SPECIFIC QUANTUM INTERACTIONS IN THE MOLECULES AND NANOPARTICLES OF ORGANIC SEMICONDUCTORS

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Quantum calculating of electron structure of organic semiconductors in the form of many-electron systems – large molecules, polymers, structures of nanotube - type and fullerenes, based on the methods of density functional and Hartree – Fock is known to result in significant discrepancy between the predicted and experimental values. The attempts of enhancing the results at the expense of improving of interparticle potentials and expansion of the base of source wave functions seem to have trimming character and represent a mathematical technique of improving the result without having precise physical substantiation. Moreover, the task of searching for the wave function at most approximated to the experiment from the point of view of mathematics, which has infinite range of solutions, is not a proper task according to Adamar – Tikhonov.

One of the reasons of falls-through of the existing methods, in the authors' opinion, is the absence of precise notion concerning the correlation of collective movement of electrons and correlated interactions of outer and inner shell electrons. The aim of the research is experimental and theoretical research of the correlation of outer shell electrons and electrons of inner shell of molecules. Using the experiment, the research was conducted for quasi – independent electrons in Hartree – Fock approximation of electrons and atoms on the basis of experimental data on the energy of ionization. The objects of the research were the molecules of nitrogen – containing, oxygen – containing, aromatic hydrocarbons and the atoms of alkaline metals.

Experiments, testifying to the correlation of outer and inner shells of atom and molecule electrons

During the last decades in the works, carried out under the guidance of Dolomatov M.Yu., the regularities testifying the interaction of outer and inner atom shells have been developed [1,2]. The connections between the energies of electron ionization and the energies of aggregation of electron states which are expressed by the integral strength of the oscillator have been ascertained. (ISO).

$$E = \alpha_1 + \alpha_2 \theta_{\lg} \quad (1); \qquad \theta_{\lg} = \int_{\lambda} \lg(\xi)\, d\lambda, \quad (2)$$

where E – the energy of boundary orbitals, IP, eV; (α_1, α_2) –empirical coefficients, dependent on the type of an orbital, constant in the given homologous series, correspondingly eV, eV ·nm^{-1}; $\theta_{\lg}$ – integral logarithmic indicator of absorption (logarithmic ISO), nm; $\xi = f(\varepsilon)$ – corresponding spectral function of electromagnetic radiation absorption for atoms and molecules; where ε – molar coefficient of absorption, dimensionality, accepted in electron spectroscopy, mol/l $^{-1}$·cm^{-1}, in SM 10^{-1}·m^{2}·mol^{-1}.

As it follows from the research [1,2], the dependence (1) has universal character, as ISO characterizes the aggregation of all the states of electrons absorbing energy in UV and visible region, we can surmise the correlation between the outer and inner electrons. The results are corroborated by the investigation of the second and third IP of the atoms of alkaline metals, defined by the method of photoelectron spectroscopy.

$$p_1 = A_1 + A_2 p_2; \quad p_2 = A_3 + A_4 p_3 \qquad (3)$$

Where A_1-A_4 –coefficients which depend on the nature of substances; p_1, p_2, p_3-first, second and third IP.

Statistic estimation of electron correlation in atom and molecular systems with statistic methods applied

Polycyclic aromatic hydrocarbons, containing from two to five annelated benzene rings, nitrogen - containing compounds series of acridine, pyridine, peredazone, quinoline, amine, indole and have been chosen as the object of the investigation.

The non empirical method of Hartree – Fock in simple Gaussian basis RHF-3-21G**has been chosen as the method of calculating energy of MO. The calculations have been carried out with the full optimization of the geometry of molecules. The distribution of the electron energy for many-electron systems is defined by the system of integro – differential equations in Hartree – Fock approximation:

$$F\Psi_i = \varepsilon_i \Psi_i, \qquad \text{where F – matrix of Fock, } \varepsilon_i \text{ – energy of MO.} \qquad (4)$$

The effect of correlation between the first vertical IP and the energies of deep MO are presented as a linear matrix equation:

$$\begin{pmatrix} \varepsilon_{i1} \\ \varepsilon_{i2} \\ \dots \\ \varepsilon_{im} \end{pmatrix} = \begin{pmatrix} 1 & -p_{11} \\ 1 & -p_{12} \\ \dots & \dots \\ 1 & -p_{1m} \end{pmatrix} \begin{pmatrix} \alpha_{1i} \\ \alpha_{2i} \end{pmatrix} + \begin{pmatrix} \omega_{i1} \\ \omega_{i2} \\ \dots \\ \omega_{im} \end{pmatrix}, \qquad (5)$$

where ε_{ij} – the element of column – matrix, which corresponds to the energy of *i* MO of *j*- compound; α_{1i}– the energy of i MO under p_{1j}=0; α_{2i} – the coefficient which characterizes the change of energy of i MO in the conditions of increasing the energy of the corresponding level by 1eV; p_{1j} – the experimental first vertical IP of *j*

compound; ω_{ij} – the parameter of disturbance, which takes account of the deviation ε_{ij} from the mean value, i=2..n, j=1..m.

As the measure of electron interaction of electron quant states (the levels of the energies of ionization), the statistic coefficient of linear correlation, which for all the systems of electron levels is expressed by the matrix correlation, has been used ***R***

For example the results of the research testify that in the lines of aromatic hydrocarbons the second (r=0,38), the third (r=0,25), the twelfth (r=0,24), the forty-seventh (r=0,23) energy levels have the maximum influence on the first vertical IP. (Fig.1).

In the lines of nitrogen – containing compounds in the frame of RHF-6-31G** method the levels 2 (r=0,88), 5 (r=0,83), 8 (r=0,76), 10 (r=0,75), 12 (r=0,68) have the maximum influence on the first vertical IP; the levels 3 (r=0,78), 4 (r=0,79), 6 (r=0,76), 9 (r=0,76), 10 (r=0,76), 11 (r=0,66), 13 (r=0,66), 14 (r=0,65) have the minimal influence. In all the correlations of 15 MO, which cover the whole line of nitrous compounds (according to the number of occupied pyrites MO – the least compound in the line), have been considered. In Fig. 2 the graphic dependence of the first vertical IP on the deep MO (down to the 15th level) is shown. [3].

Evidently, the obtained effects of electron correlation can be explained by the effects of quantum correlation and quantum entanglement of electrons, which have been investigated by Zeilinger [4-6].

So, in the molecules of polycyclic semiconductors the effects of correlative interaction of high and deep molecular levels considerably appear, therefore, such important physical characteristics as ionization energy, the work of electron yield, the level of Fermi semiconductors is in great extent determined by correlative effects. Evidently, such phenomena as the influence of outer electrons on K – capture of inner electrons by atom nuclei can be explained by such correlations. In respect to chemical interactions we can note that the energies of chemical reaction activation will be defined by the whole system of molecular electrons, but not only by valent electrons. The construction of correlated diagrams will allow to forecast the degree of influence of low energy levels on physical and chemical processes in complex information quantum molecular systems. The investigation of the dependence of the first ionization energy on the energy of deep electrons has great significance for molecular electronics. The research conducted shows that this influence is defined by the whole electronic system; therefore, the inner shell of atomic and molecular core considerably influences the work of electron yield and the width of the forbidden band in organic semiconductors.

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Figures

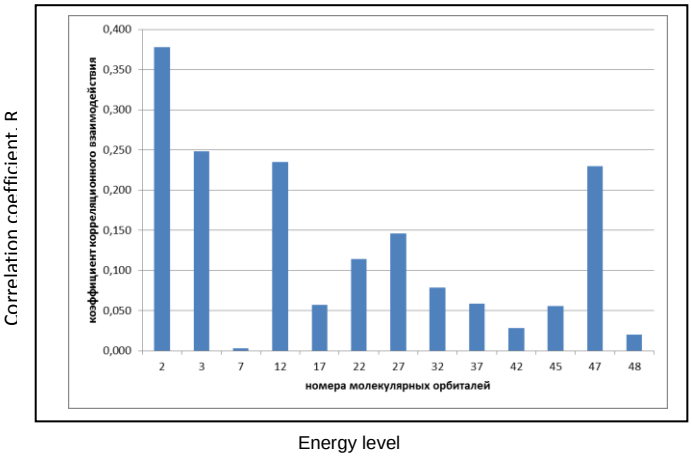

Fig.1 The correlation of the aggregate of quantum states in the series of organic semiconductors on the basis of polycyclic molecules for the first MO.

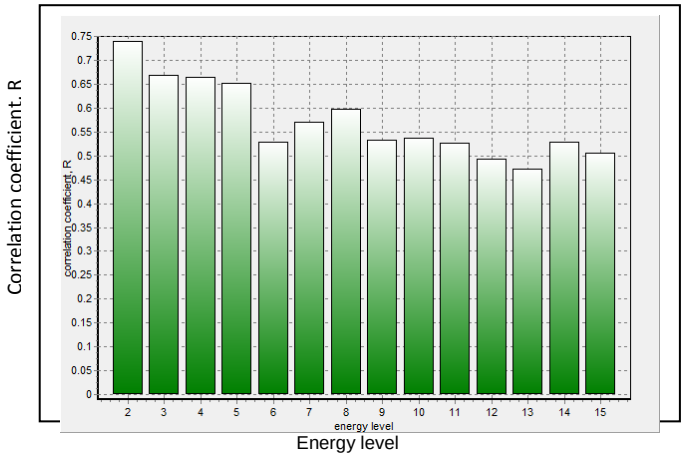

Fig.2. The dependence of the experimental first vertical PI on the energy of deep orbitals.