy spectrum of C₅₈ (C_s) fullerene at the following parameters of the Hubbard model: $U = 7.0$ eV, $B = -1.0$ eV

1.0, -6.4000	1.0, -3.1313	1.0, 0.6000	1.0, 3.8687
1.0, -6.1732	1.0, -3.0180	1.0, 0.8268	1.0, 3.9820
1.0, -6.1412	1.0, -2.7725	1.0, 0.8588	1.0, 4.2275
1.0, -6.1346	1.0, -2.4000	1.0, 0.8654	1.0, 4.6000
1.0, -5.7467	1.0, -2.0972	1.0, 1.2533	1.0, 4.9028
1.0, -5.7028	1.0, -2.0762	1.0, 1.2972	1.0, 4.9238
1.0, -5.6908	1.0, -2.0360	1.0, 1.3092	1.0, 4.9640
1.0, -5.6464	1.0, -2.0297	1.0, 1.3536	1.0, 4.9703
1.0, -5.6123	1.0, -2.0153	1.0, 1.3877	1.0, 4.9847
1.0, -5.2135	1.0, -1.8795	1.0, 1.7865	1.0, 5.1205
1.0, -5.1988	1.0, -1.8790	1.0, 1.8012	1.0, 5.1210
1.0, -5.0587	1.0, -1.8602	1.0, 1.9413	1.0, 5.1398
1.0, -4.9936	1.0, -1.7820	1.0, 2.0064	1.0, 5.2180
1.0, -4.9598	1.0, -1.6677	1.0, 2.0402	1.0, 5.3323
1.0, -4.9511	1.0, -1.6132	1.0, 2.0489	1.0, 5.3868
1.0, -4.8316	1.0, -1.5438	1.0, 2.1684	1.0, 5.4562
6.0, -4.4000	1.0, -1.4824	6.0, 2.6000	1.0, 5.5176
1.0, -4.2816	1.0, -1.2872	1.0, 2.7184	1.0, 5.7128
1.0, -4.2778	1.0, -1.2649	1.0, 2.7222	1.0, 5.7351
1.0, -4.1749	1.0, -1.0735	1.0, 2.8251	1.0, 5.9265
1.0, -4.0180	1.0, -0.8958	1.0, 2.9820	1.0, 6.1042
1.0, -3.9872	1.0, -0.8255	1.0, 3.0128	1.0, 6.1745
1.0, -3.9831	1.0, -0.8141	1.0, 3.0169	1.0, 6.1859
1.0, -3.8277	1.0, -0.8042	1.0, 3.1723	1.0, 6.1958
1.0, -3.5683	1.0, -0.7822	1.0, 3.4317	1.0, 6.2178
1.0, -3.2233	1.0, -0.7820	1.0, 3.7767	1.0, 6.2180
1.0, -3.1894		1.0, 3.8106	

Table 2. The energy spectrum of C₅₈ (C_{3v}) fullerene at the following parameters of the Hubbard model: $U = 7.0$ eV, $B = -1.0$ eV

1.0, -6.4000	2.0, -3.1386	1.0, 0.6000	2.0, 3.8614
2.0, -6.1549	1.0, -2.9284	2.0, 0.8451	1.0, 4.0716
1.0, -6.1366	3.0, -2.4000	1.0, 0.8634	3.0, 4.6000
2.0, -5.7234	1.0, -2.0529	2.0, 1.2766	1.0, 4.9471
2.0, -5.6520	2.0, -2.0298	2.0, 1.3480	2.0, 4.9702
1.0, -5.6441	2.0, -1.9823	1.0, 1.3559	2.0, 5.0177
1.0, -5.2146	2.0, -1.8623	1.0, 1.7854	2.0, 5.1377
2.0, -5.0895	1.0, -1.6822	2.0, 1.9105	1.0, 5.3178
2.0, -4.9935	1.0, -1.6238	2.0, 2.0065	1.0, 5.3762
1.0, -4.9477	2.0, -1.6061	1.0, 2.0523	2.0, 5.3939
1.0, -4.9061	2.0, -1.4731	1.0, 2.0939	2.0, 5.5269
6.0, -4.4000	1.0, -1.2472	6.0, 2.6000	1.0, 5.7528
1.0, -4.3249	1.0, -1.0443	1.0, 2.6751	1.0, 5.9557
2.0, -4.2212	2.0, -0.8925	2.0, 2.7788	2.0, 6.1075
2.0, -4.0036	1.0, -0.8064	2.0, 2.9964	1.0, 6.1936
1.0, -3.8633	2.0, -0.7887	1.0, 3.1367	2.0, 6.2113
2.0, -3.7884	1.0, -0.6826	2.0, 3.2116	1.0, 6.3174
1.0, -3.2950		1.0, 3.7050	

same width, the gap between them, known as HOMO-LUMO (Highest Occupied Molecular Orbital — Lowest Unoccupied Molecular Orbital), is equal to $\Delta \approx 1.38$ eV.

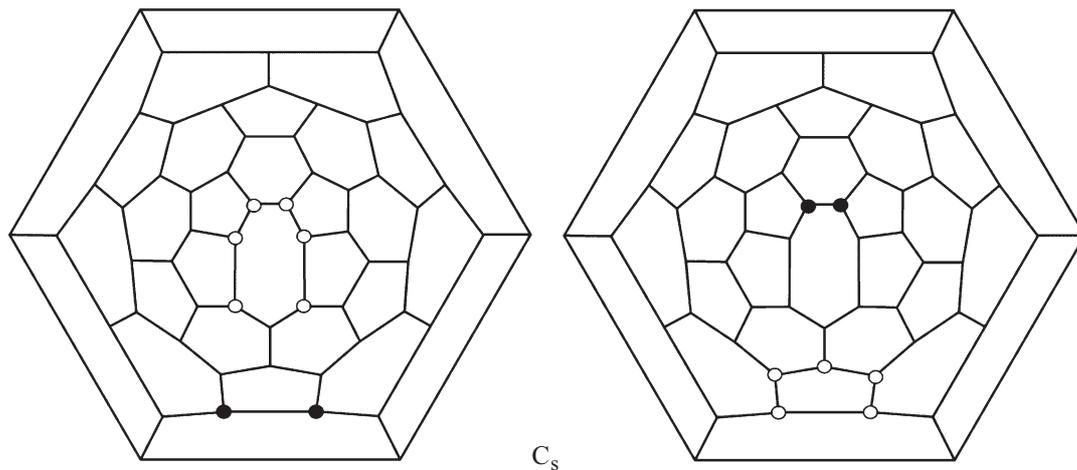


Figure 1. Schlegel diagram of C_s isomer of C_{58} fullerene with specified sites of their connection (shown with solid circles) and sites of contact with substrate surface (shown with unfilled circles).

Table 3. The energy spectrum of $C_{58}-C_{58}$ (C_s) fullerene at the following parameters of the Hubbard model: $U = 7.0$ eV, $B = -1.0$ eV

1.0, -6.5320	1.0, -4.3244	1.0, -2.0196	1.0, 0.4680	1.0, 2.6756	1.0, 4.9804
1.0, -6.3824	1.0, -4.2914	1.0, -2.0055	1.0, 0.6176	1.0, 2.7086	1.0, 4.9945
1.0, -6.2824	1.0, -4.2902	1.0, -1.9970	1.0, 0.7176	1.0, 2.7098	1.0, 5.0030
1.0, -6.1806	1.0, -4.2687	1.0, -1.9148	1.0, 0.8194	1.0, 2.7313	1.0, 5.0852
1.0, -6.1697	1.0, -4.2567	1.0, -1.8809	1.0, 0.8303	1.0, 2.7433	1.0, 5.1191
1.0, -6.1383	1.0, -4.1790	1.0, -1.8690	1.0, 0.8617	1.0, 2.8210	1.0, 5.1310
1.0, -6.1346	1.0, -4.0794	1.0, -1.8656	1.0, 0.8654	1.0, 2.9206	1.0, 5.1344
1.0, -6.0804	1.0, -4.0710	1.0, -1.8602	1.0, 0.9196	1.0, 2.9290	1.0, 5.1398
1.0, -5.8412	1.0, -4.0044	1.0, -1.8547	1.0, 1.1588	1.0, 2.9956	1.0, 5.1453
1.0, -5.7615	1.0, -3.9889	1.0, -1.8109	1.0, 1.2385	1.0, 3.0111	1.0, 5.1891
1.0, -5.7458	1.0, -3.9835	1.0, -1.7532	1.0, 1.2542	1.0, 3.0165	1.0, 5.2468
1.0, -5.7052	1.0, -3.9506	1.0, -1.6797	1.0, 1.2948	1.0, 3.0494	1.0, 5.3203
1.0, -5.6968	1.0, -3.9455	1.0, -1.6360	1.0, 1.3032	1.0, 3.0545	1.0, 5.3640
1.0, -5.6808	1.0, -3.8322	1.0, -1.6330	1.0, 1.3192	1.0, 3.1678	1.0, 5.3670
1.0, -5.6525	1.0, -3.8223	1.0, -1.5690	1.0, 1.3475	1.0, 3.1777	1.0, 5.4310
1.0, -5.6355	1.0, -3.5686	1.0, -1.5687	1.0, 1.3645	1.0, 3.4314	1.0, 5.4313
1.0, -5.6148	1.0, -3.5497	1.0, -1.5052	1.0, 1.3852	1.0, 3.4503	1.0, 5.4948
1.0, -5.5492	1.0, -3.2466	1.0, -1.4862	1.0, 1.4508	1.0, 3.7534	1.0, 5.5138
1.0, -5.2670	1.0, -3.2306	1.0, -1.4622	1.0, 1.7330	1.0, 3.7694	1.0, 5.5378
1.0, -5.2371	1.0, -3.1927	1.0, -1.2922	1.0, 1.7629	1.0, 3.8073	1.0, 5.7078
1.0, -5.2005	1.0, -3.1723	2.0, -1.2715	1.0, 1.7995	1.0, 3.8277	2.0, 5.7285
1.0, -5.1912	1.0, -3.1353	1.0, -1.2464	1.0, 1.8088	1.0, 3.8647	1.0, 5.7536
1.0, -5.1218	1.0, -3.0933	1.0, -1.1361	1.0, 1.8782	1.0, 3.9067	1.0, 5.8639
1.0, -5.0468	1.0, -3.0736	1.0, -1.0155	1.0, 1.9532	1.0, 3.9264	1.0, 5.9845
1.0, -4.9979	1.0, -2.9872	1.0, -0.8979	1.0, 2.0021	1.0, 4.0128	1.0, 6.1021
1.0, -4.9935	1.0, -2.8381	1.0, -0.8918	1.0, 2.0065	1.0, 4.1619	1.0, 6.1082
1.0, -4.9784	1.0, -2.7294	1.0, -0.8795	1.0, 2.0216	1.0, 4.2706	1.0, 6.1205
1.0, -4.9624	1.0, -2.4269	1.0, -0.8142	1.0, 2.0376	1.0, 4.5731	1.0, 6.1858
1.0, -4.9484	1.0, -2.3547	1.0, -0.8129	1.0, 2.0516	1.0, 4.6453	1.0, 6.1871
1.0, -4.9165	1.0, -2.1980	1.0, -0.8071	1.0, 2.0835	1.0, 4.8020	1.0, 6.1929
1.0, -4.8594	1.0, -2.1162	1.0, -0.8061	1.0, 2.1406	1.0, 4.8838	1.0, 6.1939
1.0, -4.7705	1.0, -2.0779	1.0, -0.7955	1.0, 2.2295	1.0, 4.9221	1.0, 6.2045
1.0, -4.5274	1.0, -2.0565	1.0, -0.7885	1.0, 2.4726	1.0, 4.9435	1.0, 6.2115
1.0, -4.5107	1.0, -2.0380	1.0, -0.7857	1.0, 2.4893	1.0, 4.9620	1.0, 6.2143
8.0, -4.4000	1.0, -2.0304	1.0, -0.7700	8.0, 2.6000	1.0, 4.9696	1.0, 6.2300
1.0, -4.3526	1.0, -2.0298	1.0, -0.4459	1.0, 2.6474	1.0, 4.9702	1.0, 6.5541

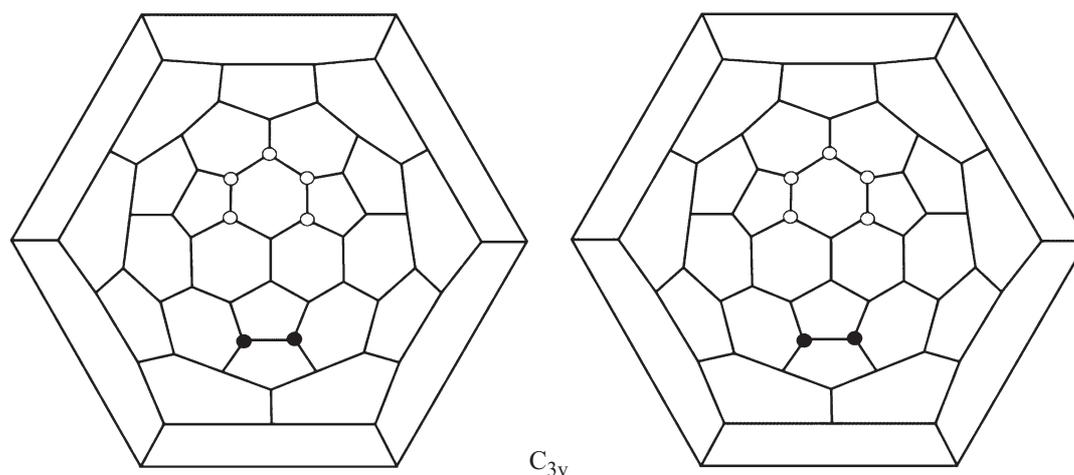


Figure 2. Schlegel diagram of C_{3v} isomer of C_{58} fullerene with specified sites of their connection (shown with solid circles) and sites of contact with substrate surface (shown with unfilled circles).

Table 4. The energy spectrum of $C_{58}-C_{58}$ (C_{3v}) fullerene at the following parameters of the Hubbard model: $U = 7.0$ eV, $B = -1.0$ eV

1.0, -6.5435	1.0, -4.3490	1.0, -2.0171	1.0, 0.4565	1.0, 2.6510	1.0, 4.9829
1.0, -6.3830	1.0, -4.3288	1.0, -1.9823	1.0, 0.6170	1.0, 2.6712	1.0, 5.0177
1.0, -6.2995	1.0, -4.2816	1.0, -1.9822	1.0, 0.7005	1.0, 2.7184	1.0, 5.0178
1.0, -6.1587	1.0, -4.2516	1.0, -1.9789	1.0, 0.8413	1.0, 2.7484	1.0, 5.0211
1.0, -6.1531	1.0, -4.2216	1.0, -1.9718	1.0, 0.8469	1.0, 2.7784	1.0, 5.0282
1.0, -6.1418	1.0, -4.2208	1.0, -1.8688	1.0, 0.8582	1.0, 2.7792	1.0, 5.1312
1.0, -6.1406	1.0, -4.1776	1.0, -1.8504	1.0, 0.8594	1.0, 2.8224	1.0, 5.1496
1.0, -6.0836	1.0, -4.0795	1.0, -1.7949	1.0, 0.9164	1.0, 2.9205	1.0, 5.2051
1.0, -5.8692	1.0, -4.0507	1.0, -1.7306	1.0, 1.1308	1.0, 2.9493	1.0, 5.2694
1.0, -5.7293	1.0, -3.9639	1.0, -1.6395	1.0, 1.2707	1.0, 3.0361	1.0, 5.3605
1.0, -5.7216	1.0, -3.9576	1.0, -1.6250	1.0, 1.2784	1.0, 3.0424	1.0, 5.3750
1.0, -5.6688	1.0, -3.8891	1.0, -1.6237	1.0, 1.3312	1.0, 3.1109	1.0, 5.3763
1.0, -5.6602	1.0, -3.8743	1.0, -1.6216	1.0, 1.3398	1.0, 3.1257	1.0, 5.3784
1.0, -5.6547	1.0, -3.8387	1.0, -1.6085	1.0, 1.3453	1.0, 3.1613	1.0, 5.3915
1.0, -5.6454	1.0, -3.8070	1.0, -1.6034	1.0, 1.3546	1.0, 3.1930	1.0, 5.3966
1.0, -5.6447	1.0, -3.7308	1.0, -1.5844	1.0, 1.3553	1.0, 3.2692	1.0, 5.4156
1.0, -5.6441	1.0, -3.5748	1.0, -1.5542	1.0, 1.3559	1.0, 3.4252	1.0, 5.4458
1.0, -5.6011	1.0, -3.3288	1.0, -1.4926	1.0, 1.3989	1.0, 3.6712	1.0, 5.5074
1.0, -5.2846	1.0, -3.2028	1.0, -1.4224	1.0, 1.7154	1.0, 3.7972	1.0, 5.5776
1.0, -5.1724	1.0, -3.1446	1.0, -1.3924	1.0, 1.8276	1.0, 3.8554	1.0, 5.6076
1.0, -5.1129	1.0, -3.1443	1.0, -1.3161	1.0, 1.8871	1.0, 3.8557	1.0, 5.6839
1.0, -5.0932	1.0, -3.1345	1.0, -1.0905	1.0, 1.9068	1.0, 3.8655	1.0, 5.9095
1.0, -5.0874	1.0, -3.0938	1.0, -1.0444	1.0, 1.9126	1.0, 3.9062	1.0, 5.9556
1.0, -5.0865	1.0, -2.9468	1.0, -1.0441	1.0, 1.9135	1.0, 4.0532	1.0, 5.9559
1.0, -5.0457	1.0, -2.9166	1.0, -0.9547	1.0, 1.9543	1.0, 4.0834	1.0, 6.0453
1.0, -5.0429	1.0, -2.4532	1.0, -0.8931	1.0, 1.9571	1.0, 4.5468	1.0, 6.1069
1.0, -4.9853	1.0, -2.4177	1.0, -0.8918	1.0, 2.0147	1.0, 4.5823	1.0, 6.1082
1.0, -4.9704	2.0, -2.4000	1.0, -0.8105	1.0, 2.0296	2.0, 4.6000	1.0, 6.1895
1.0, -4.9542	1.0, -2.3822	1.0, -0.8076	1.0, 2.0458	1.0, 4.6178	1.0, 6.1924
1.0, -4.9226	1.0, -2.3678	1.0, -0.7996	1.0, 2.0774	1.0, 4.6322	1.0, 6.2004
1.0, -4.9185	1.0, -2.1195	1.0, -0.7981	1.0, 2.0815	1.0, 4.8805	1.0, 6.2019
1.0, -4.8738	1.0, -2.0650	1.0, -0.7931	1.0, 2.1262	1.0, 4.9350	1.0, 6.2069
1.0, -4.5387	1.0, -2.0409	1.0, -0.7727	1.0, 2.4613	1.0, 4.9591	1.0, 6.2273
1.0, -4.5240	1.0, -2.0322	1.0, -0.6926	1.0, 2.4760	1.0, 4.9678	1.0, 6.3074
8.0, -4.4000	1.0, -2.0295	1.0, -0.6578	8.0, 2.6000	1.0, 4.9705	1.0, 6.3422
1.0, -4.3722	1.0, -2.0286	1.0, -0.5140	1.0, 2.6278	1.0, 4.9714	1.0, 6.4860

The energy spectrum of C_{3v} isomer of C_{58} fullerene (Table 2) is composed of 70 levels, two of which are levels with six order degeneracy, two levels have three-order degeneracy, 32 levels have two-order degeneracy, other levels are nondegenerated. The width of the occupied

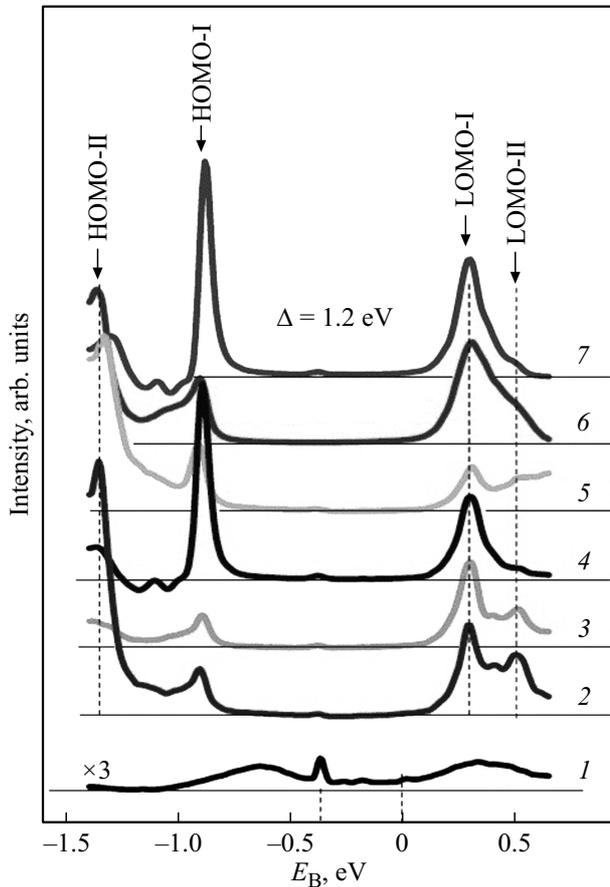


Figure 3. Densities of electron states of films synthesized in [11].

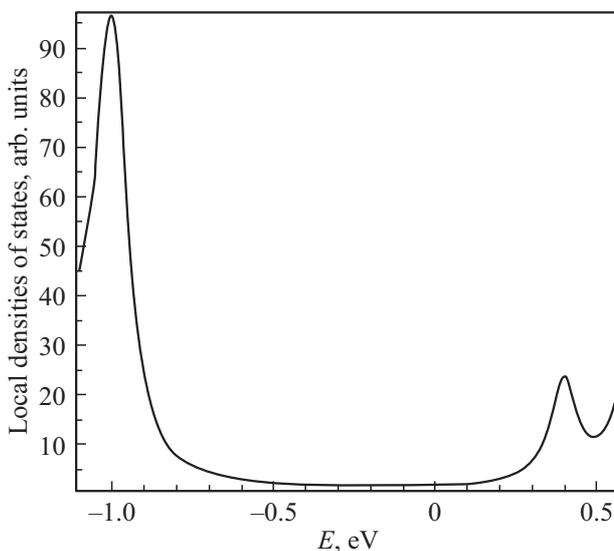


Figure 4. Density of electron states of C_s isomer of C_{58} fullerene.

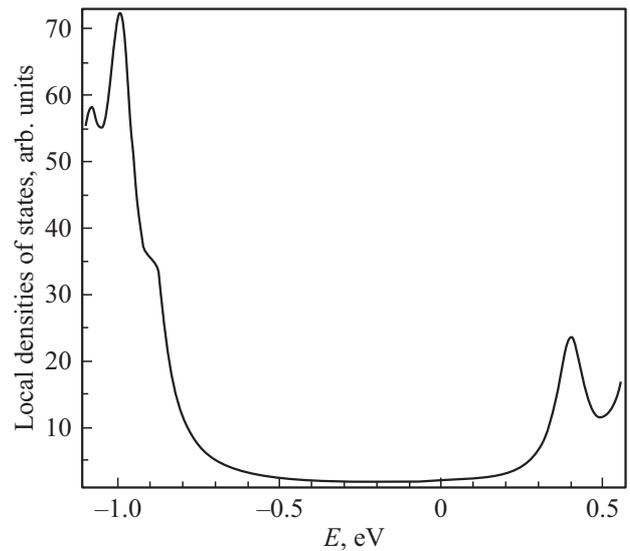


Figure 5. Density of electron states of C_{3v} isomer of C_{58} fullerene.

band is $W \approx 5.72$ eV. The unoccupied band has the same width, the gap between them, known as HOMO-LUMO, is $\Delta \approx 1.28$ eV.

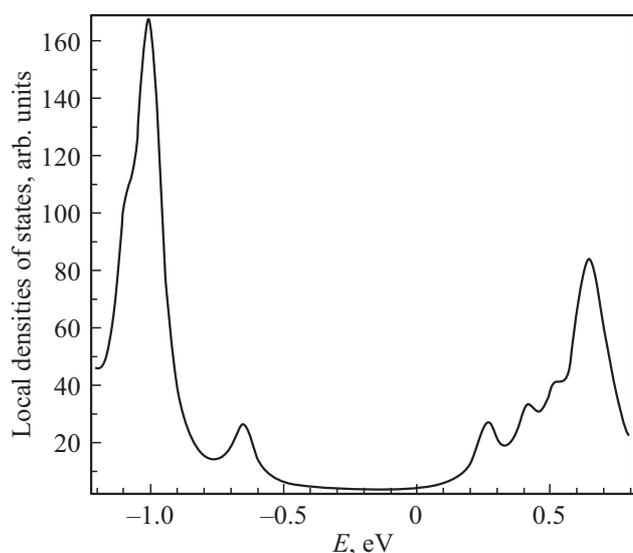
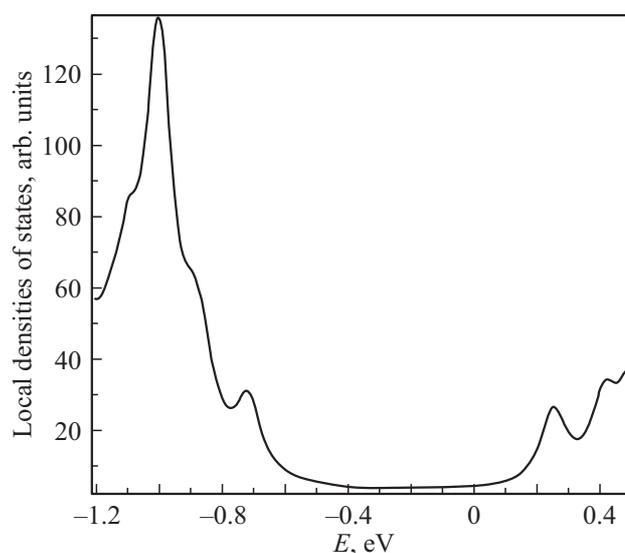
Densities of electron states of these isomers of C_{58} fullerene are shown in Fig. 3,4. Gaps on the curves of densities of electron states correspond to HOMO-LUMO gaps from Tables 1 and 2. These values are close to the experimental data reported in [11], which is indicative of the fact that electron properties of films are determined to a significant extent by the electron structure of the isolated fullerenes themselves. However, this gap anyway is 0.1–0.2 eV greater than that measured in [11]. This, to our opinion, dictates the need to take into account the effects attributable to the fact that fullerenes are bound to each other.

To take into account the effect of bond with the framework of our approximation, the energy spectra were calculated for C_s-C_s and $C_{3v}-C_{3v}$ dimers bound to each other via the sites shown in Fig. 1 and 2, that is the carbon systems composed of 106 atoms. Tables 3 and 4 present the energy spectra of these C_s-C_s and $C_{3v}-C_{3v}$ dimers. It can be seen from Table 3, that the energy spectrum of the C_s-C_s dimer contains 216 energy levels, of which: two levels have eight-order degeneracy, two levels have two-order degeneracy, other levels are nondegenerated. The occupied band has a width of $W \approx 6.1$ eV. The same width has the unoccupied band, the HOMO-LUMO gap is $\Delta \approx 0.92$ eV. Thus, from the comparison of the energy spectrum of C_s isomer of C_{58} fullerene with the energy spectrum of C_s-C_s dimer of the same fullerene, a conclusion can be made that an increase in number of sites in the system results in an increase in band width W up to ~ 6 eV and a decrease in HOMO-LUMO gap down to ~ 1 eV.

It can be seen from Table 4, where the energy spectrum of $C_{3v}-C_{3v}$ dimer is presented, that the energy spectrum

Table 5. The energy spectrum of $C_{58}-C_{58}$ (C_s) fullerene at the following parameters of the Hubbard model: $U = 6.9$ eV, $B = -1.0$ eV

1.0, -6.2659	1.0, -4.2017	1.0, -1.9228	1.0, 0.6341	1.0, 2.6983	1.0, 4.9772
1.0, -6.2648	1.0, -4.1987	1.0, -1.8823	1.0, 0.6352	1.0, 2.7013	1.0, 5.0177
1.0, -6.0633	1.0, -4.1503	1.0, -1.8459	1.0, 0.8367	1.0, 2.7497	1.0, 5.0541
1.0, -6.0549	1.0, -4.1212	1.0, -1.8318	1.0, 0.8451	1.0, 2.7788	1.0, 5.0682
1.0, -6.0383	1.0, -4.1074	1.0, -1.7812	1.0, 0.8617	1.0, 2.7926	1.0, 5.1188
1.0, -6.0346	1.0, -4.0791	1.0, -1.7636	1.0, 0.0865	1.0, 2.8209	1.0, 5.1364
1.0, -5.9139	1.0, -3.9160	1.0, -1.7623	1.0, 0.9861	1.0, 2.9840	1.0, 5.1377
1.0, -5.9130	1.0, -3.9036	1.0, -1.7602	1.0, 0.9870	1.0, 2.9964	1.0, 5.1398
1.0, -5.6457	1.0, -3.8889	1.0, -1.7196	1.0, 1.2543	1.0, 3.0111	1.0, 5.1804
1.0, -5.6234	1.0, -3.8835	1.0, -1.6444	1.0, 1.2766	1.0, 3.0165	1.0, 5.2556
1.0, -5.5967	1.0, -3.7633	1.0, -1.6323	1.0, 1.3033	1.0, 3.1367	1.0, 5.2677
1.0, -5.5528	1.0, -3.7474	1.0, -1.5822	1.0, 1.3472	1.0, 3.1526	1.0, 5.3178
1.0, -5.5520	1.0, -3.6884	1.0, -1.5513	1.0, 1.3480	1.0, 3.2116	1.0, 5.3487
1.0, -5.5476	1.0, -3.6216	1.0, -1.5061	1.0, 1.3524	1.0, 3.2784	1.0, 5.3939
1.0, -5.5349	1.0, -3.5375	1.0, -1.4880	1.0, 1.3651	1.0, 3.3625	1.0, 5.4120
1.0, -5.5148	1.0, -3.4686	1.0, -1.4067	1.0, 1.3852	1.0, 3.4314	1.0, 5.4933
1.0, -5.3453	1.0, -3.3479	1.0, -1.3879	1.0, 1.5547	1.0, 3.5521	1.0, 5.5121
1.0, -5.3105	1.0, -3.1322	1.0, -1.3731	1.0, 1.5895	1.0, 3.7678	1.0, 5.5269
1.0, -5.0964	1.0, -3.0649	1.0, -1.1933	1.0, 1.8036	1.0, 3.8351	1.0, 5.7067
1.0, -5.0888	1.0, -3.0576	1.0, -1.1906	1.0, 1.8112	1.0, 3.8424	1.0, 5.7094
1.0, -5.0550	1.0, -3.0386	1.0, -1.1810	1.0, 1.8450	1.0, 3.8614	1.0, 5.7190
1.0, -4.9895	1.0, -3.0361	1.0, -1.1472	1.0, 1.9105	1.0, 3.8639	1.0, 5.7528
1.0, -4.9459	1.0, -2.8511	1.0, -1.0761	1.0, 1.9541	1.0, 4.0489	1.0, 5.8239
1.0, -4.8935	1.0, -2.8284	1.0, -0.8945	1.0, 2.0065	1.0, 4.0716	1.0, 6.0055
1.0, -4.8840	1.0, -2.5950	1.0, -0.8086	1.0, 2.0160	1.0, 4.3050	1.0, 6.0914
1.0, -4.8808	1.0, -2.5706	1.0, -0.8028	1.0, 2.0192	1.0, 4.3294	1.0, 6.0972
1.0, -4.8477	1.0, -2.3610	1.0, -0.7925	1.0, 2.0523	1.0, 4.5390	1.0, 6.1075
1.0, -4.7926	1.0, -2.3000	1.0, -0.7376	1.0, 2.1074	1.0, 4.6000	1.0, 6.1624
1.0, -4.7743	1.0, -2.0883	1.0, -0.7143	1.0, 2.1257	1.0, 4.8117	1.0, 6.1857
1.0, -4.7679	1.0, -2.0627	1.0, -0.7067	1.0, 2.1321	1.0, 4.8373	1.0, 6.1933
1.0, -4.5711	1.0, -1.9631	1.0, -0.7064	1.0, 2.3289	1.0, 4.9369	1.0, 6.1936
1.0, -4.5211	1.0, -1.9553	1.0, -0.7040	1.0, 2.3789	1.0, 4.9447	1.0, 6.1960
8.0, -4.3000	1.0, -1.9386	1.0, -0.6950	8.0, 2.6000	1.0, 4.9614	1.0, 6.2050
1.0, -4.2249	1.0, -1.9298	1.0, -0.6887	1.0, 2.6751	1.0, 4.9702	1.0, 6.2113
1.0, -4.2027	1.0, -1.9238	1.0, -0.6880	1.0, 2.6973	1.0, 4.9762	1.0, 6.2120

**Figure 6.** Density of electron states of C_s-C_s dimer of C_{58} fullerene.**Figure 7.** Density of electron states of $C_{3v}-C_{3v}$ dimer of C_{58} fullerene.

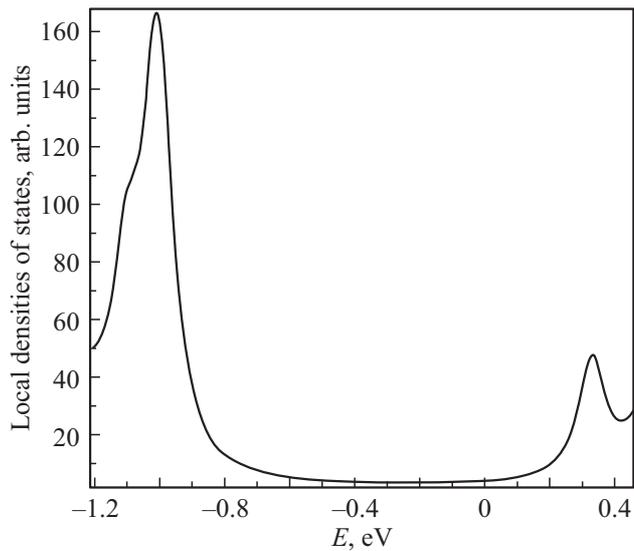


Figure 8. Density of electron states of C_s-C_s dimer of C_{58} fullerene with the exclusion of bond sites.

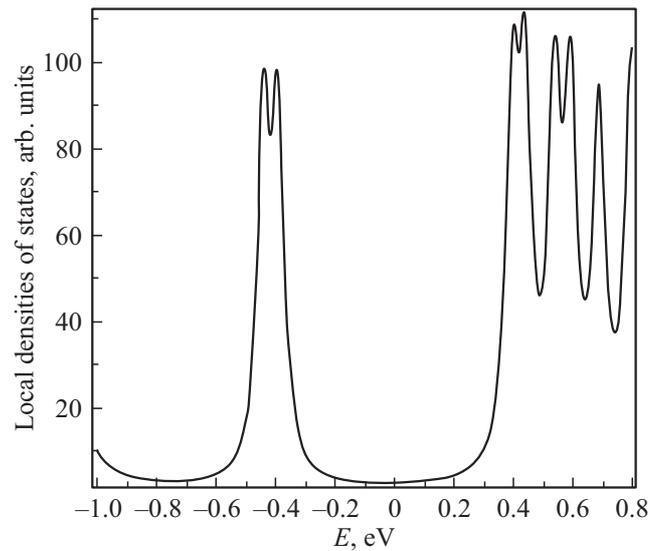


Figure 10. Density of electron states of C_s-C_s dimer of C_{58} fullerene with the exclusion of bond sites in the model with $U = 0$, $B = -2.6$ eV.

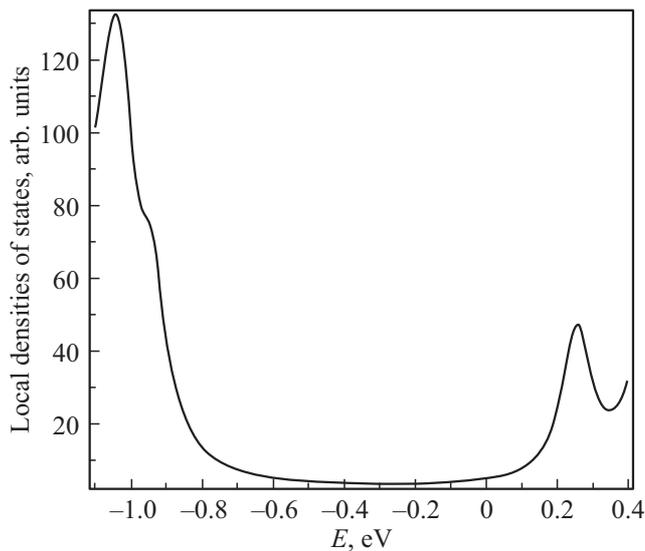


Figure 9. Density of electron states of $C_{3v}-C_{3v}$ dimer of C_{58} fullerene with the exclusion of bond sites.

of the this dimer, as well as the C_s-C_s dimer contains 216 energy levels, of which two levels have eight-order degeneracy, two levels have two-order degeneracy, other levels are nondegenerated. The occupied band has a width of $W \approx 6.0$ eV. The unoccupied band has the same width, the HOMO-LUMO gap is $\Delta \approx 1.0$ eV. From the comparison of the energy spectrum of C_{3v} isomer of C_{58} fullerene with the energy spectrum of $C_{3v}-C_{3v}$ dimer of the same fullerene, as well as for the C_s-C_s dimer, a conclusion can be made that an increase in the number of sites in the system results in an increase in the band width W up to 6 eV and a decrease in HOMO-LUMO gap Δ down to ~ 1 eV.

Fig. 6 and 7 show curves of densities of electron states for C_s-C_s and $C_{3v}-C_{3v}$ dimers, from which it can be seen that

a decrease in the gap in the energy spectrum is associated with the emergence of additional peaks for each isomer at -0.65 and 0.35 eV for the C_s-C_s system and at -0.7 and 0.3 eV for the $C_{3v}-C_{3v}$ system.

Table 6. The energy spectrum of $C_{58}-C_{58}$ (C_{3v}) fullerene at the following parameters of the Hubbard model: $U = 6.85$ eV, $B = -1.0$ eV

2.0, -6.1927	2.0, -2.9754	2.0, 0.6573	2.0, 3.8746
2.0, -5.9728	2.0, -2.9403	2.0, 0.8772	2.0, 3.9097
2.0, -5.9662	2.0, -2.6984	2.0, 0.8838	2.0, 4.1516
2.0, -5.8396	2.0, -2.2943	2.0, 1.0104	2.0, 4.5557
2.0, -5.5434	2.0, -2.2250	2.0, 1.3066	2.0, 4.6250
2.0, -5.4812	2.0, -2.1783	2.0, 1.3688	2.0, 4.6717
2.0, -5.4699	2.0, -1.9331	2.0, 1.3801	2.0, 4.9169
2.0, -5.4490	2.0, -1.8594	2.0, 1.4010	2.0, 4.9906
2.0, -5.2763	2.0, -1.8543	2.0, 1.5737	2.0, 4.9957
2.0, -4.9485	2.0, -1.8073	2.0, 1.9015	2.0, 5.0427
2.0, -4.9083	2.0, -1.8021	2.0, 1.9417	2.0, 5.0479
2.0, -4.9072	2.0, -1.7128	2.0, 1.9428	2.0, 5.1372
2.0, -4.8052	2.0, -1.5881	2.0, 2.0448	2.0, 5.2619
2.0, -4.7555	2.0, -1.5051	2.0, 2.0945	2.0, 5.3449
2.0, -4.6928	2.0, -1.4486	2.0, 2.1572	2.0, 5.4014
2.0, -4.5679	2.0, -1.4402	2.0, 2.2821	2.0, 5.4098
8.0, -4.2250	2.0, -1.4176	8.0, 2.6250	2.0, 5.4324
2.0, -4.1857	2.0, -1.3487	2.0, 2.6643	2.0, 5.5013
2.0, -4.1080	2.0, -1.1763	2.0, 2.7420	2.0, 5.6737
2.0, -4.0489	2.0, -0.8697	2.0, 2.8011	2.0, 5.9803
2.0, -4.0268	2.0, -0.8248	2.0, 2.8232	2.0, 6.0252
2.0, -3.9378	2.0, -0.7213	2.0, 2.9122	2.0, 6.1287
2.0, -3.7492	2.0, -0.6638	2.0, 3.1008	2.0, 6.1862
2.0, -3.7447	2.0, -0.6333	2.0, 3.1053	2.0, 6.2167
2.0, -3.6456	2.0, -0.6198	2.0, 3.2044	2.0, 6.2302
2.0, -3.2031	2.0, -0.5368	2.0, 3.6469	2.0, 6.3132
2.0, -3.1987		2.0, 3.6513	

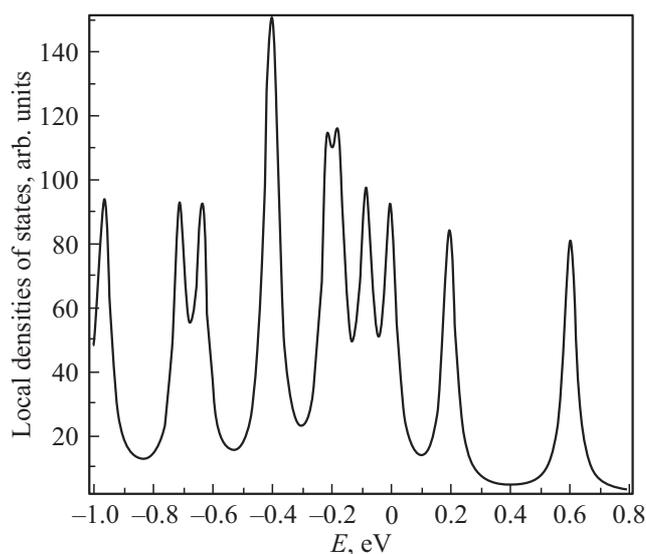


Figure 11. Density of electron states of $C_{3v}-C_{3v}$ dimer of C_{58} fullerene with the exclusion of bond sites in the model with $U = 0$, $B = -2.6$ eV.

Non-coincidence of gap values obtained within our calculations caused by the emergence of additional states with the experimental data of [11] is connected to the fact that there are neither π -electrons nor states of these electrons in the sites through which the two fullerenes are bound, because the states of these electrons and corresponding electrons both are engaged in the creation of σ -bonds connecting these isomers. The energy of these σ -electrons is much lower than the energy of π -states [13]. Hence, in our calculations performed within SFA, it is necessary to remove the sites through which two fullerenes are bound with each other.

Results of the calculation of the energy spectra taking into account the above consideration are shown in Tables 5 and 6. It can be seen from Table 5, that the energy spectrum of C_s-C_s dimer of C_{58} fullerene with removed sites of the dimer's bond is composed of 210 energy levels, two of which have eight-order degeneracy, other are nondegenerated. The width of each band is approximately equal to 5.58 eV, the HOMO-LUMO gap is about 1.32 eV.

Table 6 shows the energy spectrum of the $C_{3v}-C_{3v}$ system. It is composed of 106 energy levels, of which two have eight-order degeneracy, other have two-order degeneracy. The width of the Hubbard subbands is approximately equal to 5.67 eV, the HOMO-LUMO gap is 1.2 eV. Fig. 8 and 9 show curves of densities of electron states. There are no additional peaks on them connected with the states of electrons of the sites used to bond the fullerenes. As a consequence, the gap on the curve of density of electron states is close to the experimental values of $\sim 1.2-1.3$ eV.

The electron structure of carbon systems with sp^2 hybridization is traditionally studied within a model that does not take into account the intrasite Coulomb interaction,

and only transitions of π -electrons from one site to another are taken into account. In this case the transition integral is taken equal to 2.6 eV, that ensures the band width of π -electrons equal to $W = 6B \approx 15-16$ eV. And within our model the width of the π -electron band is $W = 6B + U$, which is also close to the traditional value of $\sim 15-16$ eV.

Due to the existence of representations alternative to our model and in order to verify both models, we have calculated the energy spectrum of systems based on C_s-C_s and $C_{3v}-C_{3v}$ isomers of C_{58} fullerene with the removal of sites through which the fullerenes are bound to each other. Results are shown in Figs. 10 and 11. It can be seen from the figures, that curves of density of electron states by no means match the experimental results of [11].

4. Conclusion

Thus, results of our calculations and their comparison with experimental data provide the strong evidence of the need to apply models taking into account ISCI of π -electrons to study electron properties of fullerenes and CNTs.

Also, from results of our work it follows, that the sites through which the isomers are bound to form dimers, should be removed from the calculations of the energy spectrum of π -electron subsystem. This is explained by the fact that in these sites there are neither π -electrons nor their states. Instead of π -states σ -states are formed, which energies, according to [13], are about 20 eV lower than the energies of π -states. These states move to the σ -band forming rigid bonds between isomers. It is the removal of these sites from the calculations of the energy spectra of the studied dimers that gave the increase in the energy gap from ~ 1.0 to ~ 1.2 eV observed in the experiment reported in [11].

Conflict of interest

The authors declare that they have no conflict of interest.

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