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Electronic structure of the chlorinated derivative $C_{72}Cl_4$

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Abstract

The electronic structure of the chlorinated derivative $C_{72}Cl_4$ is investigated taking into account the strong intrasite Coulomb interaction in this system. The energy spectrum of the $C_{72}Cl_4$ systems is calculated in the static fluctuation approximation for the Hubbard model. The density of electronic states is calculated. To verify the model used, a curve of the optical absorption spectrum based on the obtained energy spectrum, is constructed using the Kubo formula. The optical absorption spectrum curve of $C_{72}Cl_4$ coincides with the experimental curves on the good qualitative level.

Keywords: Fullerene; The Hubbard Model; Energy Spectrum; Density of Electronic States; The Intrasite Coulomb Interaction; Optical Absorption Spectrum

Introduction

Fullerenes and carbon nanotubes have been discovered for more than thirty years. These systems are still of interest to physicists, chemists, and materials scientists due to their unique structure and properties. The structure of these systems is simple and straightforward. Note that the energy spectrum of the first synthesized fullerene, C_{60}, was calculated before its synthesis [1]. The calculation was performed in the Hückel approximation, taking into account that carbon in this system is in a sp^2 hybridized state. In this calculation, the intrasite Coulomb interaction of π-electrons was completely ignored, although in the early 1970s, Levin [2] showed that this interaction is significant in carbon sp^2-hybridized systems and can reach values of ~ 20 eV. Later theoretical studies [3] based on first-principles calculations confirmed this.

Systems with a high value of the intra-nodal Coulomb interaction of π-electrons can be adequately described within the framework of the Hubbard model [4]. In a series of our works [5-10], it was shown that in fullerenes and carbon nanotubes, this interaction leads to the splitting of the π-electron energy spectrum into two groups of levels, the "upper" and "lower" Hubbard subbands. In [5-10], optical absorption spectra (OAS) were calculated, which are in good agreement with the corresponding experimental data, confirming the conclusion about the splitting of the π-electron spectrum.

According to [5-10], the "upper" Hubbard band is formed by states of electrons with double occupancy of a node, and the "lower" band is formed by states of electrons with single occupancy of a node. The gap between these subbands is $\Delta \approx U - W$, where Δ is the gap, U is the integral of the intra-node Coulomb interaction, and W is the width of the π-band. Calculations [5-10] have shown that the width of the Hubbard subbands is $W \approx 6B$, where B is the π-electron hopping integral between adjacent nodes.

Fullerene-based compounds can be divided into two groups: endohedral and exohedral. The first group includes fullerene compounds with metal atoms such as C_nMe_m. In such compounds, the metal atom, *Me*, is located inside the fullerene shell. Some of its valence electrons are used to fill the "upper" Hubbard subband. The second group includes fullerene compounds that are formed with halogen atoms or groups of atoms containing halogen atoms. They are electron acceptors. The bright representatives of the second group are C_nCl_m, C_nF_m, C_nBr_m, $C_n(CF_3)_m$.

The analysis carried out in [11-14] suggests that in such systems, impurity atoms or groups of atoms are located on the surface of fullerenes, occupying fixed nodes. As a result, a strong chemical bond with fullerenes is formed on these nodes. There is one π-electron for each such bond. Therefore, there are no π-electrons in the attachment sites. This significantly changes the structure of the π-electron subsystem. Obviously, by combining the valence of impurities in endohedral compounds and the mutual arrangement of atoms or groups of atoms in exohedral compounds, it is possible to change the electronic and optical properties of the systems under consideration over a wide range.

The most stable fullerene C_{72}, which does not obey the isolated pentagon rule, was synthesized as a chlorinated derivative $C_{72}Cl_4$, which was isolated and unambiguously characterized by X-ray crystallography [15]. The low degree of chlorination makes this compound a very promising candidate for further derivatization. Due to the low concentration of chlorine, it is possible to remove its atoms to gain access to the pristine, empty C_{72} reservoir in large quantities. The relatively high yield, which is comparable to that of the most common higher fullerenes (C_{76}, C_{78}), and the ease of separation make $C_{72}Cl_4$ not only an example of an exotic compound, but also a fullerene that is accessible for further experimental study.

A theoretical study of the structural and spectral properties of the C_{72} isomers and the chlorinated derivative $C_{72}Cl_4$ from first principles has been conducted, for example, in [16]. Our work focuses on studying the electronic and optical properties of this compound. Since there are no π electrons in the attachment sites of such systems, we will use the approach that we developed for studying the electronic structure of fullerenes [11-14,17,18].

Method, results and discussion

Carbon in fullerenes and carbon nanotubes is known to be in an sp2-hybridized state. Three of the four valence electrons are hybridized and form rigid chemical bonds that form the backbone, framework, and system. These electron states are called σ-states. The fourth, non-hybridized, electron remains partially free. Its state is called a π-state. The boundary between vacant and filled states lies in the π-state region. Therefore, all the properties that are interesting for practical applications, are determined by the π-electrons. As mentioned above, the energy spectrum of the π-electrons was calculated by Bochvar and Halpern [1] without taking into account the intra-nodal Coulomb interaction of the π-electrons, which is large according to [2] and [3]. This interaction can be most fully accounted for within the framework of the Hubbard model [4].

The Hubbard model is intuitive and conceptually simple:

$$H = \varepsilon \sum_{n,\sigma} n_{n\sigma} + B \sum_{n,k,\sigma} (a^{+}_{n\sigma} a_{k\sigma} + a^{+}_{k\sigma} a_{n\sigma}) + U \sum_{k} n_{k\uparrow} n_{k\downarrow} \,. \qquad (1)$$

Here, the first term describes the self-energy of the π-electrons, the second term describes the hopping of these electrons between neighboring nodes, and the third one describes the intra-node Coulomb interaction. The variables ε, B, and U represent the self-energy, the hopping integral, and the integral of the Coulomb electron interaction, respectively. Finally, $n_{k,\sigma} = a^{+}_{k,\sigma} a_{k,\sigma}$ is the number operator of particles in node k with spin σ, and $a^{+}_{k\sigma}$, $a_{k\sigma}$ are the creation and annihilation operators of electrons.

Despite the simplicity of the Hubbard model, its exact solution has been obtained only for a one-dimensional chain of atoms. In [5-10, 11-14,17,18], the energy spectrum of the π-electron subsystem of both pure and endo- and exohedral fullerenes was calculated using the static fluctuation approximation [19]. The OAS curves obtained on the basis of these spectra are in good qualitative agreement with the corresponding experimental curves. This suggests that both the Hubbard model and the static fluctuation approximation can be used to study fullerenes. We will use this method to study the system $C_{72}Cl_4$ whose Schlegel diagram is shown in Figure 1. Filled circles indicate nodes to which chlorine atoms are attached. These nodes do not have π-electrons.

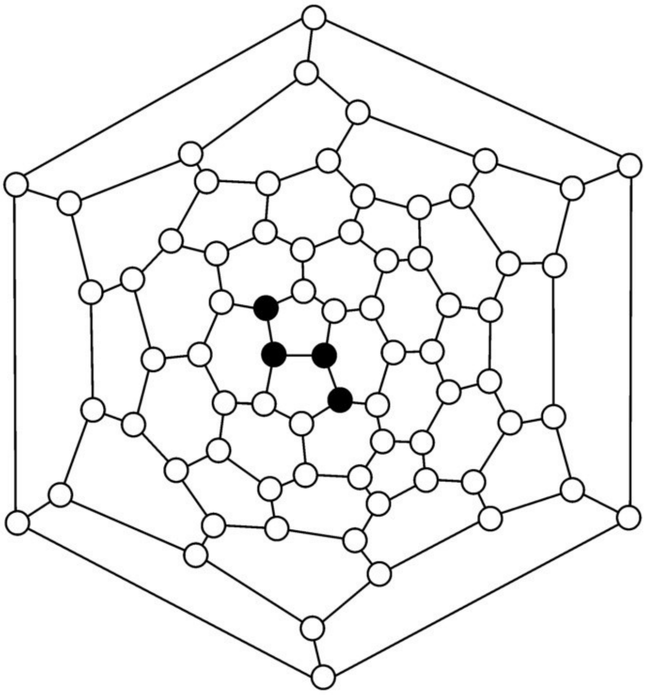

Figure 1. The Schlegel diagram of $C_{72}Cl_4$

The energy spectrum of $C_{72}Cl_4$ calculated at the values of the parameters of the Hubbard model B=-1.41 eV, U=10.7 eV, is given in Table 1. It contains 136 non-degenerate levels, of which 69 are filled and have negative energy values, and 69 are vacant and have positive energy values. From the table, we can see that the gap between the filled and empty levels is 1.787 eV. The width of each subband is 8.052 eV.

Table 1. Energy spectrum of $C_{72}Cl_4$ at the Hubbard model parameters. B=-1.41 eV, U=10.7 eV

Table 1. Energy spectrum of $C_{72}Cl_4$ at the Hubbard model parameters. *B*=-1.41 eV, *U*=10.7 eV							
-9.582	-7.191	-5.340	-3.193	1.218	3.609	5.460	7.607
-9.349	-7.157	-5.331	-3.109	1.451	3.643	5.469	7.691
-9.309	-7.118	-5.072	-3.042	1.491	3.682	5.728	7.758
-9.137	-7.102	-4.845	-2.925	1.663	3.698	5.955	7.875
-8.833	-7.019	-4.824	-2.892	1.967	3.781	5.976	7.908
-8.788	-7.018	-4.501	-2.702	2.012	3.782	6.299	8.098
-8.770	-6.743	-4.211	-2.679	2.030	4.057	6.589	8.121
-8.669	-6.669	-3.990	-2.457	2.131	4.131	6.810	8.343
-8.347	-6.545	-3.844	-2.404	2.453	4.255	6.956	8.396
-8.199	-6.541	-3.742	-2.388	2.601	4.259	7.058	8.412
-8.106	-6.454	-3.628	-1.976	2.694	4.346	7.172	8.824
-8.003	-6.442	-3.623	-1.798	2.797	4.358	7.177	9.002
-7.967	-6.418	-3.524	-1.787	2.833	4.382	7.276	9.013
-7.939	-6.384	-3.457	-1.728	2.861	4.416	7.343	9.072
-7.707	-6.330	-3.445	-1.693	3.093	4.470	7.355	9.107
-7.609	-6.189	-3.401	-1.675	3.191	4.611	7.399	9.125
-7.386	-6.028	-3.340	-1.583	3.414	4.772	7.460	9.217

The density of electronic states obtained taking into account the attenuation of the 0.15 eV levels, is shown in Figure 2, where it is more clearly visible. Unfortunately, in [15], the two most important characteristics of any system, the energy spectrum and the density of electronic states, are not presented. However, in this work, the OAS of this system has been measured, which we can compare with the OAS calculated basing on the spectrum we obtained.

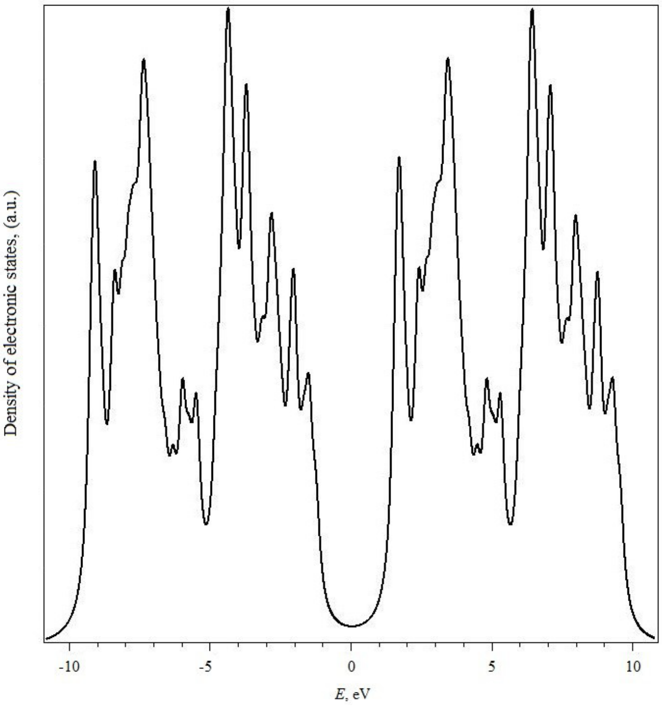

Figure 2. Density of electronic states

Figure 3 shows the theoretical (left) and experimental (right) OAS curves. It is seen that the curves are in good qualitative agreement with each other. The absorption edge on both curves lies in the 600-700 nm region, and in the 300 nm wavelength region there is a "step". In general, with the exception of the 500-600 nm region, the OAS curves are almost identical. The discrepancies in the 500-600 nm region are likely due to the influence of the solvent used in [15].

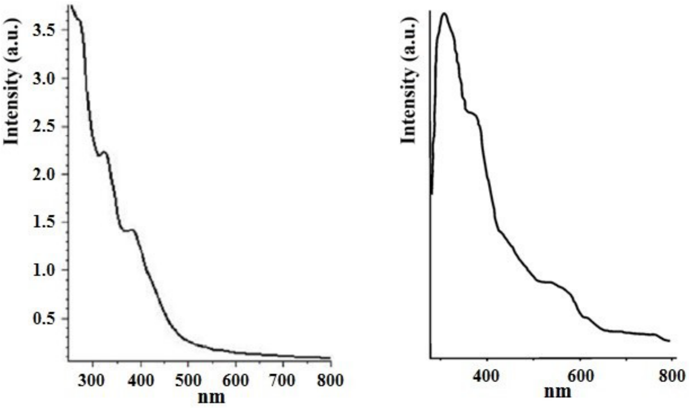

Figure 3. The calculated OAS, on the left, and the measured OAS [15], on the right

Conclusion

Thus, in the present work, the energy spectrum, density of electronic states and optical absorption spectrum of the $C_{72}Cl_4$ compound were calculated within the framework of the Hubbard model in the static fluctuation approximation. A comparison of theoretical optical absorption spectrum curve with the experimental one [15] showed good qualitative agreement. Based on this, we concluded that the intra-nodal Coulomb repulsion plays a crucial role in shaping the electronic properties of both fullerenes and their derivatives. The results of this work can be used as a theoretical basis for creating a nanoelectronics element base based on fullerene compounds.

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CRediT authorship contribution statement

Paimerov S.K.: Writing – original draft, Visualization, Investigation, Data curation.

Murzashev A.I.: Writing – review & editing, Writing – original draft, Supervision, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Zhumanazarov A.P.: Writing – original draft, Visualization, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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