ФІЗИКО-МАТЕМАТИЧНІ НАУКИ

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QUANTUM-CHEMICAL STUDIES OF QUASI-ONE-DIMENSIONAL ELECTRON SYSTEMS. 1. POLYENES

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This review is devoted to the basic problem in quantum theory of quasi-one-dimensional electron systems like polyenes (Part 1) and cumulenes (Part 2) – physical origin of the forbidden zone in these and analogous 1D electron systems due to two possible effects – Peierls instability (bond alternation) and Mott instability (electron correlation). Both possible contradiction and coexistence of the Mott and Peierls instabilities are summerized on the basis of the Kiev quantum chemistry team research projects
Keywords*: quasi-one-dimensional electron system, polyenes, 1D electron systems, local states, impurity states, generalized HF method*

В огляді на основі результатів, отриманих київською групою квантової хімії, обговорюється основна проблема квазі-одновимірних електронних систем таких як поліени (Частина 1) і кумулени (Частина 2) – фізична природа походження забороненої зони в таких і подібних їм 1D електронних системах завдяки двом можливим ефектів – нестійкість Пайерлса (чергування довжин хімічних зв'язків) і Мотта (електронна кореляція)
Ключові слова: *квазі-одновимірні електронні системи, поліени, 1D електронні системи, локальні стани, домішкові стани, узагальнений метод ХФ*

1. Introduction

This review gives detailed results and thorough discussion of basic results in quantum theory of quasi-one-dimensional electron systems like Polyenes and Cumulenes, including partly Polyacetylenes, Polydiacetylenes, and some organic crystalline conductors obtained by Kiev quantum chemistry team with my direct and consultive or conductive participation in some of the research projects below.

We begin in Part 1 of the review with local electronic states in long polyene chains in the simple tight-binding approximation [1–4]. Then will give condensed review of the Generalized Hartree-Fock method and its different versions with some demonstrative applications to atoms, molecules, and carbon polymers [5]. Further we turn to theory of electronic structure of long polyene neutral alternant radicals based on the different orbital for different spins SCF method [6]. Then we come back to local electronic states in polyene chains with an impurity atom using unrestricted Hartree-Fock approach [7].

Further in Part 2 of the review we will turn to cumulenes. Here we begin with basics of the π-electronic theory of cumulenes [8, 9]. Then long cumulene chains are treated by extended and unrestricted Hartree-Fock approaches [10]. Thus, we come close to the basic problem in quantum theory of quasi-one-dimensional electron systems – physical origin of their forbidden zone.

In connection with this basic and most intriguing problem two results will be described in details. In one case using unrestricted Hartree-Fock treatment of the Hubbard-type Hamiltonian for long one-dimensional chains two possible effects – Peierls instability (bond alternation) and Mott-type electron correlation spin ordering leading to energy gap formation are mutually exclusive [11]. On the other hand, it was recently shown that quite sophisticated theory based on the varying localized geminals approach predicts coexistence of the Mott and Peierls instabilities in real one-dimensional systems [12]. Moreover, it is stated that this approach permits to give the answer to the question what mechanism of the forbidden gap formation is more essential – the electron correlation (Mott instability) or dimerization (Peierls instability). Both treatments despite their contradictions each other will be presented in details. Finally [13], in Part 2 of the review the summary with conclusions and perspectives is given.

2. Review of local electronic states in long polyene chains in the tight-binding model

It is well known that the energy spectrum of π-electrons in the long polyene chains has two bands for allowed states – valence and conduction bands separated by the forbidden zone of width ΔE (see *e. g.* [14]). According to the Peierls theorem on nonstability of a 1dmetal with respect to nuclear displacement [15], the value ΔE must be different from zero. It was shown [8, 9, 16, 17] that the electronic interaction plays an important role in this effect.

It is reasonable to ask the following question: how would the energy picture change with the introduction of defects into the polyene chain? The defects may appear to be due to the heterogeneous atoms in the carbon chain, to the substituents of the hydrogen atoms, to the space distortion, etc. In all quantum-mechanical models based on the π-electron approximation which take account of the interaction of a limited number of the nearest neighbors the appearance of the defects is described by the change of certain parameters in the effective π-electron Hamiltonian. For the justification of the latter statement see *e. g.* [18, 19]. For a long chain this change might be considered as a local perturbation. In particular, the following problem is of interest. How much should the parameters be changed in order to obtain the local states? These are the electronic states located outside the allowed bands in the forbidden zone, above and below the allowed bands.

A general method for solving problems of this type has been worked out by Lifshits [20–23] in application to vibrations in defective crystals and by Koster and Slater [24] in a study of the impurity levels in crystals. The method gives a possibility of getting expressions in closed form for the energy and wave functions of the local states through the property of unperturbed systems and has at least the following three important aspects:

1) It permits a study of the local states without determination of the band state properties.

2) One must solve the system of equations which has an order not higher than the number of perturbed atoms.

3) In certain cases the method opens up the possibility of finding exact solutions.

In quantum-chemical applications the method was successfully used by Koutecky in his work on the theory of chemisorbtion [25, 26].

In the present chapter this method is applied to the study of the local states in long polyene chains. Wishing to obtain mainly qualitative results in terms of simple analytical formulae we restrict ourselves to the nearest neighbor orthogonal tight-binding model, known in quantum chemistry also as Hückel approximation, taking into account bond alternation.

2. 1. General Relations

If one is looking for the wave function of the local state as an expansion over AOs, χ_n, then we have the following system of equations with the expansion coefficients U_n:

$$\sum_{n'} H_{nn'} U_{n'} - EU_n = -\sum_{n'} V_{nn'} U_{n'} \ , \tag{1}$$

where $H_{nn'}$ and $V_{nn'}$ are matrix elements of the Hamiltonian of the unperturbed problem and of the perturbation in the AO's representation, respectively. Following the procedure developed in [27] for the study of the local vibrations in crystals let us introduce the Green function of the Eq. (1)

$$g_{mn}(E) = \sum_i \frac{\varphi_i^*(m)\varphi_i(n)}{E - E_i} \ , \tag{2}$$

where E_i and $\varphi_i(m)$ are the solutions of the unperturbed problem. Considering the right-hand side of (1) as a nonhomogenity one concludes that the coefficients U_n are the solutions of the following system of equations:

$$U_l = -\sum_{p,s} g_{lp}(E) V_{ps} U_s \ . \tag{3}$$

It is obvious that the sum of the right-hand side of (3) contains U_s only in the case when atom s is perturbed. Therefore, if one substitutes l in the left-hand side of (3) by the numbers of the perturbed atoms, one obtains a system of linear homogeneous equations, the order of which is equal to the rank of the perturbed matrix, whereas the order of the initial system (1) was equal to the number of atoms in the chain. The condition of solvability of the new system gives us an equation for finding energy of the local states. Thus, our first step is to calculate the Green function (2) which we obtain for a long polyene chain with and without bond alternation.

As it is well known, the wave functions ψ_k and energies E_k of the states of the unperturbed chains without bond alternation are (see *e .g.* [28])

$$\psi_k = \sqrt{\frac{2}{N+1}} \sum_n \chi_n \sin kn, \quad E_k = E_0 + 2\beta \cos k \ , \tag{4}$$

where N is the number of atoms in the chain, β is the resonance bond integrals, and

$$k = \frac{\pi s}{N+1}. \quad (s = 1, 2, ..., N)$$

For the corresponding Green function (2) one has

$$g^0_{mn}(E) = \frac{2}{N+1} \sum_k \frac{\sin kn \cdot \sin km}{E - E_0 - 2\beta \cos k} \ . \tag{5}$$

Changing the summation in (5) to integration, which for the long chain produces an error of the order $\sim 1/N$, and calculating the corresponding integral we have

$$g^0_{mn}(E) = \frac{\operatorname{sh} n\kappa \, e^{-m\kappa}}{\beta \operatorname{sh}\kappa} [(-1)^{m-n} Q(E) - Q(-E)] \ , \tag{6}$$

where a step-function

$$Q(E) = \begin{cases} 1, & if \quad E > 0 \\ 0 & if \quad E < 0 \end{cases}$$

has been used. Here we introduced a change in notation

$$E - E_0 = \pm 2\beta \operatorname{ch}\kappa$$

and without a loss in generality it is assumed that $m \geq n$.

Let us consider the polyene chain with $2N$ atoms and alternating bonds described by the resonance integrals β_1 and β_2 and assume that $|\beta_1| > |\beta_2|$. Then the wave functions $\psi_k^{(1)}$ and $\psi_k^{(2)}$, and corresponding energies $E_1(k)$ and $E_2(k)$ are

$$\psi_k^{(1)} = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} \left[\chi_{2n} \sin kn - \chi_{2n-1} \frac{\beta_1 \sin kn + \beta_2 \sin k(n-1)}{\sqrt{\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos k}} \right],$$

$$E_1(k) = E_0 - \sqrt{\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos k}, \quad (7)$$

$$\psi_k^{(2)} = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} \left[\chi_{2n} \sin kn + \chi_{2n-1} \frac{\beta_1 \sin kn + \beta_2 \sin k(n-1)}{\sqrt{\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos k}} \right],$$

$$E_2(k) = E_0 + \sqrt{\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos k}. \quad (8)$$

The values of k are determined as solutions of the following transcendental equation

$$\sin kN + \frac{\beta_1}{\beta_2} \sin k(N+1) = 0. \quad (9)$$

The functions $\psi_k^{(1)}$ and their energies $E_1(k)$ describe the states of the lower filled (valence) band, and $\psi_k^{(2)}$ and $E_2(k)$ – the upper empty (conduction) band. Both bands have a width $2|\beta_2|$ and are separated by the forbidden zone

$$\Delta E = 2|\beta_1 - \beta_2|.$$

Inserting the corresponding coefficients $\varphi_k(m)$ from (7) and (8) into (2), changing the summation over k to integration, and summing up over both allowed bands, one obtains the following expressions for those Green functions which will be used later:

$$g_{2m,2n}(E) = (-1)^{n-m} \frac{E' \operatorname{sh} m\kappa e^{-\kappa n}}{\beta_1 \beta_2 \operatorname{sh}\kappa}, \quad (10)$$

$$g_{2m-1,2n}(E) =$$
$$= (-1)^{n-m+1} [\beta_1 \operatorname{sh} m\kappa - \beta_2 \operatorname{sh}(m-1)\kappa] \frac{e^{-\kappa n}}{\beta_1\beta_2 \operatorname{sh}\kappa}, \quad (11)$$

$$g_{2n+1,2n}(E) = \frac{\beta_2 - \beta_1 e^{-\kappa}}{2\beta_1\beta_2 \operatorname{sh}\kappa}, \quad (12)$$

$$g_{2m-1,2m-1}(E) = \frac{E'}{2\beta_1\beta_2 \operatorname{sh}\kappa} \times$$
$$\times \left[1 - \frac{e^{-(2m-1)\kappa}}{E'^2} \left(\beta_2 e^{\kappa/2} - \beta_1 e^{-\kappa/2} \right)^2 \right], \quad (13)$$

where $E' = E - E_0 = \pm\sqrt{\beta_1^2 + \beta_2^2 - 2\beta_1\beta_2 \operatorname{ch}\kappa}$.

We shall mainly consider the local states in the forbidden zone because this case is the most physically interesting. Therefore, we have written down only Green functions for $|E'| < |\beta_1 - \beta_2|$.

It is obvious that any real defect is connected with a simultaneous change of certain Coulomb and resonance integrals of the chain. However, wishing to obtain an analytical description of the local states we shall consider certain models, namely: change of one Coulomb integral (single substitution), simultaneous identical change of two Coulomb integrals (double substitution), and change of one resonance integral (perturbed bond). We may hope that a qualitative description of the real situation can be realized by the combination of the present results.

2. 2. Single Substitution

Let the perturbation be described by the change $\Delta\alpha$ of the Coulomb integral of an atom n

$$V_{ps} = \Delta\alpha \, \delta_{pn} \delta_{sn}.$$

Then Eq. (3) becomes

$$U_n = -\Delta\alpha g_{nn}(E) U_n,$$

the condition of solvability of which

$$1 + \Delta\alpha g_{nn}(E) = 0 \quad (14)$$

determines the energies of the local states.

We first consider the chain without bond alternation. Substituting the function $g_{nn}^0(E)$ from (6) into (14), one obtains

$$1 + \Delta\alpha \frac{1 - e^{-2n\kappa}}{2\beta \operatorname{sh}\kappa} [Q(E) - Q(-E)] = 0. \quad (15)$$

Equation (15) can be solved analytically for two limiting cases:

1) when $n \to \infty$ that is the substitution is made far away from the edge of the chain;

2) when $n = 1$ (surface state).

When $n \to \infty$, neglecting in Eq. (15) the term $\sim e^{-n\kappa}$ and solving the corresponding equation, one obtains the known expression for the energy of the state localized in the middle of the chain [24]

$$E = E_0 + \operatorname{sign}(\Delta\alpha)\sqrt{(\Delta\alpha)^2 + 4\beta^2}. \quad (16)$$

Putting $n = 1$ into (15) one also obtains the known expression for the energy of the surface state

$$E = E_0 + \operatorname{sign}(\beta/\Delta\alpha)(\Delta\alpha + \beta^2/\Delta\alpha). \quad (17)$$

It is easy to show that the state with an energy given by (17) exists only when

$$|\Delta\alpha/\beta| > 1,$$

where as in the case of the removal of the local level in the middle of the chain, as it follows from (16), the perturbation $\Delta\alpha$ might be infinitely small.

For $n \neq 1$ and $n \neq \infty$ Eq. (15) can be solved only numerically. Nevertheless, the asymptotic result can be found for the exact value of the minimum perturbation needed for removing the local state as a function of the value *n*. It follows from (6) that the minimal distance of the local level from the band edge corresponds to $\kappa \to 0$ (or $|E - E_0| \to |2\beta|$). Substituting $\kappa \to 0$ into (15) one concludes that perturbation of the *n*-th atom leads to the appearance of the local level only when

$$\left| \frac{\Delta\alpha}{\beta} \right| > \frac{1}{n}. \quad (18)$$

Now we shall consider the chain with alternating bonds. It follows from (10) and (13) that the results should be different for even and odd perturbed atoms. However, for $n \to \infty$ these differences are exponentially small and equations of the type (14) should be the same for the states localized in the middle of the chain. Substituting $n \to \infty$ into (10) and (13) and putting a corresponding expression into (14), one obtain an equation for the energy of the local states in the forbidden zone. An analogous equation could be obtained for the levels located above and below both allowed bands. We have not written down the Green functions which correspond to $|E|>|\beta_1+\beta_2|$. A solution of these equations gives the energy of the local states E_∞ for a single substitution in the middle of the chain, namely:

$$E_\infty = \pm \operatorname{sign}(\Delta\alpha) \times \sqrt{\beta_1^2+\beta_2^2+\frac{(\Delta\alpha)^2}{2} \pm \left[(\beta_1^2+\beta_2^2)(\Delta\alpha)^2 + \frac{(\Delta\alpha)^4}{4} + 4\beta_1^2\beta_2^2 \right]^{1/2}}. \quad (19)$$

The positive sign here corresponds to the level located above or below both allowed bands, and the negative sign corresponds to the level in the forbidden zone. It follows from (19) that even an infinitely small perturbation of the distant atom leads to two local levels. One of them is located outside of the bands, and the other in the forbidden zone. When $\Delta\alpha > 0$, the level in the forbidden zone is filled, and the other is empty. When $\Delta\alpha < 0$, the substitution is reserved. If $\Delta\alpha$ is small, the energy of both levels depends quadratically upon the perturbation. When $|\Delta\alpha|>|\beta_1|$ and $|\Delta\alpha|>|\beta_2|$, the energy of the out-of-band level depends linearly on $\Delta\alpha$; whereas, the energy of the other level is approximately proportional to $1/\Delta\alpha$. The latter means that one must apply an infinitely large perturbation in order for the local level to reach the middle of the forbidden zone. Thus, the level removed from the edge of the valence band cannot be transferred to the district $E>0$ by any single substitution, and *vice versa*.

Now we shall consider the dependence of the minimal value of the perturbation needed for an appearance of the local level, on the number of the perturbed atom. Subsituting (10) for the even atoms into (14), one obtains

$$1+\Delta\alpha \frac{E' \operatorname{sh} m\kappa e^{-m\kappa}}{\beta_1\beta_2 \operatorname{sh}\kappa} = 0, \quad (20)$$

where $2m \equiv l$ is the number of the perturbed atom. Approaching $E \to \pm|\beta_1-\beta_2|$ in Eq. (20), one concludes that the minimal perturbation by its absolute value needed for removing the level in the forbidden zone is

$$\Delta\alpha_{\min}^{in}(l) = -\operatorname{sign}(E) \left| \frac{2\beta_1\beta_2}{\beta_1-\beta_2} \right| \frac{1}{l}, \quad (21)$$

and for the out-of-band levels

$$\Delta\alpha_{\min}^{out}(l) = \operatorname{sign}(E) \left| \frac{2\beta_1\beta_2}{\beta_1+\beta_2} \right| \frac{1}{l}. \quad (22)$$

Thus, if a perturbation is such that $|\Delta\alpha|>|2\beta_1\beta_2/(\beta_1-\beta_2)|/l$, then this leads to an appearance of two local states. When

$$\left| \frac{2\beta_1\beta_2}{\beta_1+\beta_2} \right| \frac{1}{l} < |\Delta\alpha| < \left| \frac{2\beta_1\beta_2}{\beta_1-\beta_2} \right| \frac{1}{l},$$

only one out-of-band level appears. If

$$\left| \frac{2\beta_1\beta_2}{\beta_1+\beta_2} \right| \frac{1}{l} > |\Delta\alpha|,$$

the local states do not appear at all.

Following the same procedure for the case when the perturbation is localized on an odd atom with the number $l \equiv 2m-1$, one obtains the following condition for removing the local level into the forbidden zone

$$\Delta\alpha_{\min}^{in}(l) = -\operatorname{sign}(E) \left| \frac{\beta_1-\beta_2}{2\beta_1\beta_2} l + \frac{\beta_1+\beta_2}{2\beta_1\beta_2} \right|^{-1}, \quad (23)$$

and for the out-of-band level

$$\Delta\alpha_{\min}^{out}(l) = \operatorname{sign}(E) \left| \frac{\beta_1+\beta_2}{2\beta_1\beta_2} l + \frac{\beta_1-\beta_2}{2\beta_1\beta_2} \right|^{-1}. \quad (24)$$

Comparing (23) and (24) with (21) and (22) one sees that for large values of *l* the criteria for the appearance of the local states on even and on odd atoms coincide. It is also seen from (23) and (24) that the appearance conditions for the surface level (*l*=1) outside the bands and in the forbidden zone are the same, namely:

$$|\Delta\alpha_{\min}^{in}(1)| = |\Delta\alpha_{\min}^{out}(1)| = |\beta_2|, \quad (25)$$

that is the surface states always appear in pairs.

Let us now suppose that the polyene chain begins with the weak bond with $|\beta_1|<|\beta_2|$. This may happen, *e. g.*, if an unpaired electron is located at the edge of the chain [29]. We shall see how the results will change. In this case besides volume solutions (7) and (8) of an unperturbed problem (the number of solutions in the even chain is equal to $2N-2$) there are two more surface solutions localized at the edges of the chain. For a long chain when interaction of both surface states could be neglected, their energy is equal to zero, and the wave function of the state localized, say at the left edge of the chain, is

$$\psi^{(3)} = \sum_l \varphi_3(l)\chi_l,$$

$$\varphi_3(l) = \begin{cases} \sqrt{\beta_2^2-\beta_1^2}(\beta_1/\beta_2)^{l-1}/\beta_2, & \text{if } l = 2m+1, \\ 0, & \text{if } l = 2m, \end{cases}$$

and Eq. (14) leads to the following equation for the energy of the local states

$$\frac{2\cdot\Delta\alpha\cdot E}{\pi} \int_0^\pi \frac{|\varphi_1(k,l)|^2}{E^2-E_1^2(k)} dk + \frac{\Delta\alpha}{E} |\varphi_3(l)|^2 = 1, \quad (26)$$

where l is the number of the perturbed atom, and $\varphi_1(k,l)$ are the coefficients of AOs in (7). For even values of l: $\varphi_3(l)=0$. This means that the formulae (20)–(22) remain valid. For $l=2m+1$ the condition for removing the local level outside of the bands coincides with (24). However, for the existence of the level near the edge of the forbidden zone it is now necessary to have

$$\Delta\alpha = \mathrm{sign}(E)\left(\frac{\beta_2-\beta_1}{2\beta_1\beta_2}l - \frac{\beta_1+\beta_2}{2\beta_1\beta_2}\right)^{-1} \quad (27)$$

instead of (23).

Equation (27) gives an appearance condition of the local state only for

$$l > \frac{\beta_1+\beta_2}{\beta_2-\beta_1}.$$

In the opposite case it gives a disappearance condition of the local state genetically linked to the surface state of the unperturbed chain. To illustrate the situation let us consider an exact solution of (26) for l=1 (perturbed surface level). The energy of the level in the forbidden zone

$$E = \mathrm{sign}(\Delta\alpha)\sqrt{\beta_1^2+\beta_2^2-2\beta_1\beta_2\,\mathrm{ch}\kappa}\,, \quad (28)$$

where

$$\kappa = \ln\left\{\frac{1}{2}\left[\frac{\beta_2}{\beta_1}-\frac{(\Delta\alpha)^2}{\beta_1\beta_2}\right]+\sqrt{\frac{1}{4}\left[\frac{\beta_2}{\beta_1}-\frac{(\Delta\alpha)^2}{\beta_1\beta_2}\right]^2+\frac{(\Delta\alpha)^2}{\beta_2^2}}\right\}. \quad (29)$$

It is seen from (28), (29) that when $\Delta\alpha=0$, then $E=0$ (level in the center of the forbidden zone). With an increase of $|\Delta\alpha|$ the level is moving to the edge of one of the allowed bands, and if $|\Delta\alpha|\to|\beta_2|$, then $|E|\to|\beta_2-\beta_1|$ which is in agreement with the criteria (27). Further increase of $|\Delta\alpha|>|\beta_2|$ leads to the infusion of the local level into the allowed band. It follows from (24), the surface level appears with an energy $|E|\geq|\beta_1+\beta_2|$, which means that it is located above or below both allowed bands. In other words for any value of $|\Delta\alpha|$ in the chain with a broken edge-bond there may be one and only one surface state. As it is seen from (27), for

$$l < \frac{\beta_1+\beta_2}{\beta_2-\beta_1}$$

an increase of l requires an increase of $|\Delta\alpha|$ in order to move the level to the edges of the forbidden zone. It is obviously connected with the exponential decrease of the wave function of the surface state when the distance from the chain edge is increasing. In other words it is difficult to move the level by substitution at the point where the electron density is small. Comparatively larger values of $|\Delta\alpha|$ needed for an appearance of a new (besides the surface level) local level for the smallest l satisfied by the inequality

$$l > \frac{\beta_1+\beta_2}{\beta_2-\beta_1}$$

is in agreement with the known fact [25, 26] of the difficulty of producing two local states which are situated in the immediate neighborhood of one another. The extent of the chain region in which this effect can be observed is greater if the width of the forbidden zone is smaller.

2. 3. Double Substitution

As the simplest example of the mutual influence of two identical defects we shall consider the case where a perturbation consists of an identical change $\Delta\alpha$ of the Coulomb integrals of the chain atoms m and n. Then

$$V_{ps} = \Delta\alpha(\delta_{mp}\delta_{ms}+\delta_{pn}\delta_{sn})$$

and (3) is reduced to

$$U_l + \Delta\alpha[g_{lm}(E)U_m + g_{ln}(E)U_n] = 0. \quad (30)$$

Substituting consequently $l=m$ and $l=n$ into (30), one obtains a system of two homogeneous linear equations, the solvability condition of which

$$[1+\Delta\alpha g_{mn}(E)][1+\Delta\alpha g_{nn}(E)] - (\Delta\alpha)^2 g_{mn}^2(E) = 0 \quad (31)$$

gives an equation for the determination of the local level energies.

Let us first consider the chain without bond alternation. Substituting the necessary Green function from (5) into (31), one obtains

$$\left(1+\frac{\Delta\alpha}{\beta}e^{-m\kappa}\frac{\mathrm{sh}m\kappa}{\mathrm{sh}\kappa}\right)\left(1+\frac{\Delta\alpha}{\beta}e^{-n\kappa}\frac{\mathrm{sh}n\kappa}{\mathrm{sh}\kappa}\right) = \left(\frac{\Delta\alpha}{\beta}e^{-m\kappa}\frac{\mathrm{sh}n\kappa}{\mathrm{sh}\kappa}\right)^2. \quad (32)$$

When $|n-m|$ increases, the right-hand side of (32) decreases approximately as $\exp[-(m-n)\kappa]$. So for a large distance between defects it might be assumed equal to zero. Then Eq. (32) is transformed to Eq. (15) for the energy of the local state in the case of single substitution, and for $m,n\gg1$ there are two degenerate local states with an energy

$$E = E_0 + \mathrm{sign}(\Delta\alpha)\sqrt{4\beta^2+(\Delta\alpha)^2}\,.$$

For $m,n\gg1$, but $|m-n|{\sim}1$, then neglecting terms like $\sim\exp(-m\kappa),\exp(-n\kappa)$, one obtains from (32)

$$\left|\frac{\Delta\alpha}{\beta}\right|\frac{1\pm e^{-|m-n|\kappa}}{\mathrm{sh}\kappa} = 1. \quad (33)$$

The solution of (33) with the positive sign exists for any value of $|\Delta\alpha/\beta|$ and $\kappa\to0$, that is an appearance of the local level corresponds to $|\Delta\alpha/\beta|\to0$. If one considers the negative sign in (33), then a solution does not always exist. An appearance of solution $(\kappa\to0)$ which corresponds to the second local level is possible only when $|\Delta\alpha/\beta|>1/(m-n)$. Thus, if in the case of infinitely distant impurities located in the middle of a chain, there are always two (degenerate) local states, but when defects approaching one another, degeneracy is removed, and if the perturbation is not large enough, *i. e.*,

$$\left|\frac{\Delta\alpha}{\beta}\right| < \frac{1}{m-n},$$

mutual repulsion of the two split levels leads to the situation where one of them flows back into the band. There are two local states only when

$$\left|\frac{\Delta\alpha}{\beta}\right| > \frac{1}{m-n}. \quad (34)$$

If condition (34) is fulfilled and the splitting of two local states is small, then Eq. (33) can be solved by the iteration method. For the zero approximation one can take the solution when $|m-n| \to \infty$, namely:

$$\text{ch}\kappa_0 = \sqrt{1+\left(\frac{\Delta\alpha}{2\beta}\right)^2}.$$

The corresponding value of κ_0 is substituted into (33), then κ_1 is found, *etc*. After the first iteration the solution is as follows:

$$E = E_0 + \sqrt{4\beta^2+(\Delta\alpha)^2}\times$$
$$\times\left\{1 \pm \frac{1}{2}\frac{(\Delta\alpha)^2}{4\beta^2+(\Delta\alpha)^2}\left[\sqrt{1+\left(\frac{\Delta\alpha}{2\beta}\right)^2} - \left|\frac{\Delta\alpha}{2\beta}\right|\right]^{m-n}\right\}\times$$
$$\times \text{sign}(\Delta\alpha). \quad (35)$$

To analyse the appearance conditions of the local states when both perturbed atoms are located not far from the chain edge, we should return to (32). Letting $\kappa \to 0$, one obtains the following appearance conditions for one

$$\left|\frac{\Delta\alpha}{\beta}\right| \geq \frac{m+n-\sqrt{(m+n)^2-4n(m-n)}}{2n(m-n)} \quad (36)$$

and for two local levels

$$\left|\frac{\Delta\alpha}{\beta}\right| \geq \frac{m+n+\sqrt{(m+n)^2-4n(m-n)}}{2n(m-n)}. \quad (37)$$

It is easy to see that the right-hand side of (36) is smaller than $1/m$ but that of (37) is larger than $1/n$. Thus, the perturbation needed for an appearance of one local level in the case of two interacting impurities is smaller, but for the appearance of two levels is larger than the perturbation needed for an appearance of one local level on any of the two (n and m) single impurities.

Considering the chain with bond alternation we restrict ourselves to the physically interesting case of local states in the forbidden zone. We shall consider separately the interaction of even perturbed atoms and the mutual interaction of even and odd perturbed atoms. The interaction of odd atoms is qualitatively the same as for even atoms and will not be considered here.

Let us first consider the interaction of two even atoms. Substituting (10) into (31) one obtains an equation for the determination of local state energies, namely:

$$\left(1+\frac{\Delta\alpha E'}{\beta_1\beta_2}e^{-m\kappa}\frac{\text{sh}m\kappa}{\text{sh}\kappa}\right)\left(1+\frac{\Delta\alpha E'}{\beta_1\beta_2}e^{-n\kappa}\frac{\text{sh}n\kappa}{\text{sh}\kappa}\right) =$$
$$= \left(\frac{\Delta\alpha E'}{\beta_1\beta_2}e^{-m\kappa}\frac{\text{sh}n\kappa}{\text{sh}\kappa}\right)^2. \quad (38)$$

Analysis of the appearance conditions having one or two solutions of (38) is analogous to the analysis of Eqs. (32) and (33). In fact, this analysis was based on the consideration of these equations in the limiting case where $\kappa \to 0$ which in the present case corresponds to an approach up to the edges of the allowed bands, that is $|E| \to |\beta_1 - \beta_2|$. Comparing asymptotic expressions for (32) and (33) we see that they become the same if $1/\beta$ is changed to $(\beta_1-\beta_2)/(\beta_1\beta_2)$. Thus, by analogy with (34)–(37) we have the following conclusions. The value of the perturbation $|\Delta\alpha|$ needed for an appearance of one local state in the forbidden zone is

$$|\Delta\alpha_1| \geq \left|\frac{\beta_1\beta_2}{\beta_1-\beta_2}\right|\frac{m+n-\sqrt{(m+n)^2-4n(m-n)}}{2n(m-n)} \quad (39)$$

and for a perturbation which leads to the two local states

$$|\Delta\alpha_2| \geq \left|\frac{\beta_1\beta_2}{\beta_1-\beta_2}\right|\frac{m+n+\sqrt{(m+n)^2-4n(m-n)}}{2n(m-n)}. \quad (40)$$

In the case when $m,n \gg 1$, but $|m-n| \sim 1$, Eqs (39) and (40) give

$$|\Delta\alpha_1| \geq 0, \quad |\Delta\alpha_2| \geq \left|\frac{\beta_1\beta_2}{\beta_1-\beta_2}\right|\frac{1}{m-n}. \quad (41)$$

In the latter case Eq. (38) is simplified to\

$$\frac{\Delta\alpha}{2\beta_1\beta_2}\frac{E'}{\text{sh}\kappa}(1 \pm e^{-|m-n|\kappa}) = -1, \quad (42)$$

and can be solved by the iteration method if the second term of the left-hand side of (42) is small enough. As a zero approximation, we may take the values of E' and κ_0 for infinitely distant impurities given by (19). The solution after the first iteration is

$$E = -\text{sign}(\Delta\alpha)\sqrt{\beta_1^2+\beta_2^2+\frac{(\Delta\alpha')^2}{2}-\sqrt{\frac{(\Delta\alpha')^4}{4}+(\beta_1^2+\beta_2^2)(\Delta\alpha')^2+4\beta_1^2\beta_2^2}}, \quad (43)$$

where

$$(\Delta\alpha')^2 = (\Delta\alpha)^2(1 \mp 2e^{-(m-n)\kappa_0}).$$

It should be noted that perturbed atoms in the formulae (38)–(43) have numbers 2*m* and 2*n*.

Finally considering the interaction of two even defects we note, as is seen from (38), that the local level cannot be shifted to the center of the forbidden zone $(E'=0)$ by any finite perturbation $\Delta\alpha$.

Now we shall consider the behavior of the local states in the case of the interaction of even and odd defects. Substituting (12)–(13) into (31), one obtains the following equation for the energies of the local states:

$$\left(1+\frac{\Delta\alpha E'}{\beta_1\beta_2}e^{-m\kappa}\frac{\text{sh}m\kappa}{\text{sh}\kappa}\right)\times$$
$$\times\left\{1+\frac{\Delta\alpha E'}{2\beta_1\beta_2}\left[1-\frac{e^{-(2m-1)\kappa}}{E'^2}(\beta_2 e^{-\kappa/2}-\beta_1 e^{\kappa/2})^2\right]\right\}=$$
$$=\left(\frac{\Delta\alpha}{\beta_1\beta_2}\right)^2\frac{[\beta_1\,\text{sh}m\kappa-\beta_2\,\text{sh}(m-1)\kappa]^2}{\text{sh}^2\kappa}e^{-2n\kappa}. \qquad (44)$$

It is seen from (44) that unlike to the interaction of even impurities, an increase of $|\Delta\alpha|$ may shift the local level to the center of the forbidden zone and one may even pass through the whole forbidden zone from the bottom to the top. However, it may be shown that the perturbation needed for this increases exponentially with the increase of the distance between the impurities. Therefore, an analysis of (44) when $\kappa\to 0$ should be carried out with care for here we meet cases of not only the appearance of the local states (removing from the bands) but also disappearance of the local states when for large $|\Delta\alpha|$ they are removed from one of the allowed bands, going through the whole of the forbidden zone, and flow into another band.

It is obvious for physical reasons (see also results for single substitution), that when approaching the lower edge of the upper band ($E'\to-(\beta_1-\beta_2)$) the perturbation $\Delta\alpha<0$ corresponds to an appearance of the local level and a $\Delta\alpha>0$ to an infusion of the previously existing level into the band. The situation is reversed when approaching the upper edge of the lower band. Substituting $\kappa\to 0$ and $E\to(\beta_1-\beta_2)$ into (44), one obtains a quadratic equation with respect to $\Delta\alpha$, namely:

$$\left(\frac{\Delta\alpha}{\beta_1\beta_2}\right)^2[m(\beta_1-\beta_2)+\beta_2][(\beta_1-\beta_2)(n-m)-\beta_2]+$$
$$+\frac{\Delta\alpha}{\beta_1\beta_2}[(n+m)(\beta_1-\beta_2)+\beta_2]-1=0. \qquad (45)$$

As it is seen from (45), for $|n-m|>\beta_2/(\beta_1-\beta_2)$ both roots are positive. This means that for sufficiently large $\Delta\alpha$ two local levels may be removed from the lower band. The value of $\Delta\alpha$ needed for removing one or two levels should satisfy the inequalities $\Delta\alpha\geq\alpha_1$ and $\Delta\alpha\geq\alpha_2$, where α_1 and α_2 are the larger and smaller roots of (45) in the absolute sense.

If $|m-n|<\beta_2/(\beta_1-\beta_2)$, then one solution of (45) is positive, and the other which is larger in the absolute sense is negative. The value $\Delta\alpha\geq\alpha_1$ leads to an appearance of one local level, and any further increase in $\Delta\alpha$ cannot lead to removing the second level. The value $\alpha_2<\Delta\alpha<-\alpha_1$ corresponds to the local level which is removed from the lower edge of the upper band when $\Delta\alpha=-\alpha_1$ and shifted to the upper edge of the lower band when $\Delta\alpha\to\alpha_2$. Thus, if the perturbed even and odd atoms are located sufficiently close to one another so that their numbers $2n$ and $2m-1$ satisfy the inequality

$$|n-m|<\frac{\beta_2}{\beta_1-\beta_2}, \qquad (46)$$

then any identical perturbation of both atoms cannot lead to an appearance of more than one local level in the forbidden zone. In particular, as it follows from (46), two neighboring perturbed atoms (*n* = *m*) linked by a stronger bond for any values of β_1 and β_2 can give only one local level in the forbidden zone. It may also be shown that there is another situation for the levels located above and below the edges of both bands, namely: it is always possible to find such a value $|\Delta\alpha|$ that two levels will be removed.

2. 4. Perturbed bond

Let the perturbation be described by changing the resonance integral between the atoms *n* and *n*+1

$$V_{ps}=\Delta\beta(\delta_{pn}\delta_{s,n+1}+\delta_{p,n+1}\delta_{sn}).$$

Then Eq. (3) is transformed to

$$U_l=-\Delta\beta[g_{ln}(E)U_{n+1}+g_{l,n+1}(E)U_n]. \qquad (47)$$

Following the same procedure used for the derivation of Eq. (31), one obtains from (47) an equation determining the energy of the local states

$$[1+\Delta\beta g_{n,n+1}(E)]^2-(\Delta\beta)^2 g_{n,n}(E)g_{n+1,n+1}(E)=0. \qquad (48)$$

It follows from (5) and (10)–(13) that Eq. (48) has the same pattern for both signs of the energy. It means that the present local states always appear in pairs and that their energies differ only in the sign.

We shall first consider the chain without bond alternation. Substituting the necessary Green functions from (5) into (48), one obtains

$$\left[1-\frac{\Delta\beta}{\beta}\frac{\text{sh}n\kappa}{\text{sh}\kappa}e^{-(n+1)\kappa}\right]^2-$$
$$-\left(\frac{\Delta\beta}{\beta}\right)^2\frac{\text{sh}n\kappa\cdot\text{sh}(n+1)\kappa}{\text{sh}^2\kappa}e^{-(2n+1)\kappa}=0. \qquad (49)$$

If the perturbation is localized in the middle of the chain, then neglecting terms like $\exp(-n\kappa)$ in (49) and solving the corresponding equation, one obtains

$$E=E_0\pm\left(\beta'+\frac{\beta^2}{\beta'}\right),\quad \beta'=\beta e^{\kappa}. \qquad (50)$$

It follows from (50) that an appearance of a pair of local states is possible only when the bond is strengthened.

An analytical solution can also be found if the perturbed bond is located at the end of the chain. Substituting $n=1$ into (49) and solving the corresponding equation, one obtains

$$E=E_0\pm\frac{\left(1+\dfrac{\Delta\beta}{\beta}\right)^2}{\sqrt{\left(\dfrac{\Delta\beta}{\beta}\right)^2+2\dfrac{\Delta\beta}{\beta}}},\quad e^{\kappa}=\sqrt{\left(\frac{\Delta\beta}{\beta}\right)^2+2\frac{\Delta\beta}{\beta}}. \qquad (51)$$

It follows from (51) that the local states exist only when the end-bond is sufficiently strengthened, namely, when $|\beta'/\beta|>\sqrt{2}$.

It should be noted that an analytical expression for the energy of the surface states can also be derived for a more general case when besides changing the resonance integral of the end-bond one also changes the Coulomb integral of the end-atom. In this case

$$V_{ps}=\Delta\alpha\,\delta_{p1}\delta_{s2}+\Delta\beta(\delta_{p1}\delta_{s2}+\delta_{p2}\delta_{s1}). \qquad (52)$$

Substituting (52) into (3) and following the same standard procedure as before, one obtains

$$E_{\pm}=E_0\pm 2\beta\mathrm{ch}\kappa, \qquad (53)$$

where

$$e^{\kappa}=\pm\frac{\Delta\alpha}{2\beta}+\sqrt{\left(\frac{\Delta\alpha}{2\beta}\right)^2+\left(\frac{\Delta\beta}{\beta}\right)^2+2\frac{\Delta\beta}{\beta}}.$$

It follows from (53) that an appearance of the local state with an energy E_- located above the valence band is possible when

$$\left(\frac{\beta'}{\beta}\right)^2-\frac{\Delta\alpha}{\beta}>2,$$

and for the level E_+ located below the same band

$$\left(\frac{\beta'}{\beta}\right)^2+\frac{\Delta\alpha}{\beta}>2.$$

It means that there are two local levels if

$$\left(\frac{\beta'}{\beta}\right)^2>2+\left|\frac{\Delta\alpha}{\beta}\right|,$$

and only one if

$$2-\left|\frac{\Delta\alpha}{\beta}\right|<\left(\frac{\beta'}{\beta}\right)^2<2+\left|\frac{\Delta\alpha}{\beta}\right|.$$

The Eq. (49) permits the derivation of a relationship between the minimum perturbation needed for the appearance of paired local states and the number n of the perturbed bond. Letting $\kappa\to 0$ in (49) we see that the local states appear only if

$$\left|\frac{\beta'}{\beta}\right|\geq\sqrt{1+\frac{1}{n}}. \qquad (54)$$

Now we shall turn to the local states in the forbidden zone of the alternating chain and shall consider two cases: perturbation of weaker and stronger bonds.

Substituting corresponding Green functions from (10)–(13) into (48), the following equation is obtained for the local levels appearing under the perturbation of the weaker bond

$$\left[1+\frac{\Delta\beta}{\beta_1\beta_2}(\beta_2-\beta_1 e^{-\kappa})\frac{\mathrm{sh}n\kappa e^{-n\kappa}}{\mathrm{sh}\kappa}\right]^2=$$
$$=\frac{(\Delta\beta)^2E'^2\mathrm{sh}n\kappa}{2\beta_1^2\beta_2^2\mathrm{sh}^2\kappa}\times$$
$$\times e^{-n\kappa}\left[1-\frac{e^{-(2n+1)\kappa}}{E'^2}(\beta_2e^{\kappa/2}-\beta_1e^{-\kappa/2})^2\right], \qquad (55)$$

where $2n$ is the number of the perturbed bond. This equation can be solved exactly for the limiting case $n\gg 1$. Letting $n\to\infty$ in (55) and solving the corresponding equation, one obtain the energies of the two states localized far away from the chain edge

$$E'=\pm\sqrt{\beta_1^2+\beta_2^2-2\beta_1\beta_2\mathrm{ch}\kappa}, \qquad (56)$$

where

$$e^{\kappa}=-\frac{\alpha'\beta_2}{2}+\sqrt{1+\alpha'\beta_1+\left(\frac{\alpha'\beta_2}{2}\right)^2},$$

$$\alpha'=\frac{2\Delta\beta}{\beta_1\beta_2}\left(1+\frac{\Delta\beta}{2\beta_2}\right),\quad \Delta\beta=\beta_2'-\beta_2.$$

An analysis of (56) shows that this solution exists only when $|\beta_2'|>|\beta_2|$. This means that any small strengthening of the weaker bond in the middle of the chain always leads to the appearance of two local states in the forbidden zone.

Equation (55) also permits the derivation of the dependence of the perturbation needed for an appearance of paired local states on the number of the perturbed bond. Letting $\kappa\to 0$ in (55), the following condition for their appearance is obtained

$$\left|\frac{\beta_2'}{\beta_2}\right|>\sqrt{1+\frac{2\beta_1}{l(\beta_1-\beta_2)}}, \qquad (57)$$

where l is the number of the perturbed bond.

An analogous consideration can be carried out for the perturbation of the stronger bond. Using corresponding Green functions, one obtains the following equation for the energies of the local states

$$\left\{1+\frac{\Delta\beta}{\beta_1\beta_2}\frac{e^{-m\kappa}}{\mathrm{sh}\kappa}[\beta_1\,\mathrm{sh}m\kappa-\beta_2\,\mathrm{sh}(m-1)\kappa]\right\}^2=$$
$$=\frac{1}{2}\left(\frac{\Delta\beta}{\beta_1\beta_2\mathrm{sh}\,\kappa}\right)^2e^{-m\kappa}\times$$
$$\times\mathrm{sh}m\kappa[E^2-e^{-2m\kappa}(\beta_2e^{-\kappa}-\beta_1)^2], \qquad (58)$$

which can be solved exactly in two limiting cases: when $m\to\infty$ (change of a bond in the middle of the chain) and when $m=1$ (surface level). In the first case setting $m\to\infty$ and solving the corresponding equation, one obtains

$$E_{\pm}=\pm\sqrt{\beta_1^2+\beta_2^2-2\beta_1\beta_2\mathrm{ch}\kappa}, \qquad (59)$$

where

$$e^{\kappa}=\frac{\alpha\beta_1}{2}+\sqrt{1+\alpha\beta_2+\left(\frac{\alpha\beta_1}{2}\right)^2},$$

$$\alpha=\frac{2\Delta\beta}{\beta_1\beta_2}\left(1+\frac{\Delta\beta}{2\beta_1}\right),\quad \Delta\beta=\beta_1'-\beta_1.$$

An analysis of (59) shows that any small weakening of the stronger bond located far away from the chain edge is sufficient for an appearance of the local levels.

Substituting $m=1$ into (58) one obtains for the surface state

$$E_{surf}=\pm\sqrt{\beta_1^2+\beta_2^2-2\beta_1\beta_2\operatorname{ch}\kappa}\,, \qquad (60)$$

where

$$e^{\kappa}=-\left[2\frac{\Delta\beta}{\beta_2}+\frac{(\Delta\beta)^2}{\beta_1\beta_2}\right].$$

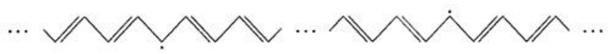
It is easy to see that the solution of (60) as well as the surface state exists only when the first bond is sufficiently relaxed, namely, when

$$\left|\frac{\beta'}{\beta_1}\right|\le\sqrt{1-\frac{\beta_2}{\beta_1}}\,.$$

From Eq. (58) the relationship of a perturbation needed for the appearance of the local states on the number *m* of the perturbed bond can be obtained. It follows from (58) that the local states appear only if

$$\left|\frac{\beta'}{\beta_1}\right|<\sqrt{1-\frac{2\beta_2}{\beta_1+\beta_2+m(\beta_1-\beta_2)}}\,. \qquad (61)$$

The characteristic nontrivial property of polymers with conjugated bonds is the presence of paramagnetic centers. This was repeatedly proved experimentally by the ESR method [30–32]. A satisfactory explanation of the general regularities of this phenomena is possible in terms of the local defect centers and the charge transfer between macromolecules [29, 33–37]. In particular it was suggested [29] that an experimentally observed ESR signal in long conjugated systems may be connected with an appearance of a pair of defects of the type



These defects have been interpreted [29] as radicals. The energy of the unpaired electrons localized on the defects situated at large distance from one another is equal to zero (Fig. 1).

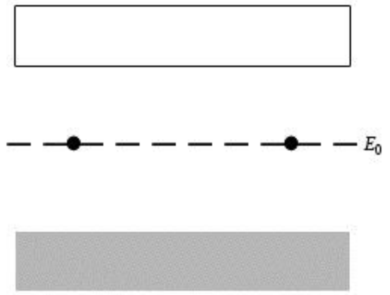
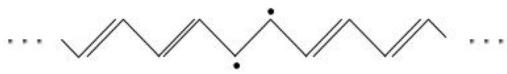


Fig. 1. Energy pattern of electrons when defects are infinitely distant from one another

Pople and Walmsley [29] noted that when defects approach each other, due to vibrations of the nuclear core, the zero degenerate level is split and both electrons should drop to the lower level. The following valence scheme is obtained when the defects approach one another as closely as possible



This state is not a triplet state. In fact this defect may originate simply by the weakening of one of the double bonds so that its resonance integral becomes equal to β_2 instead of β_1. This could be obtained, *e. g.*, by a distortion of the chain co-planarity. The energies of these local states thus obtained, are given by formulae (59) with $\beta'=\beta_2$. The picture of the energy levels is given in Fig. 2, *a*.

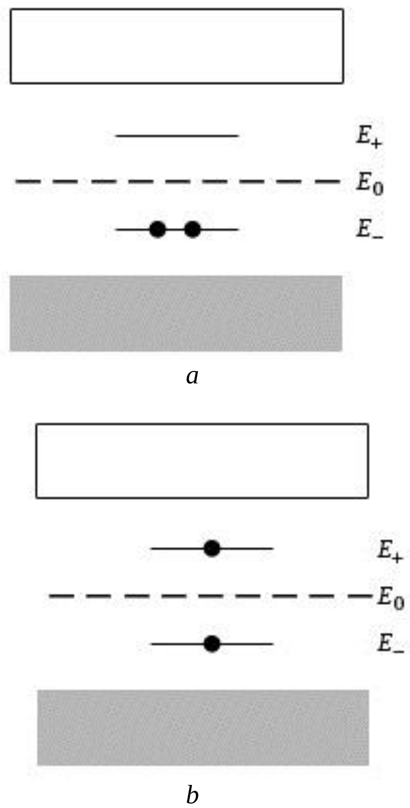


Fig. 2. Energy pattern of electrons when defects are close to each other: *a* – ground state; *b* – excited state

Transition to the lowest excited state (Fig. 2, *b*) requires an energy E_+-E_-. If one assumes that spontaneous (thermal) appearance of such states is possible only for the scheme 2b, then it is obvious that within the framework of the method used here and by the authors of [29] the energies of the states pictured in Fig. 1 and Fig. 2 are the same and are equal to the energy of the transition of one electron from the valence band to the conduction band. This simply means that a consideration of such defects without accounting for the deformation of the σ-core [38, 39] and the electronic interaction would not be correct. All next paragraphs are devoted to different methods for accounting of interaction between electrons.

3. The Generalized Hartree-Fock Method and Its Versions

Exact solution of the Schrodinger equation is known for only a few problems, mostly model ones. In practical molecular calculations different approximation methods are used. We shall review only those approximation approaches to solve molecular Schrodinger equations which permit obvious one-particle interpretation of many-electron wave function and at the same time account for the most of the electronic interactions. These approaches are known as the self-consistent field (SCF) methods based on pioneering works of Hartree and Fock [40–42]. The SCF methods revised below are mostly known as Generalized Hartree-Fock (GHF) approach with several different computational schemes having their own traditional names.

The wave function of the system of interacting electrons in general case must possess the following symmetry properties. First of all, in order the theory to be in agreement with the experimental facts the wave function must be antisymmetric relative to interchange of any pair of electrons. When molecular Hamiltonian

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\Delta_i + \sum_{i=1}^{N} V(\vec{r}_i) + \sum_{i>j=1}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

does not depend on spin variables the many-electron wave function must be an eigenfunction of $\hat{S}^2$ and $\hat{S}_z$ operators.

One of the methods for constructing many-electron wave functions that possess the required symmetry conditions is based on mathematical apparatus of the symmetric group S_N [43–45]. Irreducible representations of S_N are classified by Young schemes and are numbered by symbol $[\lambda] \equiv [\lambda_1, \lambda_2, \lambda_3, ..., \lambda_n]$ of corresponding Young schemes [43], where λ_i is the length of the *i-th* row of the Young scheme under condition that $\lambda_{i+1} \le \lambda_i$. Dimensionality of irreducible representation $[\lambda]$ is defined by a number of standard Young tables possible for a given Young scheme $[\lambda]$ and is equal to [43, 45]

$$f^{[\lambda]} = \frac{N! \prod_{i<j} (h_i - h_j)}{h_1! h_2! h_3! ... h_m!}, \qquad (62)$$

where $h_i = \lambda_i + m - i$, and m is the number of rows in the Young scheme $[\lambda]$.

Let us take a wave function of N electrons in the form

$$\Psi = \hat{G}\Phi \mathrm{X}, \qquad (63)$$

where Φ is a function of the spatial coordinates of N electrons, X – function of the spin coordinates of electrons, and operator $\hat{G}$ is chosen in a way that the function Ψ obey the necessary symmetry properties. In particular, the operator $\hat{G}$ can be chosen as [46–52]

$$\hat{G} \equiv \hat{G}_i^{\mu} = \sum_r \xi_{\hat{\sigma}_{ri}} \hat{O}_{ri}^{\mu} \hat{\omega}_{\bar{r}\bar{i}}^{\bar{\mu}}, \qquad (64)$$

where index μ defines an irreducible representation of the group S_N, index i corresponds to the *i-th* standard Young table for the Young scheme μ, $\xi_{\hat{\sigma}_{ri}}$ is the parity of the permutation $\hat{\sigma}_{ri}$, and the Young operators $\hat{O}_{ri}^{\mu}$ and $\hat{\omega}_{\bar{r}\bar{i}}^{\bar{\mu}}$ are given by [43–45]:

$$\hat{O}_{rs}^{\mu} = \frac{f^{\mu}}{N!}\sum_{\hat{\tau}} U_{rs}^{\mu}(\hat{\tau})\hat{\tau}, \qquad \hat{\omega}_{\bar{r}\bar{s}}^{\bar{\mu}} = \frac{f^{\bar{\mu}}}{N!}\sum_{\hat{\tau}} U_{\bar{r}\bar{s}}^{\bar{\mu}}(\hat{\tau})\hat{\tau}, \qquad (65)$$

where $U_{rs}^{\mu}(\hat{\tau})$ are matrix elements of the matrix of the standard orthogonal Young – Yamanouchi representation, and summation in (65) is taken over all $N!$ permutations of the group S_N, index $\bar{\mu}$ denotes an irreducible representation conjugative with μ, operators $\hat{O}_{ri}^{\mu}$ are acting on the spatial coordinates of the electrons, and $\hat{\omega}_{ri}^{\mu}$ – on the spin coordinates. Since the spin coordinates of the electrons take only two values, then the Young scheme $\bar{\mu}$ can contain not more than two rows, and scheme μ – not more than two columns: $\mu = [2^m, 1^{n-m}]$, $\bar{\mu} = [n, m]$ with $n \ge m, n + m = N$. The dimensionality of this representation according to (62) is equal to:

$$f^{[2^m,1^{n-m}]} = f^{[n,m]} \equiv f = \frac{N!(2S+1)}{\left(\frac{N}{2}+S+1\right)!\left(\frac{N}{2}-S\right)!}, \qquad (66)$$

where $2S = n - m$.

Fig. 3 shows two conjugate standard Young tables $S_f^{[2^m,1^{n-m}]}$ и $S_1^{[n,m]}$.

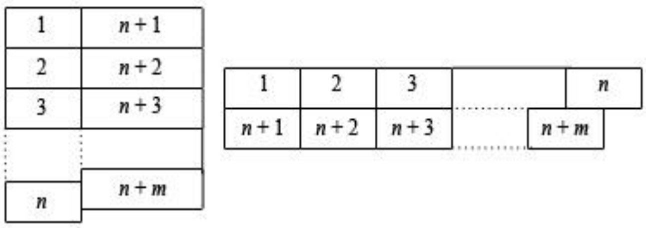


Fig. 3. Standard Young tables $S_f^{[2^m,1^{n-m}]}$ (left) and $S_1^{[n,m]}$ (right)

Standard tables are numbered in order of deviation of the sequences of numbers in the cells of the Young schemes relative to the natural numbers sequence, if you read row by row from the top to the bottom.

Consider the structure of the operators $\hat{O}_{ff}^{[2^m,1^{n-m}]}$ and $\hat{\omega}_{11}^{[n,m]}$, which will be needed later. Let $\hat{\tau}_a$ be a certain permutation of the first n symbols (a subset a), $\hat{\tau}_b$ be a certain permutation of the last m symbols (a subset b). Next, let $\hat{\tau}_r$ be the product of r different transpositions, each of which transposes one symbol from the a subset with a single symbol from the b subset. Any permutation in the group SN for any $\hat{\tau}_a, \hat{\tau}_b, \hat{\tau}_r$ can be written as

$$\hat{\tau} = \hat{\tau}_a \hat{\tau}_b \hat{\tau}_r . \quad (67)$$

The corresponding matrix elements are given by [46]

$$U_{ff}^{[2^m,1^{n-m}]}(\hat{\tau}_a \hat{\tau}_b \hat{\tau}_r) = \xi_{\hat{\tau}_a} \xi_{\hat{\tau}_b} \begin{pmatrix} n \\ r \end{pmatrix}^{-1}, \quad (68)$$

$$U_{11}^{[n,m]}(\hat{\tau}_a \hat{\tau}_b \hat{\tau}_r) = (-1)^r \begin{pmatrix} n \\ r \end{pmatrix}^{-1}, \quad (69)$$

where $\begin{pmatrix} n \\ r \end{pmatrix} \equiv \frac{n!}{(n-r)!r!}$ – binomial coefficients.

As shown by Goddard [46], the function $\hat{G}_i^{\mu}\Phi\mathrm{X}$ satisfies the Pauli principle

$$\hat{\tau}\hat{G}_i^{\mu}\Phi\mathrm{X}=\xi_{\hat{\tau}}\hat{G}_i^{\mu}\Phi\mathrm{X}$$

and is an eigenfunction of $\hat{S}^2$, namely:

$$\hat{S}^2\hat{G}_i^{\mu}\Phi\mathrm{X}=S(S+1)\hat{G}_i^{\mu}\Phi\mathrm{X} .$$

Thus it follows that the choice of the Young's scheme is determined by the value of the total spin S. The choice among $i = 1,2,3,..., f$ to construct the function

$$\Psi^{(GI)} = \hat{G}_i^{\mu}\Phi\mathrm{X} \quad (70)$$

is arbitrary to a certain extent; later we shall examine the effect of this choice on the results of calculations.

Note also that the operators $\hat{G}_i^{\mu}$ satisfy [46] the following relation

$$\sum_{\mu} \frac{1}{f^{\mu}} \sum_i \hat{G}_i^{\mu} = \hat{\Omega}_{11}^{[1^N]} \equiv \frac{1}{N!} \sum_{\hat{\tau}} \hat{\xi}_{\hat{\tau}} \hat{\tau} , \quad (71)$$

where antisimmetrizator $\hat{\Omega}_{11}^{[1^N]}$ is the Young operator corresponding to Young scheme of a single column.

Molecular Hamiltonian $\hat{H}$ does not depends on the spins and commutes with all permutations of the electron coordinates. Then, the energy value [47]

$$E = \left\langle \hat{G}_i^{\mu}\Phi\mathrm{X} \middle| \hat{H} \middle| \hat{G}_i^{\mu}\Phi\mathrm{X} \right\rangle / \left\langle \Psi^{(GI)} \mid \Psi^{(GI)} \right\rangle =$$
$$= \left\langle \Phi \middle| \hat{H} \middle| \hat{O}_{ii}^{\mu}\Phi \right\rangle / \left\langle \Phi \mid \hat{O}_{ii}^{\mu}\Phi \right\rangle. \quad (72)$$

We will be further interested in such an approximation of the functions (9) that functions Φ and X can be written as:

$$\Phi = \varphi_1(\vec{r}_1)\,\varphi_2(\vec{r}_2)\cdots\varphi_N(\vec{r}_N),$$
$$\mathrm{X} = \chi_1(s_1)\chi_2(s_2)\cdots\chi_N(s_N), \quad (73)$$

where

$$\chi_i(s_i) = \begin{cases} \alpha(s_i), \\ \beta(s_i). \end{cases}$$

Substituting (73) into (72) and varying the functional

$$I = E - \sum_j \varepsilon_j \left\langle \varphi_j \mid \varphi_j \right\rangle$$

by φ_j, one obtains an equation for the normalized orbitals minimizing (72), namely:

$$\hat{H}_k(\vec{r})\varphi_k(\vec{r}) = \varepsilon_k\,\varphi_k(\vec{r}), \quad (k = 1,2,...,N) \quad (74)$$

where $\hat{H}_k(\vec{r})$ is rather complicated effective Hamiltonian, which depends on the functions φ_k. Equations (74) is a set of nonlinear integro-differential SCF equations for variation function (63). In other words, the orbitals $\varphi_k(\vec{r})$ can be considered as eigenfunctions, which describe the state of an electron in the field of the nuclei and a certain averaged field of the remaining $N-1$ electrons.

It is easy to establish connection between the function (70) and variational Fock function [42] in the form of Slater determinant [53, 54]. Let us select Φ and X in the form

$$\Phi_0 = \hat{\tau}_{1i}\varphi_1(\vec{r}_1)\varphi_1(\vec{r}_2)\cdots\varphi_m(\vec{r}_{2m-1})\varphi_m(\vec{r}_{2m})\varphi_{m+1}(\vec{r}_{2m+1})\cdots\varphi_n(\vec{r}_N),$$
$$\mathrm{X}_0 = \hat{\tau}_{fi}\alpha(1)\beta(2)\cdots\alpha(2m-1)\beta(2m)\alpha(2m+1)\cdots\alpha(n+m), \quad (75)$$

where $\hat{\tau}_{ji}$ is a permutation by which one obtains table *j* from table *i*. The function $\hat{G}_i^{\mu}\Phi_0\mathrm{X}_0$ coincides up to a phase factor with the Slater determinant. Thus, equations (74) are a generalization of the Hartree-Fock approximation, since during transition from (73) to (75) we superimpose additional constraints on the form of the variation function. This implies that

$$E^{(GI)} = \frac{\left\langle \hat{G}_i^{\mu}\Phi\mathrm{X} \middle| \hat{H} \middle| \hat{G}_i^{\mu}\Phi\mathrm{X} \right\rangle}{\left\langle \hat{G}_i^{\mu}\Phi\mathrm{X} \mid \hat{G}_i^{\mu}\Phi\mathrm{X} \right\rangle} \le \frac{\left\langle \Psi^{(HF)} \middle| \hat{H} \middle| \Psi^{(HF)} \right\rangle}{\left\langle \Psi^{(HF)} \mid \Psi^{(HF)} \right\rangle} . \quad (76)$$

When solving equations (74) it is convenient to use the Roothaan's method [56]. Let us expand the orbitals φ_k over a certain basis functions χ_{ν}:

$$\varphi_k = \sum_{\nu=1}^{M} C_{\nu k}\chi_{\nu} \quad (M \ge N) . \quad (77)$$

Then from (74) one obtains the equations for the expansion coefficients $C_{\nu k}$ of the form

$$\sum_{\nu=1}^{M} H_{\mu\nu}^{(k)} C_{\nu k} = \sum_{\nu=1}^{M} \varepsilon_k S_{\mu\nu} C_{\nu k} , \quad (78)$$

where $S_{\mu\nu}$ are overlap integrals of the basis functions. Equation (78) is solved by the method of successive approximations [55]. It should be noted that in the general case (for any *i* in the formula (70)) the matrices $H_{\mu\nu}^{(k)}$ depend on *k* [47], which considerably complicates the solution of the equations (78) in comparison with the analogous equations for the Fock variational function. However, if *i=f*, thus a variation function $\hat{G}_f^{\mu}\Phi\mathrm{X}$ is used, equations (78) take the form [48]

$$\sum_{\nu=1}^{M} H_{\mu\nu}^{(a)} C_{\nu k}^{(a)} = \sum_{\nu=1}^{M} \varepsilon_k^{(a)} S_{\mu\nu} C_{\nu k}^{(a)} , \quad (79)$$

$$\sum_{\nu=1}^{M} H_{\mu\nu}^{(b)} C_{\nu k}^{(b)} = \sum_{\nu=1}^{M} \varepsilon_k^{(b)} S_{\mu\nu} C_{\nu k}^{(b)} . \quad (80)$$

Thus, if one uses the operator $\hat{G}_f^{\mu}$ for the construction of the wave function (70), then one obtains only two sets of equations for the expansion coefficients $C_{\nu k}$. Solving the system of equations (79)–(80), we obtain two sets of orthonormal vectors $\{ C_{\nu k}^{(a)} \}$ and $\{ C_{\nu k}^{(b)} \}$. If $i \neq f$, in the general case, these vectors are not orthogonal. Thus the wave function of the GF method is represented in the form

$$\Psi^{(GF)} = \hat{G}_f^{\mu} \Phi_1 \mathrm{X}_1 , \quad (81)$$

where

$$\Phi_1 = \varphi_{1a}(1) \cdots \varphi_{na}(n) \varphi_{1b}(n+1) \cdots \varphi_{mb}(N) , \quad (82)$$

$$\mathrm{X}_1 = \alpha(1) \cdots \alpha(n) \beta(n+1) \cdots \beta(n+m) , \quad (83)$$

$$\varphi_{ia} = \sum_{\nu} C_{\nu i}^{(a)} \chi_{\nu} , \quad \varphi_{ib} = \sum_{\nu} C_{\nu i}^{(b)} \chi_{\nu} . \quad (84)$$

Expansion vectors of different subsets, in general, are not orthogonal:

$$\left\langle \varphi_{ia} \mid \varphi_{jb} \right\rangle \neq 0 \quad (i, j = 1,2,...,M) . \quad (85)$$

Amos and Hall have shown [56] that it is always possible to make such a unitary transformation of the functions in (82):

$$\varphi'_{ia} = \sum_{l=1}^{n} \varphi_{la} V_{li} \quad (\hat{V}\hat{V}^{+} = \hat{I}), \quad (86)$$

$$\varphi'_{jb} = \sum_{l=1}^{m} \varphi_{lb} U_{lj} \quad (\hat{U}\hat{U}^{+} = \hat{I}), \quad (87)$$

that

$$\left\langle \varphi'_{ia} \mid \varphi'_{jb} \right\rangle = \lambda_i \delta_{ij} , \quad \lambda_i \leq 1 \quad \begin{pmatrix} i = 1,2,...,n \\ j = 1,2,...,m \end{pmatrix} . \quad (88)$$

A method to obtain matrices $\hat{V}$ and $\hat{U}$ is explicitly described in [56, 57]. Functions that satisfy equations (88), are usually referred to as the *corresponding orbitals* [58].

Goddard [48] has shown that the function (81) and the matrices of the operators $\hat{H}^{(a)}$ and $\hat{H}^{(b)}$ appearing in the equations (79) and (80) are invariant under the transformation (86)–(87). However, if you require that the self-consistent solutions of the equations (79) and (80) satisfy (88), you'll lose the one-particle interpretation of the solutions. In other words, the orbitals φ'_{ia} and φ'_{ib} can not be interpreted as a state of an electron in the field of the nuclei and the average field of the other electrons. Moreover, matrices of operators $\hat{H}^{(a)}$ and $\hat{H}^{(b)}$, will depend on *k*. On the other hand, it is much easier to calculate the matrices of operators $\hat{H}^{(a)}$, $\hat{H}^{(b)}$ and corresponding energies over orbitals φ'_{ia} and φ'_{ib}, rather than over orbitals φ_{ia} and φ_{ib}.

Matrix elements of operator $\hat{H}^{(a)}$ are the following [48]:

$$\begin{aligned} H_{\mu\nu}^{(a)} &\equiv \left\langle \mu \mid \hat{h} \mid \nu \right\rangle \wp_a^a + \\ &+ \sum_{i,\nu} \left[\left\langle \mu \mid \hat{h} \mid i \right\rangle \left\langle vb \mid \nu \right\rangle \wp_{i,a}^{a,vb} + \left\langle \mu \mid vb \right\rangle \left\langle i \mid \hat{h} \mid \nu \right\rangle \wp_{vb,a}^{a,i} \right] + \\ &+ \sum_{u,v} \left\langle \mu \mid ub \right\rangle \left\langle vb \mid \nu \right\rangle \sum_{i,j} \left\langle i \mid \hat{h} \mid j \right\rangle \wp_{ub,a,j}^{a,vb,i} + \\ &+ \sum_{i,j} \left[\left\langle \mu, i \mid \hat{g} \mid \nu, j \right\rangle \wp_{a,j}^{a,i} + \left\langle \mu, i \mid \hat{g} \mid j, \nu \right\rangle \wp_{j,a}^{a,i} \right] + \\ &+ \sum_{i,j,t;\nu} \left[\left\langle \mu, i \mid \hat{g} \mid j, t \right\rangle \left\langle vb \mid \nu \right\rangle \wp_{j,a,t}^{a,vb,i} + \right. \\ &\left. + \left\langle \mu \mid vb \right\rangle \left\langle j, t \mid \hat{g} \mid \nu, i \right\rangle \wp_{vb,a,i}^{a,j,t} \right] + \\ &+ \sum_{u,v} \left\langle \mu \mid ub \right\rangle \left\langle vb \mid \nu \right\rangle \sum_{i<j;s,t} \left\langle i, j \mid \hat{g} \mid s, t \right\rangle \wp_{ub,a,s,t}^{a,vb,i,j} - \\ &- E \sum_{u,v} \left\langle \mu \mid ub \right\rangle \left\langle vb \mid \nu \right\rangle \wp_{ub,a}^{a,vb} , \end{aligned} \quad (89)$$

and similarly for $\hat{H}^{(b)}$, where

$$\left\langle \mu \mid \hat{A} \mid vb \right\rangle \equiv \int d\vec{r} \, \chi_{\mu}^{*}(\vec{r}) \hat{A}(\vec{r}) \varphi_{vb}(\vec{r}) ,$$

$$\hat{h}(r) = -\frac{1}{2}\Delta + \hat{V}(r) ,$$

$$\left\langle i, j \mid \hat{g} \mid t, s \right\rangle = \int d\vec{r}_1 \, d\vec{r}_2 \, \varphi_i^{*}(\vec{r}_1) \varphi_t(\vec{r}_1) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \varphi_j^{*}(\vec{r}_2) \varphi_s(\vec{r}_2) .$$

The quantities $\wp$ are quite complicated functions of overlap integrals λ_i defined by (88), for example:

$$\wp_a^a = \sum_{p=0}^{m-1} \binom{n}{p}^{-1} A_p \equiv T00 ,$$

$$A_p = \sum_{\substack{\{k_1, k_2, ..., k_p\} \\ (k_i \neq k_j)}} x_{k_1} x_{k_2} \cdots x_{k_p} , \quad x_k = \lambda_k^2 .$$

It follows from (89) that there are all together 78 matrices of the operators $\hat{\wp}$. Expressions for all matrices given in [48] for Hamiltonians $\hat{H}^{(a)}$ and $\hat{H}^{(b)}$ are based on orbitals satisfying (88).

Normalization integral for the function (81)

$$\left\langle \Psi^{(GF)} \mid \Psi^{(GF)} \right\rangle = T00 . \quad (90)$$

With the assumption that the unitary transformations (86) and (87) were performed and $\varphi_i^{*} = \varphi_i$ the average energy value over the function $\Psi^{(GF)}$ is the following [5]:

$$E^{(GF)} = \left\langle \Psi^{(GF)} \mid \hat{H} \mid \Psi^{(GF)} \right\rangle / T00 =$$
$$= \{\{\sum_{i=1}^{m}[(\left\langle ia \mid \hat{h} \mid ia \right\rangle + \left\langle ib \mid \hat{h} \mid ib \right\rangle)T01(i) + 2\lambda_i \left\langle ia \mid \hat{h} \mid ib \right\rangle T11(i)] +$$
$$+\frac{1}{2}\sum_{i,j=1}^{m}\left\{\begin{array}{l} T02(i,j)[(ia,ia+ib,ib \mid ja,ja+jb,jb)-(ia,ja \mid ja,ia)-(jb,ib \mid ib,jb)] \\ +T12(i,j)\{2\lambda_i[(ia,ib \mid ja,ja+jb,jb)-(ja,ia \mid ib,ja)-(ia,jb \mid jb,ib)] \\ +2\lambda_j[(ia,ia+ib,ib \mid ja,ja)-(ia,jb \mid ja,ia)-(ib,ja \mid jb,ib)] \\ +2\lambda_i\lambda_j(ia,ja \mid jb,ib)+(ib,ja \mid ja,ib)+(ia,jb \mid jb,ia)\} \\ +2T22(i,j)\lambda_i\lambda_j[2(ia,ib \mid ja,jb)-(ia,jb \mid ja,ib)] \end{array}\right\} +$$
$$+\sum_{i=1}^{m}[T01(i)(ia,ia \mid ib,ib)+T11(i)(ia,ib \mid ib,ia)] +$$
$$+\sum_{l=m+1}^{n}\sum_{i=1}^{m}\left\{\begin{array}{l} T01(i)[(ia,ia \mid l,l)+(ib,ib \mid l,l)-(ia,l \mid l,ia)] \\ +T11(i)\{(ib,l \mid l,ib)+2\lambda_i[(ia,ib \mid l,l)-(ia,l \mid l,ib)]\} \end{array}\right\}\}\} \times T00^{-1} +$$
$$+\sum_{l=m+1}^{n}\left\langle l \mid \hat{h} \mid l \right\rangle + \sum_{k>l=m+1}^{n}[(l,l \mid k,k)-(l,k \mid k,l)], \qquad (91)$$

where

$$(i,j \mid s,t) \equiv \left\langle i,s \mid \hat{g} \mid j,t \right\rangle,$$

$$\left.\begin{array}{l} TIJ = \sum_{p=0}^{m-J}\binom{n}{p+I}^{-1} A_p, \\ TIJ(i) = \sum_{p=0}^{m-J}\binom{n}{p+I}^{-1} A_p(i), \\ TIJ(i,j) = \sum_{p=0}^{m-J}\binom{n}{p+I}^{-1} A_p(i,j), \end{array}\right\} \qquad (92)$$

$$\left.\begin{array}{l} A_p(i) = A_p - x_i A_{p-1}(i) = A_p \mid_{x_i=0}, \\ A_p(i,j) = A_p(i) - x_j A_{p-1}(i,j) = A_p \mid_{x_i=x_j=0}, \\ A_0 = A_0(i) = A_0(i,j) = 1. \end{array}\right\} \qquad (93)$$

Iterative procedure for solving equations (79) and (80) is as following. Compute the eigenvectors $C_k^{(a)}(i)$ and $C_k^{(b)}(i)$ of the equations (79) and (80) on the *i*-th iteration. Then, being performed the transformations (86) and (87) and defined the corresponding vectors $C_k'^{(a)}(i)$ and $C_k'^{(b)}(i)$, we build new matrices $H^{(a)}(i+1)$ and $H^{(b)}(i+1)$. Compute the eigenvectors on the ($i+1$)-th iteration and so on unless the self-consistent vectors $C_k^{(a)}$ и $C_k^{(b)}$ are obtained. Thus, the procedure for solving the equations (79) and (80) is just similar to the solution of the Hartree-Fock single-determinant wave function in the algebraic approach [55]. The only difference lies in the fact that it is necessary to solve two coupled equations (79) and (80) and to perform the transformations (86) and (87) at each iteration. Nevertheless note that the matrices of operators $\hat{H}^{(a)}$ and $\hat{H}^{(b)}$ are much more complicated than the corresponding matrix in the Hartree-Fock-Roothaan method [55]. Thus, if the latter contains only three types of the matrix elements: one-electron, Coulomb and exchange ones, the matrices of the operators $\hat{H}^{(a)}$ and $\hat{H}^{(b)}$ in general case contain 2×78 types of matrix elements.

As a final result of the self-consistent procedure described above one obtains the orbitals φ_{ia} and φ_{ib} minimizing the energy expression (91). According to (76) a value of the total energy of the system obtained in this way is always not higher than the energy in the Hartree – Fock – Roothaan approach. Note also that the average values of the electron and spin densities can also be calculated with the function (81) built on corresponding orbitals since the function (81) is invariant under transformations (86) and (87) [56].

The Goddard' GF-functions method relates to other similar methods proposed earlier. Pople and Nesbet [59] proposed to vary the energy over a function of the form

$$\Psi^{(UHF)} =$$
$$= \hat{\Omega}_{11}^{[1^N]}\psi_{1\alpha}(1)\cdots\psi_{n\alpha}(n)\psi_{1\beta}(n+1)\cdots\psi_{m\beta}(N) =$$
$$= \frac{1}{N!}\sum_{i=1}^{N!}\xi_{\hat{\tau}_i}[\hat{\tau}_i\varphi_{1a}(\vec{r}_1)\cdots\varphi_{na}(\vec{r}_n)\varphi_{1b}(\vec{r}_{n+1})\cdots\varphi_{mb}(\vec{r}_N)]\times$$
$$\times[\hat{\sigma}_i\alpha(s_1)\cdots\alpha(s_n)\beta(s_{n+1})\cdots\beta(s_{n+m})] = \hat{\Omega}_{11}^{[1^N]}\Phi_1 X_1, \qquad (94)$$

where

$$\psi_{i\alpha}(k) = \varphi_{ia}(\vec{r}_k)\alpha(s_k),$$
$$\psi_{i\beta}(k) = \varphi_{ib}(\vec{r}_k)\beta(s_k), \quad (\varphi_{ia} \neq \varphi_{ib}),$$

$\hat{\tau}_i$ – permutation operator of electron spatial coordinates, $\hat{\sigma}_i$ – permutation operator of spin coordinates of the electrons, and the summation is taken over all *N*! permutations of the group S_N, $\xi_{\hat{\tau}_i}$ – parity of the permutation $\hat{\tau}_i$.

Optimizing orbitals φ_{ia} and φ_{ib}, appearing in (94), one can obtain the energy lower than the Hartree-Fock energy value. This method was named as *unrestricted Hartree-Fock method* (UHF). However, as it follows from (71), the wave function (94) is a mixture of various multiplets, as a consequence it is not an eigenfunction of the operator $\hat{S}^2$. Therefore, the application of the variational function (94) to calculate the electronic structure of molecules in a rigorous approach is not justified.

To eliminate this shortcoming Lowdin [60–62] proposed to pick out the required spin component from the function (94) by projection operators $\hat{O}_l$:

$$\Psi_l = \hat{O}_l\Psi^{(UHF)}, \qquad (95)$$

where

$$\hat{O}_l = \prod_{k\neq l} \frac{\hat{S}^2 - k(k+1)}{l(l+1)-k(k+1)}. \quad (96)$$

It is also possible to vary the orbitals φ_{ia} and φ_{ib} entering the function Ψ_l by minimization the expression

$$E^{(EHF)} = \langle \Psi_l | \hat{H} | \Psi_l \rangle / \langle \Psi_l | \Psi_l \rangle. \quad (97)$$

This approach was named as *extended Hartree – Fock method* (EHF).

The wave function (95) can be represented [62] as

$$\Psi_l^{(EHF)} = \hat{\Omega}_{11}^{[1^N]} \Phi_1 \hat{O}_l \chi_1 = \hat{\Omega}_{11}^{[1^N]} \Phi_1 \sum_{p=0}^{m} C_p(l, M_S) \chi_1^{(p)}, \quad (98)$$

where $M_S = (n-m)/2$ is the projection of the total spin of the electrons on a choosen direction,

$$\chi_1^{(p)} = \sum_{\sigma_p} \hat{\sigma}_p \chi_1, \quad (99)$$

with $\hat{\sigma}_p$ being the operator interchanging *p* indices of the subset *a* with *p* indices of the subset *b*, i.e. $\hat{\sigma}_p$ is similar to $\hat{\tau}_p$ in (67). The explicit form of the coefficients $C_p(l, M_S)$ for different cases was obtained by Lowdin [62], Sasaki and Ohno [63], and Smith [64]. The most general expression of these coefficients is [63]:

$$C_p(S, M_S) = \\ = (2S+1)\frac{(m+S-M_S-p)!(S+M_S)!}{(S-M_S)!}\sum_t \frac{(-1)^t}{t!}\frac{[(S-M_S+t)!]^2}{(S-M_S+t-p)!(m-t)!(2S+1)!}$$

There is hold more simple expression for the case $S = M_S$ [63]:

$$C_p(M_S, M_S) \equiv C_p(S) = (-1)^p \frac{2S+1}{n+1}\binom{n}{p}^{-1}. \quad (100)$$

Calculation of average values of operators over wave functions of the form (95) is quite complicated even when the operators are not spin dependent. This is due to the fact that the summation over the spin variables in expressions such as (97) is a rather cumbersome task.

Nevertheless, there were obtained a number of general expressions for the EHF method – expressions for the electron and the spin density matrices as well as for energy [60, 61, 65–67].

As shown by Goddard [47], the wave function (98) for the case $S = M_S$ can be represented as

$$\Psi^{(EHF)} = \hat{O}_S \hat{\Omega}_{11}^{[1^N]} \Phi_1 X_1 = \hat{\Omega}_{11}^{[1^N]} \Phi_1 \hat{\omega}_{11}^{[n,m]} X_1 = \\ = \frac{1}{f} \hat{G}_f^{[2^m, 1^{n-m}]} \Phi_1 X_1 = \frac{1}{f} \Psi^{(GF)}. \quad (101)$$

This is easily seen by comparing the expressions (65) and (69) for the operators $\hat{\omega}_{ri}^{\mu}$ and matrix elements $U_{11}^{[n,m]}$ with the expression (100) for the coefficients $C_p(S)$ in (98). Thus, the EHF wave function is equivalent to the Goddard GF wave function if $S = M_S$. However, taken into account the expression (72), we note that the calculation of the average values of the spin-independent operators much simpler to perform by Goddard's method due to summation over the spin variables in (72) is taken out of the brackets and canceled. Furthermore, the using of the theory of the permutation group in general facilitates the reduction of the equations for the optimum orbitals φ_{ia} and φ_{ib}, entering in $\Psi^{(EHF)}$, to the eigenvalue equation of the form (79)–(80) [48].

In connection with the difficulties described above in calculating the optimum EHF orbitals for specific calculations of π-electronic molecular structures the simplified EHF version named as the *alternant molecular orbitals* (AMO) method has been used much wider. This method was proposed by Lowdin [60, 68–70]. The method consists in the following. Suppose that the orthonormal set of orbitals $\{a_k\}$ that are solutions of the Hartree – Fock – Roothaan equation or even in the worst case of the Huckel equation [28, 71, 72] is known. Suppose further that the ground state of a molecular system is described in this approximation by single determinant wave function which contains *m* doubly filled orbitals $a_1, a_2, a_3, ..., a_m$ and $n-m$ singly occupied orbitals $a_{m+1}, ..., a_n$. Under these assumptions, the wave function of the AMO method is constructed as following. Each of the doubly occupied orbitals $a_k (1 \le k \le m)$ according to a certain rule is matched with one of the vacant orbitals $a_{\bar{k}} (\bar{k} > m)$ and thus two orthonormal AMO sets are constructed:

$$\left.\begin{aligned} \varphi_{ka} &= \cos\theta_k a_k + \sin\theta_k a_{\bar{k}}, \quad (k = 1,2,3,...,m) \\ \varphi_{kb} &= \cos\theta_k a_k - \sin\theta_k a_{\bar{k}}, \quad (k = 1,2,3,...,m) \\ \varphi_{ka} &= a_k. \quad (k = m+1,...,n) \end{aligned}\right\} \quad (102)$$

Substituting Φ_1 in (98) as

$$\Phi_1 = \varphi_{1a}(1)\cdots\varphi_{na}(n)\varphi_{1b}(n+1)\cdots\varphi_{mb}(N),$$

one obtains the wave function $\Psi^{(AMO)}$ of the *multi-parameter AMO method.* Since orbitals (102) satisfy (88) due to orthogonality of orbitals a_k, the average energy value

$$E^{(AMO)} = \langle \Psi^{(AMO)} | \hat{H} | \Psi^{(AMO)} \rangle / \langle \Psi^{(AMO)} | \Psi^{(AMO)} \rangle \quad (103)$$

will be determined by the expression (91). Varying $E^{(AMO)}$ over θ_k, one obtains optimal AMO of the form (102). If the above procedure is performed with all θ_k being the same ($\theta_k = \theta$), the corresponding method is called a *single-parameter AMO* method.

Let us consider certain features of the AMO method applied to alternant systems. Molecular systems are called alternant ones if their atoms can be split into two subsets such as the nearest neighbors of an atom of one subset are being only atoms of the other subset [73]. In the case of π-electron system of the alternant hydrocarbons to obtain AMO (48) complementary orbitals a_k and $a_{\bar{k}}$ are pairing in the following way [74]:

$$\begin{aligned} a_k &= \sum_{\nu^*} C_{\nu k}\chi_\nu + \sum_{\nu^{**}} C_{\nu k}\chi_\nu, \\ a_{\bar{k}} &= \sum_{\nu^*} C_{\nu k}\chi_\nu - \sum_{\nu^{**}} C_{\nu k}\chi_\nu, \end{aligned} \qquad (104)$$

where $\sum_{\nu^*}$ means that the summation is taken over the atoms of a one subset, and $\sum_{\nu^{**}}$ – over the atoms of another subset. A detailed description of the AMO method and its applications is given in [67].

It is easy to establish a connection between EHF and AMO methods [56, 68]. If the energy (103) is minimized not only over θ_k, but also over the orbitals a_k, one obtains the wave function and energy of the EHF nethod. In fact, the orbitals φ_{ka} and φ_{kb} in (98) can always be transformed in a way as to hold the relation (88). Orbitals that satisfying (88) can be represented in a form of (102) [56] if

$$\left.\begin{aligned} a_k &= (\varphi_{ka}+\varphi_{kb})(2+2\lambda_k)^{-1/2}, \quad (k=1,2,3,...,m) \\ a_{\bar{k}} &= (\varphi_{ka}-\varphi_{kb})(2-2\lambda_k)^{-1/2}, \quad (k=1,2,3,...,m) \\ a_k &= \varphi_{ka}, \qquad\qquad\qquad\qquad (k=m+1,...,n) \end{aligned}\right\} \qquad (105)$$

where

$$\lambda_k = \langle \varphi_{ka} | \varphi_{kb} \rangle = \cos 2\theta_k. \qquad (106)$$

Minimization of the expression (103) represents a problem to find an extremum over for many nonlinear parameters. This is as already mentioned above the main shortage of the computational AMO scheme compared to the method proposed by Goddard.

Thus establishing the connection between different approaches of the SCF theory on variational function with "*different orbitals for different spins*/DODS», namely, between AMO, EHF, and GF methods, we proceed further to discuss the properties of the corresponding solutions, as well as some applications of these methods.

3. 1. Properties of solutions of the generalized Hartree-Fock equations and their applications

We first consider the properties of the EHF self-consistent solutions and focus mostly on the single-particle interpretation of the EHF wave function (81). Equations (74) or (79)–(80) for orbitals φ_{ka} and φ_{kb} can be transformed [50] to

$$\begin{aligned} (\hat{h}+\hat{V}^{GF}_{ka})\varphi_{ka} &= \varepsilon_k^{(a)}\varphi_{ka}, \\ (\hat{h}+\hat{V}^{GF}_{kb})\varphi_{kb} &= \varepsilon_k^{(b)}\varphi_{kb}, \end{aligned} \qquad (107)$$

where $\hat{h}$ – operator of the kinetic energy and potential energy of an electron in the field of the nuclei, $\hat{V}^{GF}$ – effective potential operator of the remaining N–1 electrons. It follows from (107) that the functions φ_{ka} and φ_{kb} can be interpreted as the state of an electron in the field of the nuclei and the average field of the other electrons. In this sense there is a complete analogy with the Hartree-Fock approximation. This important result means the following. Rather than to operate with the Ψ-function of N electrons in the abstract 3N-dimensional space, we can consider certain single-electron function in a real three-dimensional space. In general case, this is not eligible even if one decomposes many-electron wave function into the one-electron functions. One must have equations of the form (107) in order their solutions obey a single-particle interpretation. Considering molecules or solids, we are talking, for example, about an electron of the oxygen atom, inner and valence electrons, conductivity electron, localized electron, π- and σ-electrons, d-electron etc. There is always tacitly assumed that there do exist equations of the form (107), since it is impossible to distinguish between the electrons themselves and therefore can not be said that a certain electron is in a particular state that can appear in the expansion of the exact many-electron Ψ-function. Equations (107) as well as the HF equations do not assume the actual assignment of electrons to particular states. These equations are obtained by approximating the exact wave function (81) with further variation of its orbitals in a way as to minimize the energy. Analyzing the corresponding equations, we note that each orbital is an eigenfunction of a certain operator mapping with the Hamiltonian of an electron moving in the field of the nuclei and the average field of the other N – 1 electrons. Naturally, all these arguments, no matter how convincing they are, do not strictly prove that the solutions of the SCF equations are directly related to the physical quantities and, therefore, make sense of themselves. However, it is clear that these solutions have a number of convenient and useful properties.

Goddard has shown [50] that the energy (91) of N-electron system can be represented as a sum of two terms:

$$E^{(GF)} = E(N) = E(N-1) + e_k, \quad e_k = \varepsilon_k / D_k^k, \qquad (108)$$

where the term $E(N-1)$ does not depend on the state of the N-th electron. This expression is valid for all orbitals φ_{kb}, *i. e.* orbital energies $\varepsilon_k^{(b)}$ have a meaning of ionization potentials predicted by EHF. This statement is known as Koopmans' theorem [75]. In all fairness, we note that Koopmans' theorem is just approximate: ionization potentials predicted close to the experimental values if an error in the description of N – 1 electrons is compensated by a change of correlation energy passing from N–1 to N electrons. It is also obvious that the Koopmans' theorem is asymptotically exact.

If one uses the Roothaan method [55], than each of the equations (79) and (80) will have $M \geq N$ solutions φ_{ka} and φ_{kb}, respectively. The question arises as which of these solutions should be used to construct the EHF Ψ-function. It is shown in [50] that there should be selected n orbitals φ_{ka} and m orbitals φ_{kb} with minimal Lagrange multiplier $\varepsilon_k^{(a)}$ and $\varepsilon_k^{(b)}$, *i. e.* procedure for orbital selection is the same as in the Hartree-Fock-Roothaan method. Exceptions to this rule may be accounted in a case of multiple degeneration of ε_k [50], for example, when treating the heavy atoms.

If one of the orbitals in the EHF wave function (81), for example $\varphi_{ka}(k \le n)$ or $\varphi_{kb}(k \le m)$ is replaced by one of the vacant orbitals $\varphi_{k'a}(k' > n)$ or $\varphi_{k'b}(k' > m)$ respectively, we obtain some kind of the excited configuration $\Psi^{(EHF)}(k,k')$, where k – the number of the orbital replaced, and k' – the number of replacing orbital. Goddard has shown [50] that

$$\left\langle \Psi^{(EHF)}(k,k') \,|\, \hat{H} \,|\, \Psi^{(EHF)} \right\rangle = 0 . \qquad (109)$$

Thus, the Brillouin theorem [76–79] is hold in the frame of the EHF approach, which is simply equivalent to the variational principle. Note also that in the general case

$$\left\langle \Psi^{(EHF)}(k,k') \,|\, \Psi^{(EHF)} \right\rangle \ne 0 . \qquad (110)$$

The spatial symmetry of the one-electron orbitals within EHF approach was discussed by Goddard [50] and Popov [80] for the singlet state. It was shown that the requirement of non-degeneracy of the ground state wave function $\Psi^{(EHF)}$ imposes the limitations of one of two possible types on the symmetry properties of the orbitals. The first possibility corresponds to the case when orbitals of each of the sets $\{\varphi_{ka}\}$ and $\{\varphi_{kb}\}$ should be the basis functions of the irreducible representations of the symmetry group *G*. In this case partitioning of sets into irreducible subsets may not be equivalent. Eigenvalues $\varepsilon_k^{(a)}$ and $\varepsilon_k^{(b)}$ in (79) and (80) may also be different.

The second possibility is feasible for symmetry groups having at least one subgroup *g* of index 2. In this case orbitals of each sets must be the basis functions of the irreducible representations of the subgroup *g*, and partitioning of sets into irreducible subsets should be equivalent. Eigenvalues $\varepsilon_k^{(a)}$ and $\varepsilon_k^{(b)}$ in (79) and (80) have to be equal, while the corresponding eigenfunctions φ_{ka} and φ_{kb} may be different. Thus, the restrictions imposed on orbitals in EHF approach by symmetry are less severe than similar restrictions in the Hartree – Fock approximation. This conclusion is valid for all *GI*-methods $(I \ne F)$ [47].

To illustrate the methods considered above and the pecularities of their solutions let us consider some typical examples. Different orbitals for different spins φ_{ia} and φ_{ib} have been proposed for the first time by Hylleraas [81] and Eckart [82] for He atom. In this case, the coordinative part of the function (63) for the singlet ground state

$$\Phi(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{2}}[\varphi_a(\vec{r}_1)\varphi_b(\vec{r}_2) + \varphi_b(\vec{r}_1)\varphi_a(\vec{r}_2)],$$

with $\varphi_a = \varphi_b$ corresponds to the traditional method of Hartree-Fock approximation. In the frame of the EHF method with this function it is accounted 93 % of the radial correlation energy [83, 84]. Within the UHF method with functions φ in exponential form

$$\varphi_a(\vec{r}_i) \sim \exp(-\alpha \vec{r}_i), \quad \varphi_b(\vec{r}_i) \sim \exp(-\beta \vec{r}_i)$$

80 % of the correlation energy is accounted for, and exponents are $\alpha = 2.183$ and $\beta = 1.189$. Calculations in this approximation for the isoelectronic series H^-, He and Li^+ are made in [85, 86], and for large values of the nuclear charge Z up to Z=10 are published in [87]. It was found that orbital splitting is decreased with increasing of Z. The exponents α and β should not be interpreted as the effective charges. In particular, the assumption that an «effective charge of the outer electron" β will be striving for *Z*–1 with increasing Z [85], was not confirmed [87].

Consider the calculation of the H_2 molecule in the framework of GF approach and compare results with similar calculations by the Hartree-Fock-Roothaan method [47]. Function (70) of the ground state of the hydrogen molecule is $(m = n = 1)$

$$\Psi^{(G1)} = \hat{G}_1^{[2]}\varphi_a(1)\varphi_b(2)\alpha(1)\beta(2) . \qquad (111)$$

In this case, the *GF* and *G1* methods are equivalent, since there is only one standard Young's table. Molecular orbitals were expanded over the basis consisted of the Slater atomic orbitals (AO) *1s*, *2s*, and *2pσ* of each of the hydrogen atoms. Table 1 shows the expansion coefficients of the self-consistent orbitals φ_a and φ_b appearing in the expression (111) for the equilibrium internuclear distance *R=1.4* and *R=6 a.u*. The letters A and B denote different hydrogen atoms. The second column shows the optimal values of the Slater function exponents.

Table 1

EHF orbitals for the hydrogen molecule

AO	Exponents	φa	φb
R=1.4 a.u.			
A1s	1.3129	0.775023	0.121577
A2s	1.1566	0.111130	0.042025
A2pσ	1.9549	0.003120	0.037667
B1s	1.3129	0.121577	0.775023
B2s	1.1566	0.042025	0.111130
B2pσ	1.9549	0.037667	0.003120
R=6.0 a.u.			
A1s	1.0045	0.993720	0.002525
A2s	0.850	0.007571	0.002730
A2pσ	0.820	0.001209	–0.000870
B1s	1.0045	0.002525	0.993720
B2s	0.850	0.002730	0.007571
B2pσ	0.820	–0.000870	0.001209

As seen from Table. 1, the density $|\varphi_a|^2$ as well as $|\varphi_b|^2$ has different values at different protons even at the equilibrium internuclear distance. When separating nuclei apart molecular orbital φ_a is urging towards the atomic orbital 1s localized on one of the protons, and orbital φ_b – towards an atomic orbital 1s, localized on the other proton. As noted above, such a behavior of self-consistent EHF/GF molecular orbitals is possible due to the fact that the spatial symmetry (in this case the symmetry of the H_2 molecule) does not impose the requirements

$$|\varphi_i(\vec{r} = \vec{R}_A)|^2 = |\varphi_i(\vec{r} = \vec{R}_B)|^2$$

on the EHF orbital. Therefore, the contribution of ionic configurations into the H_2 ground state wave function tends to zero as the nuclei are moving apart. In the Hartree-Fock approach the H_2 ground state wave function has the form $\Psi^{(HF)}=\hat{G}_{11}^{[1^2]}\varphi_1(1)\varphi_1(2)\alpha(1)\beta(2)$, and due to the symmetry of the H_2 molecule

$$|\varphi_1(\vec{r}=\vec{R}_A)|^2=|\varphi_1(\vec{r}=\vec{R}_B)|^2 .$$

Table 2 shows the energy of H_2 for different internuclear distances obtained by the Hartree-Fock method and the GF approach. Slater atomic basis for both calculations are shown in Table 1.

Table 2
The energy of the hydrogen molecule for different internuclear distances, *a.u.*

R	Method		
	HF	GF	Exact
1.4	–1.133449 [88]	–1.151526	–1.174475 [89]
6.0	–0.82199 [88]	–1.000552	
∞	–0.7154 [61]	–1.000000	–1.000000

As follows from Table 2, the GF method in contrast to the Hartree-Fock approximation shows the correct asymptotic behavior of the H_2 energy with moving nuclei apart. We shall see below that this result remains valid for $N>2$. It gives us a possibility to use the GF method to calculate the interaction of atoms and molecules, and this is one of the advantages of EHF approach.

Consider spin density calculations at the nucleus of a lithium atom [47]:

$$\rho_z(\vec{R})=\left\langle\Psi\left|\sum_{i=1}^{N}\hat{s}_z(i)\,\delta(\vec{r}_i-\vec{R})\right|\Psi\right\rangle / S\left\langle\Psi\,|\,\Psi\right\rangle, \quad (112)$$

where $\hat{s}_z(i)$ – spin projection operator of the *i-th* electron, $\delta(\vec{r}\,)$ – three-dimensional Dirac δ-function, *S* – total spin ($S\neq 0$),the nucleus coordinate $\vec{R}=0$.

Table 3 shows the values of $4\pi\rho_z(0)$ and energy of the ground state ^2S of the lithium atom calculated by different methods.

Table 3
Energy and spin density at the nucleus of a lithium atom

Method	$4\pi\rho_z(0)$	Abs. error, %	Energy, *a.u.*
HF	2.094	28	–7.432725
UHF	2.825	2.8	–7.432751
UHF with projection	2.345	19.3	–7.432768
GF/EHF	3.020	3.9	–7.432813
Experiment	2.906	–	–7.4780

The table shows that in contrast to the Hartree-Fock approach EHF and UHF methods give good results for the $\rho_z(0)$ value. If you select a doublet component from the UHF function (94), then after variation of orbitals (UHF with projection), the result obtained for $\rho_z(0)$ is being much worse than in the traditional UHF method.

Among the various applications of the AMO method to alternant hydrocarbons (AH), we note the paper of Swalen and de Heer [90]. It compares the results obtained by a single-parameter and multi-parameter AMO method to conjugate AH with different numbers of π-electrons. We introduce the notation

$$\Delta\varepsilon=\frac{E^{(HF)}-E^{(AMO)}}{N}\geq 0 .$$

It is shown in [90] that in the case of single-parameter AMO method $\Delta\varepsilon$ value decreases with increasing *N*, while in the case of multi-parameter AMO approach $\Delta\varepsilon$ value increases with increasing *N* for the same set of molecules. It can be concluded that the single-parameter AMO method should only be used when calculating small molecules and its application to large electronic systems is not efficient.

We turn now to a possibility of further generalizations of the EHF approach. As already noted, when using the expression (70) for constructing the function Ψ of *N* electrons one can choose *f* different operators $\hat{G}_i^{\mu}$ $(i=1,2,3,...,f)$. The choice of the *i* value can be arbitrary from the physical point of view. This is related to the existence of the so-called spin degeneracy due to the fact that for a given value of the total spin *S* of the *N* electron system and its projection S_z one can construct *f* correct spin functions, where *f* is defined by (66). Selecting *i* value one just defines the type of spin-functions [51]. Ladner and Goddard [51] investigated the effect of the choice of the *i* value to the computational results for the ground state of Li, H_3, and H_4. They were also suggested a generalization of the method which consists in the following – in the expression (70) for the wave function instead of using just one particular operator $\hat{G}_i^{\mu}$ a linear combination of these operators is used whose coefficients are being optimized as well as the corresponding one-electron orbitals. This method was named as *spin-optimized GI* method (SOGI). There were obtained equations for optimal orbitals [51], which of course are much more complicated than in the GI methods. This fact makes the practical applications of the SOGI method difficult. The basic results of [51] are the following. Self-consistent energies and orbitals of the different GI methods are weakly dependent on the choice of the *i* values. The most changes occur in the density matrices, in particular, the spin density (112). Table 4 shows the energies and spin and electron densities for the ground state ^2S of the lithium atom.

Table 4
The energy, spin and electron densities at the nucleus of Li atom depending on the choice of spin-functions

Method	$\rho_z(0)$	$\rho\,(0)$	Energy, *a.u.*
G1	0.2096	13.8646	–7.447560
G2 (GF/EHF)	0.2406	13.8159	–7.432813
SOGI	0.2265	13.8646	–7.447565
HF	0.1667	13.8160	–7.432725
Exp.	0.2313	–	–7.47807

In the third column of table 4 there are shown the values of the electron density at the nucleus of a lithium atom

$$\rho\ (\vec{R}) = \langle \Psi | \sum_{i=1}^{N} \delta(\vec{r}_i - \vec{R}) | \Psi \rangle / \langle \Psi | \Psi \rangle .$$

As seen from Table 4, the G1 method gives better results for the electron density and energy, whereas the GF method best describes the spin density. The energy dependence of the *i* value in (70) is connected with the fact that the equations for optimal orbitals (74) in different GI methods are different. However, as it follows from Table 4, these differences are small.

Thus, we can conclude the following. Improving of the results obtained when going from the GI methods to SOGI approach, is not so important as with transition from Hartree-Fock method to GI, in particular, to GF/EHF method. On the other hand, the computational procedure in the SOGI method is much more complicated than in the EHF method. Therefore, to our opinion EHF method in its various versions and modifications will have more broad application in practical calculations of the electronic structure of molecules.

As noted above, the UHF approach is the simplest method to account for electron correlation and is widely used in the calculations of the electronic structure of molecules and radicals [47, 51, 56, 58, 91, 92]. The UHF wave function (94) is not an eigenfunction of the $\hat{S}^2$ operator. To eliminate this shortage there are usually applying so called total or partial projection of the UHF wave function to the state with the required spin multiplicity [56, 91]. It should be kept in mind that the projected wave function is no longer optimum relative to the variational principle. Therefore, its adequacy to the real situation, in general, is not evident [56]. The next consisting procedure should be further variation of projected wave function to obtain the minimum of the total energy, namely, to use the EHF approach. Nevertheless, the UHF method with partial or complete projection leads often to good agreement with various experimental data, including the hyperfine splittings in the ESR spectra of free radicals. In [58, 91, 92], The results of calculations in the UHF framework with partial projection of the wave function for organic free radicals with a small number of electrons is given in [58, 91, 92].

Benzyl radical $C_6H_5CH_2$ contains already quite a large number of electrons. There are known our results of *ab initio* calculations of benzyl in the basis of Gaussian functions under the UHF framework with full projection on the ground doublet state [57] and without projection [93–95]. It is useful to compare the results in both approximations.

The contribution of the doublet component in the non-projected wave function $\Psi^{(UHF)}$ of the benzyl radical [93–95] turned out be equal 95.4 %, and the remaining 4.6 % belongs to the quartet and the higher spin components. Contribution of the doublet component to the $\langle \hat{S}^2 \rangle$ is 84 %, and the quartet component is 15.7 % [57]. This means that the spin projection in the UHF framework can substantially affect only spin characteristics of a radical but distribution of the electron density is almost not influenced. This conclusion is confirmed by numerical calculations [57].

Table 5 shows the distribution of the spin densities $\rho_z^{\pi}(\mathrm{C})$ and $\rho_z(\mathrm{H})$ at the atomic nuclei of the benzyl radical calculated without projection [93–95] and there is also given a comparison of the calculated hyperfine splitting on protons with the experimental data.

Table 5

The spin densities and hyperfine splittings a^H in the benzyl radical calculated according to the UHF framework without projection

Atom	$\rho_z^{\pi}(\mathrm{C})$	a^{H}, *Oe*					$\rho_z(\mathrm{H})$	Atom
		Calculation*	Experiment			Calculation**		
			[96]	[97]	[98]			
C_o	0.276_0	–7.45	5.14	5.15	5.08	–5.88	$–0.011_6$	H_o
C_m	$–0.191_6$	5.17	1.79	1.75	1.7	3.95	0.007_8	H_m
C_p	0.275_7	–7.44	6.14	6.18	6.18	–6.18	$–0.012_2$	H_p
C_α	0.767_1	–18.72	16.35	16.35	15.7	–17.74	$–0.035_0$	H_α

** Calculated according to the McConnell equation [99, 100] with the constants* $Q^{\mathrm{H}}_{\mathrm{CH}} = -27$ *and* $Q^{\mathrm{H}}_{\mathrm{CH_2}} = -24.4$ *Oe [101]*

***Calculated according to the equation* $a^{\mathrm{H}} = Q^{\mathrm{H}} \rho_z(\mathrm{H})$ *with constant* Q^{H}*, equal to the hyperfine splitting in the free hydrogen atom (506.82 Oe)*

As many calculations in the π-electron approximation [102–104], *ab initio* calculations have led to similar values of π-spin density $\rho_z^{\pi}(\mathrm{C})$ at the *ortho* and *para* carbon atoms. Using the simple McConnell equation [99, 100], we obtain the same splittings at the *ortho* and *para* protons which is inconsistent with the experimental data [96–98]. However, the direct calculation of the spin density at the protons $\rho_z(\mathrm{H})$ leads to the correct ratio of the corresponding splittings. From the analysis of the occupation numbers of natural orbitals calculated from UHF wave functions before and after projection, it was shown that the evaluation of the spin density after projection can be performed practically without loss of accuracy from non-projected values multiplied by $S/(S+1)$ [57]. It was shown that this rule is asymptotically exact at $N \to \infty$ [6, 10, 105].

Significant progress in understanding the properties of carbon-chain polymeric systems has been achieved due to the use of different versions of the Generalized HF approaches [106]. Thus, the relative simplicity of UHF equations has allowed to perform a number of analytical calculations of infinite polyene chains [16, 107–110], long polyene radicals [6, 105], cumulenes, polyacenes, and graphite [17, 111], long polyene chains with impurity atoms [7] and take into account the end effects in long polyenes and cumulenes [10]. These calculations have allowed, in particular, to make conclusions about the physical nature of the dielectric properties of such systems [16], which was further confirmed for polyenes by exact solutions [112]. However, the use of the instant UHF approach leaves some doubt primarily because the wave function in this method does not have the correct spin symmetry. Fortunately, this difficulty was overcame surprisingly easily in the calculations of systems with a large number of electrons ($N \gg 1$). It was found [10] that the self-consistent equations for the orbitals in the EHF method asymptotically ($N \to \infty$) coincide with the similar equations in the UHF methods:

$$E_0^{EHF} = E_0^{UHF} + \mathrm{O}\left(\frac{1}{N}\right).$$

Consequently, the energy characteristics of long polyene chains (the ground state energy, the spectrum of low-lying excitations) obtained by UHF methods are preserved if passing to EHF approach.

Now we turn to theory of electronic structure of long polyene neutral alternant radicals based on the different orbital for different spins SCF method.

4. Electronic Structure of Long Neutral Polyene Alternant Radicals by the DODS Method

As shown above the simplest method to account for correlation between electrons with different spins consists in using different orbitals for different spins (DODS). McLachlan [113], considering the polarization of closed shells in a radical due to the field of its unpaired electron, suggested a simple method for the calculation of the spin density based on the DODS approach. His method is restricted by applicability conditions of perturbation theory [14, 34, 114]. In this chapter we suggest a method for the calculation of alternant radicals which is free from this defect and which is more congruous from the point of the self-consistency procedure. This method will be applied to long neutral polyene radicals with the emphases to the spin properties of the wave functions in the DODS approximation. The second quantization formalism [115] will be used.

4.1. The DODS method for alternant radicals

Consider a system with $2n$ electrons in the state with closed shells. In the one-particle approximation the corresponding Hamiltonian correct to a constant is

$$\hat{H}_0 = \sum_{i\sigma} \varepsilon^0(i) \hat{A}^+_{i\sigma} \hat{A}_{i\sigma}\ , \qquad (113)$$

where $\hat{A}^+_{i\sigma}$ and $\hat{A}_{i\sigma}$ are creation and annihilation operators of an electron in the state $\varphi_i(\vec{r})$ with spin σ, the real functions $\varphi_i(\vec{r})$ form a complete orthonormal set, the variable σ takes two values +1/2 and –1/2 (in units of $\hbar$), and $\varepsilon^0(i)$ is the orbital energy in the state i. The corresponding wave function for the ground state is

$$\left|\Psi_0\right\rangle = \prod_{i=1}^{n} \hat{A}^+_{i\uparrow} \hat{A}^+_{i\downarrow} \left|0\right\rangle . \qquad (114)$$

Let us add one more electron to this system filling the state with $i = p$, $\sigma = \uparrow$ and choose as zero approximation the function

$$\left|\Psi^{(0)}\right\rangle = \hat{A}^+_{p\uparrow} \left|\Psi_0\right\rangle . \qquad (115)$$

The corresponding Hamiltonian for a system with $N = 2n+1$ electrons in the SCF approximation will be written as

$$\hat{H} = \hat{H}_0 + \hat{V} = \sum_{i\sigma} \varepsilon^0(i) \hat{A}^+_{i\sigma} \hat{A}_{i\sigma} + \sum_{ij\sigma} V_\sigma(i,j) \hat{A}^+_{i\sigma} \hat{A}_{j\sigma}, \qquad (116)$$

where, using standard notations for the integrals,

$$V_\sigma(i,j) = \left\langle ip\right| \left. jp\right\rangle - \delta_{\sigma\uparrow} \left\langle ip\right| \left. pj\right\rangle . \qquad (117)$$

To the first order of the perturbation $\hat{V}$ the following expression for the spin density is obtained

$$\rho^{(1)}(\vec{r}) = R^{(1)}_\uparrow(\vec{r},\vec{r}) - R^{(1)}_\downarrow(\vec{r},\vec{r}), \qquad (118)$$

$$\rho^{(1)}(\vec{r}) = \varphi_p^2(\vec{r}) - \sum_{ij} \left\langle ip\right| \left. pj\right\rangle \frac{\varphi_i(\vec{r})\varphi_j(\vec{r})}{\varepsilon^0(i) - \varepsilon^0(j)} (n_i - n_j), \qquad (119)$$

where n_i are the occupation numbers for the state $\left|\Psi_0\right\rangle$, and the one-particle density matrix is

$$R^{(1)}_\sigma(\vec{r},\vec{r}\,') = \sum_{ij} \left\langle \Psi^{(1)} \right| \hat{A}^+_{i\sigma} \hat{A}_{j\sigma} \left| \Psi^{(1)} \right\rangle \varphi_i(\vec{r}\,')\varphi_j(\vec{r}), \qquad (120)$$

where $\left|\Psi^{(1)}\right\rangle$ is the first-order wave function for N electrons.

Using a representation of orthogonal AOs

$$\varphi_i(\vec{r}) = \sum_\mu C_{\mu i} \chi_\mu(\vec{r}), \qquad (121)$$

one obtains from (119) the familiar McLachlan expression for the elements of the spin density matrix

$$\rho^{(1)}_{\mu\nu} = \rho^{(0)}_{\mu\nu} - \sum_{ij\kappa\lambda} \gamma_{\kappa\lambda} \frac{C_{\kappa i} C_{\lambda j} C_{\mu i} C_{\nu j}}{\varepsilon^0(i) - \varepsilon^0(j)} (n_i - n_j) C_{\kappa p} C_{\lambda p}, \qquad (122)$$

$$\rho^{(0)}_{\mu\nu} = C_{\mu p} C_{\nu p}, \qquad (123)$$

$$\gamma_{\kappa\lambda} = \left\langle \kappa\lambda\right| \left. \kappa\lambda\right\rangle . \qquad (124)$$

Expressions (119) and (122) are valid if the applicability conditions of perturbation theory

$$|\varepsilon^0(i) - \varepsilon^0(j)| \gg V_\sigma(i,j) \quad (i \neq j) \qquad (125)$$

are satisfied. To eliminate conditions (125) we shall account for the polarization of closed shells of a radical without the use of the perturbation theory.

We shall consider large neutral alternant radicals ($N \gg 1$) for which conditions (125) break down.

For these systems Hamiltonian (116), neglecting terms of order N^{-2}, can be written as

$$\hat{H} = \sum_{\substack{i\sigma \\ (1\le i\le (N+1)/2)}} [\varepsilon'_\sigma(i)(\hat{A}^+_{i\sigma}\hat{A}_{i\sigma} + \hat{A}^+_{\bar{i}\sigma}\hat{A}_{\bar{i}\sigma}) + $$
$$+a_\sigma(i)(\hat{A}^+_{i\sigma}\hat{A}_{\bar{i}\sigma} + \hat{A}^+_{\bar{i}\sigma}\hat{A}_{i\sigma})], \qquad (126)$$

where

$$\varepsilon'_\sigma(i) = \varepsilon^0(i) + \Delta\varepsilon_\sigma(i), \quad \Delta\varepsilon_\sigma(i) = V_\sigma(i,i),$$
$$a_\sigma(i) = V_\sigma(i,\bar{i}), \quad \varepsilon^0(\bar{i}) = -\varepsilon^0(N-i),$$

and we suppose in the following that the unpaired electron occupies the non-bonding orbital

$$p = (N+1)/2 \text{ with } \varepsilon^0(p) = 0.$$

The Hamiltonian (126) can be diagonalized by the following canonical transformation of the annihilation operators

$$\hat{A}_{i\sigma} = [\hat{B}_{i\sigma} + \xi_\sigma(i)\tilde{\hat{B}}_{\bar{i}\sigma}]\Im^{-1/2}_\sigma(i), \qquad (127)$$

$$\hat{A}_{\bar{i}\sigma} = [\tilde{\hat{B}}_{\bar{i}\sigma} - \xi_\sigma(i)\hat{B}_{i\sigma}]\Im^{-1/2}_\sigma(i), \qquad (128)$$

$$\hat{B}_{i\sigma} = [\hat{A}_{i\sigma} - \xi_\sigma(i)\hat{A}_{\bar{i}\sigma}]\Im^{-1/2}_\sigma(i), \qquad (129)$$

$$\tilde{\hat{B}}_{\bar{i}\sigma} = [\hat{A}_{\bar{i}\sigma} + \xi_\sigma(i)\hat{A}_{i\sigma}]\Im^{-1/2}_\sigma(i), \qquad (130)$$

and similar expressions for the creation operators, where

$$\Im_\sigma(i) = 1 + \xi^2_\sigma(i),$$

and $\xi_\sigma(i)$ are certain real values. It is easy to show that the operators $\hat{B}_{i\sigma}$, $\hat{B}^+_{i\sigma}$ as well as the operators $\hat{A}_{i\sigma}$, $\hat{A}^+_{i\sigma}$ satisfy the same commutation rules.

The transformation (127)–(130) mixes orbital $\varphi_i(\vec{r})$ only with its complementary orbital, and the mixing coefficients $\xi_\sigma(i)$ may be different for different spins. See also [116] where a charge-density wave state has been discussed using a phasefactor in (127)–(130) which may depend on spin.

Substituting (127)–(130) into (126) one obtains

$$\hat{H} = \sum_{\substack{i\sigma \\ (1,2,\ldots,n+1)}} \{\varepsilon_\sigma(i)\hat{B}^+_{i\sigma}\hat{B}_{i\sigma} + \tilde{\varepsilon}_\sigma(i)\tilde{\hat{B}}^+_{\bar{i}\sigma}\tilde{\hat{B}}_{\bar{i}\sigma} +$$
$$+[2\xi_\sigma(i)\varepsilon^0(i) + a_\sigma(i)(1-\xi^2_\sigma(i))]\times$$
$$\times\Im^{-1}_\sigma(i)(\hat{B}^+_{i\sigma}\tilde{\hat{B}}_{\bar{i}\sigma} + \tilde{\hat{B}}^+_{\bar{i}\sigma}\hat{B}^+_{i\sigma})\}, \qquad (131)$$

where

$$\varepsilon_\sigma(i) = \{\varepsilon^0(i)[1-\xi^2_\sigma(i)] -$$
$$-2\xi_\sigma(i)\,a_\sigma(i)\}\Im^{-1}_\sigma(i) + \Delta\varepsilon_\sigma(i), \qquad (132)$$

$$\tilde{\varepsilon}_\sigma(i) = \{-\varepsilon^0(i)[1-\xi^2_\sigma(i)] +$$
$$+2\xi_\sigma(i)\,a_\sigma(i)\}\Im^{-1}_\sigma(i) + \Delta\varepsilon_\sigma(i). \qquad (133)$$

Adjusting the coefficients of the non-diagonal terms in (131) to zero an equation for $\xi_\sigma(i)$ is obtained

$$\xi^2_\sigma(i) - 2\xi_\sigma(i)\varepsilon^0(i)/a_\sigma(i) = 1, \quad (a_\sigma(i) \ne 0) \qquad (134)$$

$$\xi_\sigma(i) = 0. \qquad (a_\sigma(i) = 0) \qquad (135)$$

Equation (134) has always a root not exceeding 1 by module $(i = 1,2,3,\ldots,n)$, which will be used in the following. The non-bonding orbital $\varphi_p(\vec{r})$ is not affected by the transformation (127)–(130). Nevertheless the energy levels $\varepsilon_\sigma(p)$ may be displaced. It can be shown from (126)–(135) that the results are not changed if one formally says that the orbital $\varphi_p(\vec{r})$ mixes with itself. It follows from (134)–(135) that $|\xi_\sigma(p)| = 1$.

For the values $\xi_\sigma(i)$ satisfying the Equations (134)–(135) the Hamiltonian $\hat{H}$ has a diagonal form and the ground state wave function is

$$|\Psi\rangle = \prod_{\substack{i\sigma \\ (i=1,2,\ldots,n)}} \hat{B}^+_{i\sigma}\hat{B}^+_{p\uparrow}|0\rangle. \qquad (136)$$

In the state (136) the first order density matrix and the spin density are

$$R_\sigma(\vec{r},\vec{r}') = \sum_{ij}\langle\Psi|\hat{A}^+_{i\sigma}\hat{A}_{j\sigma}|\Psi\rangle\varphi_i(\vec{r})\varphi_j(\vec{r}') =$$
$$= \delta_{\sigma\uparrow}\varphi_p(\vec{r})\varphi_p(\vec{r}') +$$
$$+\sum_{k=1}^{n}\Im^{-1}_\sigma(k)\{\varphi_k(\vec{r})\varphi_k(\vec{r}') + \xi^2_\sigma(k)\varphi_{\bar{k}}(\vec{r})\varphi_{\bar{k}}(\vec{r}') -$$
$$-\xi_\sigma(k)[\varphi_k(\vec{r})\varphi_{\bar{k}}(\vec{r}') + \varphi_{\bar{k}}(\vec{r})\varphi_k(\vec{r}')]\}, \qquad (137)$$

$$\rho(\vec{r}) = R_\uparrow(\vec{r},\vec{r}) - R_\downarrow(\vec{r},\vec{r}). \qquad (138)$$

Substituting (121) into (138) and using the pairing relation

$$C_{\mu\bar{k}} = (-1)^{\mu+1}C_{\mu k},$$

one obtains for the spin density on atom μ

$$\rho_\mu = C^2_{\mu p} + (-1)^\mu 2\sum_{k=1}^{n}C^2_{\mu k}\left[\frac{\xi_\uparrow(k)}{\Im_\uparrow(k)} - \frac{\xi_\downarrow(k)}{\Im_\downarrow(k)}\right]. \qquad (139)$$

It should be noted that in the general case the Hamiltonian (126) and the wave function (136) are not self-consistent. In other words, the Hamiltonian in the Hartree-Fock approximation built on function (136) does not coincide in the general case with (126). The problem of self-consistency is to be solved accounting for the specific form of the matrix elements $\langle ij|ks\rangle$.We shall consider below a case when self-consistent values of $a_\sigma(k)$ can be determined for a Hamiltonian of type (126).

4. 2. Calculation of Properties of Long Neutral Polyene Radicals by the DODS Method

The Hartree-Fock solution of the Schrodinger equation for long polyene radicals will be found and the corresponding expression for the spin density will be compared with the McLachlan formula [113]. The eigenvalues and eigenfunctions of the Hamiltonian (113) are taken as

$$\varepsilon^0(i) = -2|\beta|\cos(i\theta), \qquad (140)$$

$$\varphi_i(\vec{r}) = \sqrt{\frac{2}{N+1}}\sum_{\mu=1}^{N}\sin(\mu i\theta)\,\chi_\mu(\vec{r}), \qquad (141)$$

where $\theta = \pi/(N+1)$, N is the number of atoms in the polyene chain. In the following we will consider a case when $N \gg 1$ and omit all terms $\sim 1/N^2$. For large N the solution (140)–(141) are close to the self-consistent ones. The matrix elements $V_\sigma(i,j)$ in (116) will be calculated in the zero differential overlap approximation accounting for Coulomb integrals $\gamma_{\mu\nu}$ only for nearest neighbors and using the following notations: $\gamma_{\mu\mu} \equiv \gamma_1$, $\gamma_{\mu,\mu\pm1} \equiv \gamma_2$. The last approximation is based on [117–119].

The first case to be considered is that when $\gamma_2 = 0$. Substituting (140)–(141) into (116) the following parameters of the Hamiltonian (126) are obtained

$$a_\sigma(k) = \Delta\varepsilon_\sigma(k) = \frac{\gamma_1}{N}\delta_{\sigma\downarrow}. \quad \left(0 < k \le \frac{\pi}{2}\right). \qquad (142)$$

The Hamiltonian (126) with the parameters (142) is not self-consistent since it is built on the zero order wave function (115) and its diagonalization corresponds to the first iteration of the self-consistency procedure. Performing the latter step-by-step the following expression for the Hamiltonian on the rth iteration is obtained

$$\hat{H}^{(r)} = \sum_{\substack{k\sigma\\(0<k\le\pi/2)}} [\varepsilon^0(k)(\hat{n}_{k\sigma} - \hat{n}_{\bar{k}\sigma}) + \Delta\varepsilon_\sigma(k)(\hat{n}_{k\sigma} - \hat{n}_{\bar{k}\sigma}) +$$
$$a_\sigma^{(r)}(k)(\hat{A}^+_{k\sigma}\hat{A}_{\bar{k}\sigma} + \hat{A}^+_{\bar{k}\sigma}\hat{A}_{k\sigma})] + \hat{W}^{(r)}, \qquad (143)$$

where

$$\hat{n}_{k\sigma} = \hat{A}^+_{k\sigma}\hat{A}_{k\sigma},$$

$$a_\sigma^{(r+1)}(k) = -\frac{\gamma_1}{2N}\sum_{k'}(1+\frac{1}{2}\delta_{kk'})\frac{a_{-\sigma}^{(r)}(k')n_{-\sigma}^{(1)}(k')}{\sqrt{4\beta^2\cos^2 k' + [a_{-\sigma}^{(r)}(k')]^2}}, \qquad (144)$$

and $n_\sigma^{(1)}(k')$ are the occupation numbers in the state (115),

$$\hat{W}^{(r)} = \frac{\gamma_1}{N}\sum_{\lambda=1}^{4}\sum_{ks} f^{(r)}(s,k)\hat{A}^+_{k\sigma}\hat{A}_{s_\lambda\sigma},$$
$$f^{(0)}(s,k) \equiv 0, \quad |f^{(r)}(s,k)| < 1, \qquad (145)$$
$$s_1 = 2k - s, \quad s_2 = 2k + s,$$
$$s_3 = 2\pi - 2k - s, \quad s_4 = 2\pi - 2k + s.$$

The final solution will be found in the following way. Taking $\hat{W}^{(r)} = 0$ and using Equations (144) the self-consistent values of $a_\sigma(k)$ are determined. Diagonalizing the Hamiltonian (126) with the self-consistent parameters $a_\sigma(k)$ the ground state wave function is obtained in the form (136). Then $\hat{W}^{(r)}$ is taken into account by perturbation theory. The convergence of the perturbation series will indicate the correctness of this treatment. In other words, the method of compensation of "dangerous" diagrams developed by Bogolyubov [120, 121] for solving problems in the theory of superconductivity is used. It will be clear later that the "dangerous" diagrams in the sense of the convergence of perturbation series are the non-diagonal terms in (126). This means that (134)–(135) is the equation for the compensation of "dangerous" diagrams.

We shall now find the self-consistent values of the parameters $a_\sigma(k)$. Neglecting in the left part of (144) terms $\sim 1/N$ one obtains

$$a_\sigma^{(r+1)} = -\frac{\gamma_1}{2\pi}a_{-\sigma}^{(r)}\int_0^{\pi/2}\frac{dx}{\sqrt{4\beta^2\cos^2 x + [a_{-\sigma}^{(r)}]^2}}. \qquad (146)$$

The values of $a_\sigma^{(r)}$ for $r = 0,1,2$ and $N \to \infty$ are given in Table 6.

Table 6

Values of the parameters $a_\sigma^{(r)}$ for Hamiltonian (143)

r	$a_\uparrow^{(r)}$	$a_\downarrow^{(r)}$
0	0	$\frac{\gamma_1}{N}$
1	$-\frac{\gamma_1}{N}\ln N$	$\frac{\gamma_1}{N}$
2	$-\frac{\gamma_1}{N}\ln N$	$\frac{\gamma_1}{N}\ln N(\ln N - \ln\ln N)$

It is seen that $|a_\sigma^{(r)}|$ increases as r becomes larger. The reason is that the integral in the right part of (146) has a logarithmic singularity at $a_\sigma^{(r)} \to 0$. If one takes $a_\downarrow^{(r)} = -a_\uparrow^{(r)} = a^{(r)}$ then the self-consistency condition $a_\sigma^{(r)} = a_\sigma^{(r+1)} = a$ leads to the equation

$$xK(x) = \frac{4\pi|\beta|}{\gamma_1}, \qquad (147)$$

where $K(x)$ – elliptical integral of the first order, and $x^2 = 4\beta^2/(4\beta^2 + a^2)$.

Equation (147) has a root for a certain $a > 0$ [122]. For reasonable choices of parameters $(\gamma_1/|\beta| < 5)$ the value of a satisfying Equation (147) is limited by $2|\beta|/3 > a > 0$. Thus, certain self-consistent values of the parameters of the Hamiltonian (143) exist:

$$a_\downarrow(k) = -a_\uparrow(k) = a. \qquad (148)$$

Substituting (148) into (132)–(133) the following expressions for the energy levels correct to $\sim 1/N$ are obtained

$$\varepsilon_\sigma(k) = \varepsilon\ (k) = -\sqrt{4\beta^2\cos^2 k + a^2}, \qquad (149)$$

$$\tilde{\varepsilon}_\sigma(k) = \tilde{\varepsilon}(k) = \sqrt{4\beta^2\cos^2 k + a^2} \qquad (150)$$

since according to (134) and (148)

$$\xi_\downarrow(k) = -\xi_\uparrow(k) = \xi(k) =$$
$$= -\frac{2|\beta|}{a}\cos k + \sqrt{1 + \frac{4\beta^2\cos^2 k}{a^2}}. \qquad (151)$$

It follows from (149)–(150) that $\varepsilon_\uparrow(\pi/2) = -a$, $\tilde{\varepsilon}_\downarrow(\pi/2) = a$ since the levels $\tilde{\varepsilon}_\uparrow(\pi/2)$ and $\varepsilon_\downarrow(\pi/2)$ are absent according to (129) and (151).

One sees from (149)–(150) and (151) that self-consistency leads to a splitting of the energy spectrum with $2N$ levels into to bands, each with N levels. The wave function (136) corresponds to the ground state of a chain with all levels $\varepsilon_\sigma(k)$ filled and $\tilde{\varepsilon}_\sigma(k)$ empty. One notes also that according to (149)–(150) $\varepsilon_\uparrow(k)=\varepsilon_\downarrow(k)=\varepsilon(k)$ and $\tilde{\varepsilon}_\uparrow(k)=\tilde{\varepsilon}_\downarrow(k)=\tilde{\varepsilon}(k)$. The width of the forbidden zone between filled and empty bands is equal to $2a$. An analogous solution for polyenes with even number of atoms has been obtained in [16, 109, 110]. It was also established that this state is energetically more stable than the Hartree-Fock state (140)–(141). Theory of the local electronic states in long polyene chains with an account of electronic correlation as in the present approach will be discussed below in connection with the nature of the forbidden zone which is still not clear enough physically.

It can be shown that an account for perturbation (145) in the first and second orders changes the elements of the density matrix $\hat{B}^+_{k\sigma}\hat{B}_{k'\sigma}$ by values $\sim 1/N$ and that the contribution to the energy equals $\Delta E_0^{(1)}=\Delta E_0^{(2)}=Const$. Thus, the effect of the perturbation (145) can be neglected. On the other hand, as follows from Table 6, perturbation theory is not applicable to the Hamiltonian (143). The reason is that the interaction between levels with $k\sim\pi/2$ is important even for small $a(k)$. The use of the compensation principle permits to account exactly for the contribution of all terms in the Hamiltonian (143) which violate the convergence of the perturbation series.

It will be shown now that an account for the integrals γ_2 in the matrix elements of the electronic interaction does not change qualitatively the results obtained above. In this case Equation (144) becomes

$$a_\sigma(k)=-\frac{1}{2N}\sum_{k'}\left[\begin{array}{l}\gamma_1(1+\frac{1}{2}\delta_{kk'})-\gamma_2(1+\frac{1}{2}\delta_{kk'}\cos 2k')\dfrac{a_{-\sigma}(k')n^{(1)}_{-\sigma}(k')}{\sqrt{4\beta^2\cos^2 k'+a^2_{-\sigma}(k')}}\\ +\dfrac{\gamma_2}{2N}\sum_k(1+\sin k\sin k')\dfrac{a_\sigma(k')n^{(1)}_\sigma(k')}{\sqrt{4\beta^2\cos^2 k'+a^2_\sigma(k')}}\end{array}\right]. \quad (152)$$

Supposing $a_\downarrow(k)=-a_\uparrow(k)=a(k)$ and neglecting in (152) all terms $\sim 1/N$ one obtains for $a(k)$ the equation

$$a(k)=\frac{1}{2\pi}\int_0^{\pi/2}(\gamma_1+\gamma_2\sin k\sin k')\frac{a(k')dk'}{\sqrt{4\beta^2\cos^2 k'+a^2(k')}}. \quad (153)$$

The solution of (153) can be found in a form

$$a(k)=c_1+c_2\sin k, \quad (154)$$

where

$$c_1=\frac{\gamma_1}{2\pi}\int_0^{\pi/2}\frac{a(x)dx}{\sqrt{4\beta^2\cos^2 x+a^2(x)}}, \quad (155)$$

$$c_2=\frac{\gamma_2}{2\pi}\int_0^{\pi/2}\frac{a(x)\sin x\,dx}{\sqrt{4\beta^2\cos^2 x+a^2(x)}}. \quad (156)$$

The dependence of the one-particle energies $\varepsilon_\sigma(k)$ on k is determined by the following relations

$$\varepsilon_\sigma(k)=\{2\beta\cos k[1-\xi^2_\sigma(k)](1+\Re_\sigma)-2\xi_\sigma(k)a_\sigma(k)\}\Im^{-1}_\sigma(k)+\Delta\varepsilon_\sigma \quad (157)$$

with

$$0<k\ll\frac{\pi}{2}\quad(\sigma=\uparrow),\quad 0<k<\frac{\pi}{2}\quad(\sigma=\downarrow)$$

and

$$\tilde{\varepsilon}_\sigma(k)=\{-2\beta\cos k[1-\xi^2_\sigma(k)](1+\Re_\sigma)+2\xi_\sigma(k)a_\sigma(k)\}\Im^{-1}_\sigma(k)+\Delta\varepsilon_\sigma \quad (158)$$

with

$$0<k\ll\frac{\pi}{2}\quad(\sigma=\downarrow),\quad 0<k<\frac{\pi}{2},\quad(\sigma=\uparrow)$$

where

$$\Delta\varepsilon_\uparrow=\gamma_2/N,\quad \Delta\varepsilon_\downarrow=(\gamma_1+\gamma_2)/N,$$

$$\Re_\sigma=\frac{\gamma_2}{N|\beta|}\sum_k n^{(1)}_\sigma(k)\cos k\frac{\xi^2_\sigma(k)}{\Im_\sigma(k)}.$$

In this case, as follows from (157)–(158) and (154), the energy spectrum with $2N$ levels also splits into two bands, each with N levels. The distance between these bands is equal to $2a(\pi/2)$. As above, the effect of the perturbation $\hat{W}$ can be neglected.

Thus, the inclusion of the Coulomb repulsion integrals for electrons on neighboring atoms of a chain into the matrix elements does not change qualitatively the previous solution. The quantitative aspects are determined by the relations between parameters β, γ_1, and γ_2.

Expressing the parameters $\xi_\sigma(k)$ in (139) through $a_\sigma(k)$ one obtains for the spin density

$$\rho_\mu=\frac{2}{N}\sin\frac{\mu\pi}{2}+(-1)^{\mu+1}\frac{4}{N}\sum_{k=\theta}^{(\pi/2)-\theta}\frac{a(k)\sin^2\mu k}{\sqrt{4\beta^2\cos^2 k+a^2(k)}}. \quad (159)$$

We note that for $N\to\infty$ the spin density ρ_μ according to (153) and (146) has a finite limit:

$$0<|\rho_\mu|<a.$$

Now we shall consider the spin density in a long polyene chain which results from McLachlan's method

[113]. Substituting (140)–(141) into (122) and accounting only for $\gamma_1 (\gamma_2 = 0)$ one obtains

$$\rho_\mu^{(1)} = \frac{2}{N+1}\sin\frac{\mu\pi}{2} + \frac{2\lambda}{(N+1)^2}(-1)^{\mu+1}\sum_{k=\theta}^{(\pi/2)-\theta}\frac{\sin^2 \mu k}{\cos k}, \quad (160)$$

where $\lambda = \gamma_1 |\beta|/2$.

For $N \to \infty$ the second term in (160) is estimated as

$$\frac{2\lambda}{(N+1)^2}(-1)^{\mu+1}\sum_{k=\theta}^{(\pi/2)-\theta}\frac{\sin^2 \mu k}{\cos k} \sim \frac{2\lambda}{N\pi}\int_0^{\pi/2-\theta}\frac{\sin^2 \mu k\, dk}{\cos k} \cong \frac{\lambda}{\pi}\frac{\ln N}{N} \to 0. \quad (N \to \infty)$$

Thus, McLachlan's method gives incorrect asymptotic behaviour for the spin density in a polyene chain with $N \to \infty$. The reason is that McLachlan's formula was obtained in the first order of the perturbation over non-diagonal terms in the Hamiltonian (143). As we already know, perturbation theory is not applicable to the operator (143). Contribution to ρ_μ in the second order is equal to $\sim (\ln N)^2 / N \quad (N \to \infty)$ which supports our conclusion.

Results obtained so far indicate that in systems like long polyene radicals the Hartree-Fock solution (140)–(141) is unstable relative to a small perturbation caused by the spin polarization of closed shells in a radical. The existence of this perturbation in the Hamiltonian leads necessary to a state described by the wave function with different orbitals for different spins. The possibility of existence of these states in systems like alternant hydrocarbons has been discussed in [107] by the use of Green functions and thoroughly demonstrated in [67].

4. 3. Projection on Pure Spin State

It follows from (127)–(130), (136), and (151) that the solution obtained above corresponds to the DODS type and therefore is not an eigenfunction of operator $\hat{S}^2$. This fact can be expressed in the following equivalent form which seems to us more visual if the representation of occupation numbers is used, namely: in the DODS method the operator $\hat{S}^2$ does not commute with Hamiltonian. The equivalency of both statements is proved by the use of one of the main theorems in quantum mechanics: two operators commute if and only if they have a common system of eigenfunctions [123].

The following statement can also be proved: a Hamiltonian of the type

$$\hat{H}_1 = \sum_{ij\sigma} h_\sigma(i,j)\hat{A}_{i\sigma}^+\hat{A}_{j\sigma}$$

commutes with the operator $\hat{S}^2$ only if one of the following two conditions are satisfied

(1) $h_\uparrow(i,j) = h_\downarrow(i,j)$,

(2) $h_\uparrow(i,i) = h_\downarrow(i,i) = Const, \quad h_\uparrow(i,j) = h_\downarrow(i,j). \quad (i \neq j)$

To prove this it is necessary to calculate the commutator $[\hat{S}^2, \hat{H}_1]$. The expression for an operator $\hat{S}^2$ in the second quantization representation may be found in [115]. For our case

$$[\hat{S}^2, \hat{H}_1] = \sum_{lkj}[h_\uparrow(l,k) - h_\downarrow(l,k)] \times (\hat{A}_{l\downarrow}^+\hat{A}_{j\uparrow}^+\hat{A}_{j\downarrow}\hat{A}_{k\uparrow} - \hat{A}_{l\uparrow}^+\hat{A}_{j\downarrow}^+\hat{A}_{j\uparrow}\hat{A}_{k\downarrow}). \quad (161)$$

Expression (161) proves our statement. For the Hamiltonian (126) with parameters (148) and (153) conditions (1) and (2) above are not satisfied because

$$h_\uparrow(k,\bar{k}) - h_\downarrow(k,\bar{k}) = a_\uparrow(k) - a_\downarrow(k) = -2a(k).$$

Using traditional rules for the calculation of averages let us determine the average value of the operator $\hat{S}^2$

$$\langle\Psi|\hat{S}^2|\Psi\rangle = m_S^2 + \frac{N}{2} - Sp(R_\uparrow R_\downarrow) = m_S^2 + \frac{1}{2}\sum_{kl}\rho^2(k,l), \quad (162)$$

where

$$\hat{S}_z|\Psi\rangle = m_S|\Psi\rangle, \quad \rho(k,l) = R_\uparrow(k,l) - R_\downarrow(k,l), \quad R_\sigma(k,l) = \langle\Psi|\hat{A}_{k\sigma}^+\hat{A}_{l\sigma}|\Psi\rangle.$$

Expression (162) is valid for any state described by a single-determinant real function. Taking the function (136) with parameters $\xi_\sigma(k)$ from (151) one obtains the following expressions correct to $\sim 1/N$

$$\rho(k,l) = \frac{a\,\delta_{kl}}{\sqrt{4\beta^2\cos^2 k + a^2}} + \delta_{kl}, \quad (163)$$

$$\langle\Psi|\hat{S}^2|\Psi\rangle = \frac{3}{4} + \frac{dN}{2\sqrt{1+d^2}} \quad (164)$$

with $d = a|\beta|/2$.

It is seen from (163)–(164) that the average value of $\hat{S}^2$ in the states described by (134)–(136), and (146)–(159) is proportional to the number of electrons *N*. To estimate the spin density quantitatively projection on a pure spin state is important [58]. One notes that when the parameters a_σ or $a_\sigma(k)$ satisfy Equations (146) or (147) then the operators $\hat{B}_{k\sigma}$ correspond to the states described in the coordinate representation by orbitals like AMO

$$\Re_{k\uparrow}(\vec{r}) = \cos x_k \cdot \varphi_k(\vec{r}) + \sin x_k \cdot \varphi_{\bar{k}}(\vec{r}), \quad (165)$$

$$\Re_{k\downarrow}(\vec{r}) = \cos x_k \cdot \varphi_k(\vec{r}) - \sin x_k \cdot \varphi_{\bar{k}}(\vec{r}). \quad (166)$$

The parameter x_k is related to the parameters $a(k)$ by the relation

$$\sin 2x_k = \frac{a(k)}{\sqrt{4\beta^2\cos^2 k + a^2(k)}}. \quad (167)$$

Projection on the lowest doublet state of the wave function (136) with parameters $a_\sigma(k)$ satisfying Equations (147) and (153) by the method due to Harriman [124] leads to the following expression for the spin density

$$\rho_\mu = \frac{2}{N}\sin\frac{\mu\pi}{2}\left\{1+\frac{2}{3}\sum_{i=1}^{n}\left[1-\frac{\omega_{1/2}(i)}{\omega_{1/2}}\right]\right\}+$$
$$+\frac{4}{3N}\sum_{i=1}^{n}\left[\frac{\omega_{1/2}(i)}{\omega_{1/2}}-1\right]\sin^2(\mu i\theta)+$$
$$+\frac{4}{3N}(-1)^{\mu+1}\sum_{i=1}^{n}\frac{\omega_{1/2}(i)\,a(i\theta)\sin^2(\mu i\theta)}{\omega_{1/2}\cdot\sqrt{4\beta^2\cos^2(i\theta)+a^2(i\theta)}}, \quad (168)$$

where according to [124]

$$\omega_s = \sum_{k=0}^{n}(-1)^k\binom{2s+k+1}{k}^{-1}B_k\,, \quad (169)$$

$$\omega_s(i) = \sum_{k=0}^{n-1}(-1)^k\binom{2s+k+1}{k}^{-1}B_k(i)\,, \quad (170)$$

$$B_k = \sum_{\{m_1,m_2,\dots,m_k\}}^{\binom{n}{k}}\prod_{m=m_1}^{m_k}\left[\frac{a^2(m\theta)}{4\beta^2\cos^2(m\theta)+a^2(m\theta)}\right], \quad (171)$$

$$B_k(i) = \sum_{\substack{\{m_1,m_2,\dots,m_k\}\\(m_j\neq m_i)}}^{\binom{n-1}{k}}\prod_{m=m_1}^{m_k}\left[\frac{a^2(m\theta)}{4\beta^2\cos^2(m\theta)+a^2(m\theta)}\right], \quad (172)$$

$2s+1$ is the state multiplicity required, $\binom{n}{k}=\frac{n!}{k!(n-k)!}$, summation in (171)–(172) is carried out over all possible choices of k numbers from $\{1,2,\dots,n\}$. It can be shown that for $N\to\infty$ ($n = N/2$) the values of B_k from (171)–(172) may be represented as

$$B_k = \left(\frac{N}{\pi}\right)^k\int_0^\pi f(x_k)\,dx_k\int_0^{x_k} f(x_{k-1})\,dx_{k-1}\cdots\int_0^{x_2} f(x_1)\,dx_1 =$$
$$=\left(\frac{N}{\pi}\right)^k\frac{F^k(\pi)}{k!}=\frac{(N\alpha)^k}{k!}, \quad (173)$$

where

$$f(x)=\frac{d^2}{1+2d^2+\cos x}, \quad \alpha=\frac{d}{2\sqrt{1+d^2}},$$

and according to [125]

$$F(y)=\int_0^y f(x)\,dx = 2\alpha\,\mathrm{arctg}\left(2\alpha\,\mathrm{tg}\frac{y}{2}\right)$$

with

$$F(0)=0, \quad F(\pi)=\alpha\pi\,.$$

In an analogous way one obtains for $B_k(i)$

$$B_k(i)=\frac{(N\alpha)^k}{k!}-2f(i\theta)\frac{(N\alpha)^{k-1}}{(k-1)!}\,. \quad (174)$$

Thus, the expression (169)–(170) for $s=1/2$ become

$$\omega_{1/2}=2\sum_{k=0}^{n}(-1)^k\frac{(N\alpha)^k}{(k+2)!}, \quad (175)$$

$$\omega_{1/2}(i)=\omega_{1/2}+2(-1)^{n+1}\frac{(N\alpha)^n}{(n+2)!}-$$
$$-4f(i\theta)\sum_{k=1}^{n-1}(-1)^k\frac{k(N\alpha)^{k-1}}{(k+2)!}. \quad (176)$$

A general term in (175) and (176) $(N\alpha)^k/(k+2)!$ has a maximum for $k\sim N\alpha = x$

$$\frac{x^x}{(x+2)!}\sim\frac{e^x}{x^{5/2}}\,. \quad (177)$$

For $k=n=N/2$ one obtains

$$\frac{(N\alpha)^{N/2}}{\left(\frac{N}{2}+2\right)!}\sim(2e\alpha)^{N/2}N^{-5/2}<N^{-5/2}, \quad (178)$$

Since it follows from (146) that for reasonable choices of the parameters

$$2\alpha<\frac{1}{3}\,.$$

From the theory of alternating series [125, 126] increasing the upper limit of summation *n* in (175) and (176) to infinity leads to an error less than $N^{-5/2}$. Thus, the following equation is valid within this accuracy

$$\omega_{1/2}(x)=2\sum_{k=0}^{\infty}(-1)^k\frac{x^k}{(k+2)!}=2\frac{e^{-x}}{x^2}-\frac{2}{x^2}+\frac{2}{x}\,. \quad (179)$$

For $N\to\infty$, $\omega_{1/2}(x)\to 0$.

Noting that according to (176)

$$\omega_{1/2}(x)-\omega_{1/2}(x,i)=-2f(i\theta)\frac{d\omega_{1/2}(x)}{dx}$$

one obtains

$$\omega_{1/2}(x)-\omega_{1/2}(x,i)=-4f(i\theta)\left(\frac{2}{x^3}-\frac{1}{x^2}-\frac{2e^{-x}}{x^3}-\frac{e^{-x}}{x^2}\right). \quad (180)$$

It follows from (180) and (179) that

$$\frac{\omega_{1/2}(i)}{\omega_{1/2}}\sim 1+\frac{Const}{N\alpha}. \quad (N\to\infty) \quad (181)$$

Substituting (181) into (168) one obtains

$$\rho_\mu=(-1)^{\mu+1}\frac{4}{3\pi}\int_0^{\pi/2}\frac{a(x)\sin^2\mu x\,dx}{\sqrt{4\beta^2\cos^2 x+a^2(x)}}\,. \quad (182)$$

Comparing (182) and (159) one sees that the projection lowers the amplitude of alternation of the spin densities on chain atoms by a factor of three. Nevertheless, for $N\to\infty$ the amplitude of alternation of the spin densities $|\rho_\mu|$ remains different from zero. Relative values of the spin densities on different atoms are not affected by the projection.

It was shown in paragraph 4.2 that the solution of the SCF equations for long polyene radicals by the DODS method leads to lower ground state energy compared with the traditional solution (140)–(141). The state corresponding to the latter is unstable with respect to a perturbation polarizing the closed shells of a radical. Comparing expressions (147), (149)–(150), and (159) with the results of [16] one notes that the appearance of an unpaired electron in the long polyene chain does not affect the main characteristics of the system. This is a natural consequence of Koopmans' theorem [75].

However, there is a certain difference in the properties of a long polyene with an even number of electrons and in long polyene radicals. If an electronic system has zero value of the spin projection . $\hat{S}_z$. then the spin density is identically equal to zero [127, 124]. A radical has a non-zero eigenvalue of $\hat{S}_z$ and the latter conclusion is not valid. In fact, from (182) the projection of the wave function on to a doublet state leads only to quantitative changes in the spin density distribution. Therefore the DODS method predicts antiferromagnetism in long polyene radicals. There is here no contradiction with physical intuition which tells us that an addition of one electron to a large system must not affect its properties because, first of all, the spin of a system changes on a finite value and, secondly, as already mentioned above, main characteristics of the system including its energy are not changed by addition of one electron.

In the absence of experimental data we cannot compare the theory with experiment and insist on the indisputability of results obtained. In fact, the non-projected DODS method describes incorrectly the spin properties, for any non-relativistic Hamiltonian must commute with the operator $\hat{S}^2$. After projection the wave function (136) is no longer an eigenfunction of the Hamiltonian which casts doubt on its adequacy as a true solution. On the other hand the DODS methods seems to be the best one in its account of electronic correlation in the one-particle approximation. Thus, the correct way to account for the spin polarization requires repudiation of the one-particle approximation. In fact, as follows from paragraph 4.3, it is impossible to write down a one-electron Hamiltonian which accounts for the spin polarization correctly and at the same time commutes with the operator $\hat{S}^2$. It follows from (149)–(150) and (157)–(158) that a finite forbidden zone appears in the spectra of one-particle eigenvalues of the antiferromagnetic state (136) of the polyene radical, and this state is separated from the usual state (140)–(141). Extrapolation to $N \to \infty$ of the experimental data leads to a certain finite value of the frequency of the first electronic transition in the absorption spectra of polyenes [16]. It has been also shown in [16] that the correlation gap 2*a* is close to the interpolated experimental value. Nevertheless it should be noted that the interpretation of the excited states in the DODS method is still not clear. The antiferromagnetic state in long polyene radicals obtained above is, as suggested in [107], one of the phase states in systems like large alternant hydrocarbons.

Now we come back to the local electronic states in polyene chains with an impurity atom (§ 2.2) using unrestricted Hartree-Fock approach.

5. The Influence of an Impurity Atom on π-electronic Structure of Long Polyenes using the UHF Approach

It is well known from optical experiments [128] that the frequency of the first electronic transition in polyenes tends to a non-zero value when the polyene chain is lengthened. Until recently this energy gap was supposed to arise from the instability of the equal-bond polyene configuration with respect to the bond alternation [129, 130]. Nevertheless, it has recently been shown that the unrestricted Hartree-Fock (UHF) approach taking into account electron correlation can be used to describe the π-electronic spectra of large conjugated systems like polyenes, cumulenes, polyacenes, and graphite [6, 16, 17, 107, 109–111, 108]. Note that the papers [6, 16, 108] have dealt with the electronic structure of regular ideal polyene chains consisting of an even [16, 108] or odd [6] number of carbon atoms.

Comparing with experiment only the values of energy gaps, obtained in the two different models, do not make it clear which of these models or their combination [131] is more realistic. One of the possible methods of investigating the electronic structure of any periodic systems is to study the influence of the appropriately introduced defects on the energy spectra of these systems. Thus, to study the effect of disturbed periodicity on the electronic structure of polyene chains by means of the UHF method is of interest. The same problem has been discussed in [1, 2, 4] under the assumption that the energy gap is due to the bond alternation.

5. 1. The UHF Solution for Long Polyene Chains with an Impurity Atom

As follows from paragraphs 2 and 4, the UHF equations for an ideal polyene chain have the following general form in the orthogonal AO representation [6, 16, 108]

$$\begin{aligned}&\left(\alpha_0+\frac{\gamma}{2}+\varepsilon_k^{(j)}\right)C_{k\sigma}^{(j)}(\mu)=\sum_{\nu=1}^{N}\hat{H}_\sigma(\mu,\nu)\equiv\\&\equiv[\alpha_0+\gamma n_{\mu\sigma}^{(0)}]C_{k\sigma}^{(j)}(\mu)+\beta[(1-\delta_{\mu,1})\times\\&\times C_{k\sigma}^{(j)}(\mu-1)+(1-\delta_{\mu,N})C_{k\sigma}^{(j)}(\mu+1)],\qquad(183)\end{aligned}$$

where α_0 and β are the Coulomb and resonance integrals, γ is the electron repulsion integral,

$$n_{\mu\sigma}^{(0)}=\sum_{k<\pi/2}[C_{k\sigma}^{(1)}(\mu)]^2$$

are the electron populations of the μ-th AO with σ-spin, $\sigma=\uparrow,\downarrow$.

The solution of (183) is defined by the relations

$$C_{k\sigma}^{(1)}(\mu)=\sqrt{\frac{2}{N}}[1+(-1)^{\mu+1}\xi_k\tau_\sigma]\sin\mu k/\sqrt{1+\xi_k^2},\quad(184)$$

$$C_{k\sigma}^{(2)}(\mu)=\sqrt{\frac{2}{N}}[(-1)^{\mu+1}-\xi_k\tau_\sigma]\sin\mu k/\sqrt{1+\xi_k^2},\quad(185)$$

$$\varepsilon_k^{(1)}=-\varepsilon_k^{(2)}=-\sqrt{4\beta^2\cos^2 k+a^2},\qquad(186)$$

where $N \gg 1$ is the number of carbon atoms in the chain. The self-consistent value of a is found from the equation

$$\frac{\gamma}{\pi}\int_0^{\pi/2} dk(4\beta^2\cos^2 k + a^2) = 1, \qquad (187)$$

$$\xi_k = [2\beta\cos k + \sqrt{4\beta^2\cos^2 k + a^2}]/a,$$
$$\tau_\sigma = \begin{cases} 1, & (\sigma = \uparrow), \\ -1, & (\sigma = \downarrow). \end{cases} \qquad (188)$$

The width of the forbidden zone between the energy levels $\varepsilon_k^{(1)}$ occupied in the ground state and empty levels $\varepsilon_k^{(2)}$ is equal to 2a. It follows from (184)–(188) that

$$n_{\mu\sigma}^{(0)} = \frac{1}{2} + (-1)^{\mu+1}\frac{2\gamma\tau_\sigma}{\pi}\times$$
$$\times\int_0^{\pi/2} dk\frac{\sin^2 \mu k}{\varepsilon_k^{(2)}} = \frac{1}{2} + (-1)^{\mu+1}\delta_\mu. \qquad (189)$$

As seen from (189), the values of δ_μ depend on an atom number μ. The analysis of (189) shows that this dependence occurs near the chain boundary:

$$\delta_\mu \approx \delta + \left(\frac{1}{2}\right)^{\mu-1}\Delta\delta, \qquad (190)$$

where

$$\delta = a/\gamma = 0.21, \Delta\delta = 0.06$$

with $\beta = -2.4\,eV$ and $\gamma = 5.4\,eV$ [16].

Using the UHF method we now consider the electronic structure of a long polyene chain with the ν-th atom substituted. We make an assumption that such a substitution can be approximated by changing an appropriate Coulomb integral as $\alpha_\nu = \alpha_0 + t$. As seen from (183), the change of γ corresponding to perturbed atom can be taken into account by an appropriate change of the effective value of α. We shall consider here such substitutions which can be described by the change of the parameters α and γ only, i.e. the values of β are considered to be close to those for ideal polyenes. There are a number of substitutions which satisfy the conditions above, e.g. $H \rightarrow CH_3, C \rightarrow N$.

The UHF Hamiltonian for polyenes (183) is a non-linear operator since it contains $n_{\mu\sigma}^{(0)}$ (189). Therefore, a direct application of the local-perturbation theory [132] developed for linear Hamiltonians [20, 21, 24], *e.g.*, for the tight binding method, requires an justification. The correct solution involves an iteration procedure usual for the calculations by the SCF methods. Consequently, one can use the local-perturbation theory for each iteration. The equation for eigenfunctions and eigenvalues in the case of long polyenes with the substitution has the following form for the first iteration, *e.g.*, see [20, 21]

$$(\hat{H}_\sigma + t\hat{\Lambda} - z_\sigma)\varphi_\sigma = 0, \qquad (191)$$

where $\hat{H}_\sigma$ is given by (183), and operator $\hat{\Lambda}$ is defined by

$$(g, \hat{\Lambda}\varphi) \equiv \sum_{\mu,\mu'} g^*(\mu)\Lambda(\mu,\mu')\varphi(\mu') = g^*(\nu)\varphi(\nu). \qquad (192)$$

Let us present some general results which follow from [20, 21]. Eigenvalues $z_{q\sigma}^{(i)}$ of the Equation (191) are determined by

$$1 + t\sum_{k,j}\frac{[C_{k\sigma}^{(j)}(\nu)]^2}{\varepsilon_k^{(j)} - z_{q\sigma}^{(i)}} = 0. \qquad (193)$$

It follows from (193) that a perturbation of type (192) gives rise to the infinitesimal shifts of zone levels

$$z_{k\sigma}^{(i)} = \varepsilon_k^{(i)} + \frac{\pi}{N}\frac{d\varepsilon_k^{(i)}}{dk}\Theta_{k\sigma}^{(i)}. \qquad (194)$$

The perturbation of the type (193) can also give rise to a local state splitting off zones. This question will be discussed in the next section. Now, we consider the effect of the substitution of an atom placed near the end of polyene chain ($\nu \ll N$). Then the shifts in a quasi-continuous spectrum are determined by the equation (see Appendix below)

$$\mathrm{ctg}\,\pi\Theta_{k\sigma}^{(i)} =$$
$$= -\frac{\sin 2k}{2\lambda L_{k\sigma}^{(i)}(\nu)\sin^2 \nu k}\left[1 - \lambda L_{k\sigma}^{(i)}(\nu)\frac{\sin 2\nu k}{\sin 2k}\right], \qquad (195)$$

where $\lambda = t/|\beta|$, and

$$L_{k\sigma}^{(i)}(\nu) = \frac{1}{2|\beta|}[\varepsilon_k^{(i)} + (-1)^\nu a\,\tau_\sigma]. \qquad (196)$$

The eigenfunctions corresponding to the eigenvalues (194) can be written as (see Appendix below)

$$\varphi_{k\sigma}^{(i)}(\mu) = \sqrt{\frac{2}{N}}C_{k\sigma}^{(i)}(\mu)\sin(k^*\mu - \pi\Theta_{k\sigma}^{(i)}), \quad (\mu > \nu), \qquad (197)$$

$$\varphi_{k\sigma}^{(i)}(\mu) = \sqrt{\frac{2}{N}}C_{k\sigma}^{(i)}(\mu)\sin(k\nu - \pi\Theta_{k\sigma}^{(i)})\frac{\sin \mu k}{\sin \nu k}, \quad (\mu < \nu), \qquad (198)$$

$$\varphi_{k\sigma}^{(i)}(\nu) = \sqrt{\frac{1}{2N}\frac{d\varepsilon_k^{(i)}}{dk}}\sin\Theta_{k\sigma}^{(i)}/(tC_{k\sigma}^{(i)}(\nu)\sin k\nu), \qquad (199)$$

where

$$C_{k\sigma}^{(i)}(\mu) = \sqrt{\frac{2}{N}}C_{k\sigma}^{(i)}(\mu)\sin k\mu, \quad k^* = k + \frac{\pi}{N}\Theta_{k\sigma}^{(i)}.$$

It follows from (197) that the perturbation results in the phase shift of the eigenfunctions for $\mu > \nu$. In order to define under what conditions the relations (193)–(199) correspond to the self-consistent solution of Eq. (191) we evaluate $n_{\mu\sigma}$. Transforming (197) yields for the zone-state density at the μ-th atom

$$[n_{\mu\sigma}^{(1)}]_{zone} = \sum_k [\varphi_{k\sigma}^{(1)}(\mu)]^2 = \frac{1}{2} + (-1)^{\mu+1}\delta_\mu\tau_\sigma +$$
$$+\frac{a}{\pi}\int_0^{\pi/2} dk[\cos(2\mu k - 2\pi\Theta_{k\sigma}^{(i)})]/\varepsilon_k^{(2)}. \quad (\mu > \nu) \qquad (200)$$

Comparing (200) with (189) one can see that the perturbation effect on the zone-state density is transferred along the chain in the same way as the influence of its boundary, *i.e.* it sharply attenuates: $2^{|\mu-\nu|}$ times at the distance $|\mu-\nu|$. Thus, if $\mu-\nu \gg 1$ then (200) leads to $n^{(1)}_{\mu\sigma}=n^{(0)}_{\mu\sigma}$. It means that regardless of the non-linearity of the UHF equations, the impurity effect is local as in the case of linear Hamiltonians. Following (200) one can obtain for the electron density at the impurity atom (see Appendix below)

$$n^{(1)}_{\nu\sigma}=\frac{d}{dt}\sum_k (z^{(1)}_{k\sigma}-\varepsilon^{(1)}_k). \quad (201)$$

Taking into consideration Coulson's and Lonquet-Higgins' relation [73], we reduce the expression (201) to the form

$$n^{(1)}_{\nu\sigma}=\frac{d}{dt}\frac{1}{2\pi i}\oint_C z\, d\ln[M_\sigma(z)/M^{(0)}_\sigma(z)], \quad (202)$$

where the integration is in the positive direction along the infinite half-circle ($\mathrm{Re}\, z<0$) and imaginary axis in the complex plane *z*; $M_\sigma(z)$ and $M^{(0)}_\sigma(z)$ are determinants which vanish at the points $z=z^{(i)}_{k\sigma}$ and $z=\varepsilon^{(1)}_k$, respectively. The expression (202) can be written as [133]

$$n^{(1)}_{\nu\sigma}=\frac{d}{dt}\frac{1}{2\pi i}\oint_C z\, d\ln[1-t\,G_{0\sigma}(\nu,\nu;z)]=$$
$$=-\frac{1}{2\pi i}\oint_C dz\frac{d}{dt}\ln[1-t\,G_{0\sigma}(\nu,\nu;z)], \quad (203)$$

where the function

$$G_{0\sigma}(\nu,\mu;z)=\sum_{k\,j}\frac{C^{(j)}_{k\sigma}(\nu)C^{(j)}_{k\sigma}(\mu)}{z-\varepsilon^{(j)}_k} \quad (204)$$

is the Green function:

$$\sum_{\mu'=1}^{N}[\hat H_\sigma(\mu,\mu')-z\delta_{\mu\mu'}]G_{0\sigma}(\mu',\nu;z)=-\delta_{\mu\nu}.$$

The equivalence of expressions (202) and (203) results from the fact that in accordance with (193) the functions in brackets in (202) and (203) have simple poles and zeros at the same points. Having failed to obtain general analytical expressions for (200) or (202) we now discuss some limiting cases. Let $|\lambda|\ll 1$. Then the integrand in (203) can be expanded in the series of λ

$$n^{(1)}_{\nu\sigma}=\frac{1}{2\pi i}\oint_C dz\, G_{0\sigma}(\nu,\nu;z)\sum_{n=0}^{\infty}[\lambda\,|\beta|\,G_{0\sigma}(\nu,\nu;z)]^n . \quad (205)$$

According to (204) $|\beta G_{0\sigma}(\nu,\nu;z)|<1$ if $z\in C$. Therefore, the series in (205) converges regularly if $|\lambda|<1$ and $z\in C$. As a consequence, integrating (205) term by term yields

$$n^{(1)}_{\nu\sigma}=\sum_k [C^{(1)}_{k\sigma}(\nu)]^2\sum_{n=0}^{\infty}[\lambda L^{(1)}_{k\sigma}(\nu)\sin 2\nu k/\sin 2k]^n . \quad (206)$$

It follows from (206) that

$$n^{(1)}_{\nu\sigma}=n^{(0)}_{\nu\sigma}+\mathrm{O}(\lambda). \quad |\lambda|\ll 1. \quad (207)$$

Thus, if $|\lambda|$ is small, the solution of (191) given by (193)– (201) and corresponding to the first iteration of the self-consistency procedure for a long polyene chain with impurity is a self-consistent one. The equation of second iteration has the following form

$$\sum_{\mu'=1}^{N}\Big\{\hat H_\sigma(\mu,\mu')+t\Lambda(\mu,\mu')+$$
$$+\lambda[n^{(1)}_{\mu\sigma}-n^{(0)}_{\mu\sigma}]\delta_{\mu\mu'}-z\delta_{\mu\mu'}\Big\}\varphi_\sigma(\mu')=0. \quad (208)$$

Let us consider this equation for the case $\nu=1$, *i. e.* when the perturbation is localized at the first atom of the chain. It follows from (206) that

$$n^{(1)}_{1\sigma}-n^{(0)}_{1\sigma}=\sum_{n=1}^{\infty}\lambda^n(-1)^n f_{n\sigma}=-\lambda\Delta^{(1)}/\gamma, \quad (209)$$

where $\Delta^{(1)}>0$, and

$$f_{n\sigma}=\frac{1}{\pi}\int_0^{\pi/2}dk\sin^2 k\frac{(\sqrt{\cos^2 k+d^2}+d\tau_\sigma)^{n+1}}{\sqrt{\cos^2 k+d^2}}.$$

As seen from (209), the correction $-\lambda\Delta^{(1)}$ to the perturbation has the opposite sign to the initial perturbation $\lambda|\beta|$. Consequently, if λ is finite, the impurity is screened with zone electrons , as one should expect. It means that the effective value of the perturbation parameter $|\lambda'|$ is less than $|\lambda|$. It is easy to verify using (206) that this result is also valid if $\nu\neq 1$.

In order to evaluate differences $n^{(1)}_{\mu\sigma}-n^{(0)}_{\mu\sigma}$ for $\mu>\nu$ we now consider another limiting case: $|\lambda|\to\infty$. Then it follows from (195) that $\pi\Theta^{(i)}_{k\sigma}\to\nu k$. Hence, the relations (197)–(199) take the form

$$\lim_{|\lambda|\to\infty}\varphi^{(i)}_{k\sigma}(\mu)=\begin{cases}C^{(i)}_{k\sigma}(\mu-\nu), & (\mu>\nu)\\ 0. & (\mu\le\nu)\end{cases} \quad (210)$$

It follows from (210) that a strong perturbation tears the link consisting of ν atoms of the chain. It is obvious that the functions (210) are self-consistent for the chain consisting of $N-\nu\approx N$ atoms because they coincide with the self-consistent zone functions of an ideal polyene chain. Substituting (210) into (200) and using (189) and (190) one obtains

$$|n^{(1)}_{\mu\sigma}-n^{(0)}_{\mu\sigma}|=|\delta_{\mu-\nu}-\delta_\mu|\le|\delta_1-\delta_2|=0.09. \quad (211)$$

It means that the changes of values $n_{\mu\sigma}(\mu>\nu)$ are small even though the parameter $|\lambda|$ changes from zero to infinity. Thus, in order to obtain the zone functions $\varphi^{(i)}_{k\sigma}(\mu)$ of a long polyene chain with the ν-th atom substituted $(\nu\ll N)$ as $\mu>\nu$, it is quite sufficient to restrict oneself to the first iteration of the self-consistency procedure for any value of the perturbation parameter λ. In particular, if $\nu=1$ one can suppose that $n^{(1)}_{\mu\sigma}-n^{(0)}_{\mu\sigma}=\delta_{\mu 1}(-\lambda\Delta^{(1)}/\gamma)$. It means that the non-linearity of Eq. (191) can be neglected except for the fact that an initial perturbation parameter λ is to be replaced by its effective value λ', $|\lambda'|<|\lambda|$. On the other hand, if $\nu\neq 1$ and $|\lambda|\gg 1$ then functions $\varphi_\sigma(\mu)$ $(\mu<\nu)$ are to be close to the corresponding functions of a short polyene chain consisting of $\nu-1$ atoms. It should be also noted that calculating $n^{(1)}_{\mu\sigma}$-values, we neglect the contribution of local-state functions, which have the amplitude (see Appendix below)

$$|\varphi_{p\sigma}(\mu)|=Const\,(e^{-|\mu-\nu|q_0/2}+e^{-|\mu+\nu|q_0/2}), \quad (212)$$

where $q_0>0$. Hence it is clear that the functions are localized near the substituted atom. If $|\lambda|\gg 1$ then $q_0\gg 1$, *i. e.* $\varphi_{p\sigma}(\mu)\sim\delta_{\mu\nu}$; if $|\lambda|\ll 1$ then $\varphi_{p\sigma}(\mu)\sim\lambda$ (see Appendix below). Thus, we are taking into account that the local-state functions does not affect the relations (207) and (211).

5. 2. Local States

General results obtained above can be used to consider the local electronic states in polyene chains with impurity.

As stated by Lifshits [20, 21] and Koster and Slater [24], the wave functions of local states are determined by the equations

$$\varphi_\sigma(\nu)=-\sum_{\mu,\mu'}G_{0\sigma}(\nu,\mu';z)\,t_{\mu',\mu}\,\varphi_\sigma(\mu). \quad (213)$$

Here $t_{\mu\nu}$ is the matrix elements of perturbation produced by substitution. If, for example, only one of the Coulomb integrals changes $\alpha_\nu\to\alpha_{\nu 0}+t\Delta\alpha_{\nu 0}$, then $t_{\mu\mu'}=t\delta_{\mu\mu'}\,\delta_{\mu\nu_0}$. To solve (213) the following relation should be satisfied

$$\mathrm{Det}[G_{0\sigma}(\mu,\mu';z)t_{\mu\mu'}+\delta_{\mu\mu'}]=0. \quad (214)$$

The relation (214) gives the equation for evaluating the energies of local states. Substituting $\varepsilon_k^{(j)}$ and $C^{(j)}_{k\sigma}(\mu)$ from (184)–(186) into (204) one can obtain expressions for $G_{0\sigma}(\mu,\nu;z)$ for the most interesting case of local states in the forbidden zone:

$$\left.\begin{aligned}
&G_{0\sigma}(2\mu,2\nu;z_\sigma)=(z_\sigma-a\tau_\sigma)(2\beta^2\mathrm{sh}\Theta)^{-1}(-1)^{\mu-\nu}[e^{-|\mu-\nu|\Theta}-e^{-|\mu+\nu|\Theta}],\\
&G_{0\sigma}(2\mu-1,2\nu-1;z_\sigma)=(z_\sigma+a\tau_\sigma)(2\beta^2\mathrm{sh}\Theta)^{-1}(-1)^{\mu-\nu}[e^{-|\mu-\nu|\Theta}+e^{-|\mu+\nu|\Theta}],\\
&G_{0\sigma}(2\mu-1,2\nu;z_\sigma)=(-1)^{\mu-\nu}(\beta\mathrm{sh}\Theta)^{-1}[\mathrm{sh}\mu\Theta-\mathrm{sh}(\mu-1)\Theta],\quad(\nu\geq\mu)\\
&G_{0\sigma}(2\mu-1,2\nu;z_\sigma)=(-1)^{\mu-\nu}(\beta\mathrm{sh}\Theta)^{-1}[1-e^{\Theta}]e^{-\mu|\Theta}\mathrm{sh}\mu\Theta,\quad(\nu<\mu)
\end{aligned}\right\}\quad(215)$$

where Θ is given by the relation

$$\mathrm{ch}\,\Theta=\frac{-(z_\sigma^2-a^2-2\beta^2)}{2\beta^2}.$$

The Green functions determined by (215) are identical with those for a diatomic $(\cdots-\mathrm{A}-\mathrm{B}-\mathrm{A}-\mathrm{B}-\cdots)$ chain with equal bonds in tight binding approximation (see the expressions (10)–(13) in paragraph 2 above and (14)–(15) in [4] for $\beta_1=\beta_2$ and $z=a\tau_\sigma$). If the values of $n_{\nu\sigma}$ were independent of ν this fact would be considered as trivial because the Hamiltonian (183) and that which is used in paragraph 2 above and in [4] are identical. However, as follows from (189), $n_{\nu\sigma}$ depends on ν and the self-consistent field near the end of a chain differs from the one in the middle of a chain. Thus, the Hamiltonian (183) differs from the Hamiltonian of [4] and coincides with the tight-binding Hamiltonian for the diatomic chain in the case of the specific change of the Coulomb integrals α_μ^{A} and α_μ^{B} when increases. As the Green functions (215) and (10)–(13) in paragraph 2 above and (9)–(10) in [4] are identical, one can use the results of paragraph 2 and [4] to consider the conditions under which the local states arise. These conditions corresponding to the simplest perturbation, which is described by the change of the Coulomb integral of an atom or resonance integral of a bond, can be formulated as follows.

The infinitesimal change $\Delta\alpha$ of the Coulomb integral of an odd atom is sufficient to give rise to a local state in the forbidden zone.

On the other hand, the perturbation of an even atom with number $2l$ generates the local state in the forbidden zone only if

$$|\Delta\alpha|>2\beta^2(\sqrt{a^2+4\beta^2}\pm a)^{-1}\frac{1}{l}. \quad (216)$$

The wave function and the energy of the local state caused by the perturbation of the first atom will be considered in more details. Substituting $\nu=1$ and $t_{\mu\nu}=t\,\delta_{\mu\nu}\,\delta_{\mu 1}$ into (214) one can obtain

$$1+\lambda(\tilde z_{p\sigma}-d\tau_\sigma)(1+e^{-q_0})/\,\mathrm{sh}\,q_0=0 \quad (217)$$

with

$$\mathrm{ch}\,q_0=1+2(d^2-\tilde z_{p\sigma}^2),\quad \tilde z_{p\sigma}=\frac{z_{p\sigma}}{|2\beta|}<d, \quad (218)$$

and

$$1-\lambda(\tilde z_{p\sigma}-d\tau_\sigma)(1-e^{-Q_0})/\,\mathrm{sh}\,Q_0=0 \quad (219)$$

with

$$\mathrm{ch}\,Q_0=2(\tilde z_{p\sigma}^2-d^2)-1,\quad |\tilde z_{p\sigma}|>\sqrt{1+d^2}. \quad (220)$$

As seen from (217), the infinitesimal change of the Coulomb integral of the first atom actually leads to the local state appearing in the forbidden zone. Its energy distance from the edge of the gap is equal to

$$|\tilde z_{p\sigma}-a|\approx a\lambda^2=1.1\lambda^2\ eV.$$

In the case of large perturbation $\lambda\to\pm\infty$ the Eq. (219) gives for the energy of local state

$$\tilde z_{p\sigma}\to\pm\infty.$$

Using the general equation (213) one can obtain the wave function of a local state, the first atom being perturbed

$$\varphi_{p\sigma}(\mu) = \tau_{p\sigma}(-1)^{\frac{\mu-1}{2}} e^{-\frac{\mu-1}{2}q_0}, \quad (\mu \text{ is odd}) \quad (221)$$

$$\varphi_{p\sigma}(\mu) = \tau_{p\sigma}\lambda(-1)^{\frac{\mu}{2}} e^{-\frac{\mu}{2}q_0}, \quad (\mu \text{ is even}) \quad (222)$$

where

$$\tau_{p\sigma} = \frac{1-e^{-2q_0}}{1+\lambda^2 e^{-2q_0}}$$

and q_0 are determined by (218). In accordance with (219) the larger the perturbation parameter the higher the degree of the localization of the wave function of the impurity level in the region of impurity. It can be shown that the situation is exactly the same when $\nu \neq 1$.

If the perturbation of a chain can be simulated by a small change of the resonance integral of a bond, then it does not cause the local states to split off the allowed bands.

Derived above properties of local states differ essentially from those obtained under the assumption that the energy gap in the spectra of long polyene chains is due to the bond alternation. In the latter case the perturbation giving rise to the local state in the forbidden zone is $\sim 1/l$, (l being the number of a perturbed atom) both for even and odd l. Thus. In contrast to the model above, the generation of a "surface" state ($l = 1$) is most difficult. In addition, the appropriate change of the resonance integral of a bond (weakening of a stronger bond or strengthening of a weaker bond) leads to two local states appearing in the forbidden zone.

The recent theoretical results [111, 131, 134] provide an evidence in favor of the electron-correlation nature of the polyene-spectrum gap. But it appears likely that the question still remains doubtful (see, *e. g.*, [135–137]). The above mentioned differences in the properties of local states can be used to study experimentally whether the energy gap is due to electron correlations or its appearance is a consequence of the bond alternation.

The results obtained so far seem to be useful in the study of the following question. In contrast to polyenes, the first optical transition frequency in the symmetric cyanide dyes tends to zero when the conjugated chain of the dye is lengthened [138]. Nevertheless, the long conjugated chains of cyanide dyes and polyenes differ by their end groups only. Then, it is natural to correlate the above difference in the optical spectra of these two classes of molecules with the effect of nitrogen atoms of the end groups of cyanide dyes. Indeed, the insertion of nitrogen atoms into the polyene chain can give rise to a local state near the bottom of an empty zone. As a consequence, the first optical transition corresponds to the transition of an electron from this local level to an empty zone. The energy of this transition is small for long chains. Then, the extrapolation of experimental data can give zero value (or nearly zero value) of the first transition frequency. Let us also note that the conjugated chains of cyanide dyes consist of an odd number of atoms N. But, the number of π-electrons N_e is even: $N_e = N \pm 1$. If $N_e = N+1$ then the local state considered above is occupied in the ground state. If $N_e = N-1$ then there is a hole in a valence zone of cyanide dye and the explanation of optical experiments is trivial.

6. Appendix and conclusions

We first deal with the derivation of main relations used in § 5.1, namely, will consider the sum in (193):

$$-G_{0\sigma}(\nu,\nu;z_{q\sigma}^{(i)}) \equiv \sum_{k,j} \frac{|C_{k\sigma}^{(j)}(\nu)|^2}{\varepsilon_k^{(j)} - z_{q\sigma}^{(i)}} =$$
$$= \frac{4}{N}\sum_k \frac{\sin^2 k\nu[\varepsilon_q^{(i)} + a\tau_\sigma(-1)^\nu]}{\varepsilon_k^2 - \varepsilon_q^2 - \frac{2\pi}{N}\Theta_{q\sigma}^{(i)}\varepsilon_q^{(i)}\frac{d\varepsilon_q^{(i)}}{dq}} + \mathrm{O}\left(\frac{1}{N}\right) =$$
$$\equiv [\varepsilon_q^{(i)} + a\tau_\sigma(-1)^\nu]\, S^{(i)}(q,\sigma), \quad (223)$$

where we have used (194). To calculate $S^{(i)}(q,\sigma)$ we shall use the method developed by Lifshits [20, 21]. Let us denote

$$S^{(i)}(q,\sigma) = S_1^{(i)}(q,\sigma) + S_2^{(i)}(q,\sigma) \quad (224)$$

and evaluate each sum separately, namely:

$$S_1^{(i)}(q,\sigma) = \frac{4}{N^2}\sum_{k\neq q} \frac{2\pi\Theta_{q\sigma}^{(i)}(d\varepsilon_q^{(i)}/dq)\,\varepsilon_q^{(i)}\sin^2 k\nu}{(\varepsilon_k^2 - \varepsilon_q^2)\left(\varepsilon_k^2 - \varepsilon_q^2 - \frac{2\pi}{N}\Theta_{q\sigma}^{(i)}\frac{d\varepsilon_q^{(i)}}{dq}\right)} -$$
$$-\frac{2}{\pi}\frac{\sin^2 q\nu}{\Theta_{q\sigma}^{(i)}\varepsilon_q^{(i)}\frac{d\varepsilon_q^{(i)}}{dq}} =$$
$$= \frac{2\sin^2 q\nu}{\varepsilon_q^{(i)}(d\varepsilon_q^{(i)}/dq)}\left[\frac{2}{N^2}\sum_{k\neq q}\frac{\pi\Theta_{q\sigma}^{(i)}}{(k-q)\left(k-q-\frac{\pi}{N}\Theta_{q\sigma}^{(i)}\right)} - \frac{1}{\pi\Theta_{q\sigma}^{(i)}}\right] +$$
$$+\mathrm{O}\left(\frac{1}{N}\right) \approx$$
$$\approx \frac{2\sin^2 q\nu}{\varepsilon_q^{(i)}(d\varepsilon_q^{(i)}/dq)}\left(\sum_{n\neq 0}\frac{\pi\Theta_{q\sigma}^{(i)}}{n\pi(n\pi - \pi\Theta_{q\sigma}^{(i)})} - \frac{1}{\pi\Theta_{q\sigma}^{(i)}}\right) =$$
$$= -2\sin^2 q\nu\,\mathrm{ctg}\left[\frac{\pi\Theta_{q\sigma}^{(i)}}{\varepsilon_q^{(i)}(d\varepsilon_q^{(i)}/dq)}\right], \quad (225)$$

$$S_2^{(i)}(q,\sigma) = \frac{4}{N}\sum_{k\neq q}\frac{\sin^2 k\nu}{\varepsilon_k^2 - \varepsilon_q^2} =$$
$$= \frac{1}{2\pi\beta^2}\int_C \frac{1-\cos k\nu}{\cos k - \cos 2q}dk + \mathrm{O}\left(\frac{1}{N}\right), \quad (226)$$

where $\int_c$ denotes the principal value of a corresponding contour integral taken from 0 to π. In order to evaluate (226) we need to calculate

$$I \equiv \int_C \frac{\cos k\nu}{\cos k - \cos 2q}dk = I_1 + I_2, \quad (227)$$

where

$$I_1 = \frac{1}{2}\int_C dx \frac{e^{ivx}}{\cos x - \cos q}, \quad I_2 = \frac{1}{2}\int_C dx \frac{e^{-ivx}}{\cos x - \cos q}. \qquad (228)$$

The integrals (228) can be evaluated by the residue theory. The integral I_1 is taken along the contour C_1, and I_2 – along contour C_2 (Fig. 4). Calculations give

$$I = \frac{i\pi}{2}\mathrm{res}\frac{e^{ivz} - e^{-ivz}}{\cos z - \cos q}\Big|_{z=q} = \pi\frac{\sin vq}{\sin q}. \qquad (229)$$

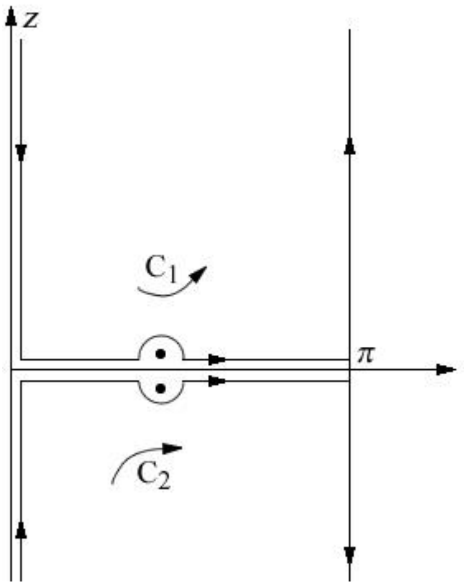


Fig. 4. The contours for the evaluation of integrals (A6)

The substitution of (229) into (227) and (226) results in the relation

$$S_2^{(i)}(q,\sigma) = -\frac{1}{2\beta^2}\frac{\sin 2vq}{\sin 2q}. \qquad (230)$$

Equation (195) can be obtained from (225), (230), (223), and (193).

The eigenfunctions of (191) are defined as [20, 21]

$$\varphi_{q\sigma}^{(i)}(\mu) = -t\,\tau_{q\sigma}^{(i)}\sum_{k,j}\frac{C_{k\sigma}^{(j)}(\mu)C_{k\sigma}^{(j)}(\nu)}{\varepsilon_k^{(j)} - z_{q\sigma}^{(i)}}. \qquad (231)$$

The sum in (231) is calculated just like as $S_1^{(i)}(q,\sigma)$.

Let us evaluate a normalization constant $\tau_{q\sigma}^{(i)}$, namely

$$\sum_{\mu=1}^{N}[\varphi_{q\sigma}^{(i)}(\mu)]^2 = \left[\frac{\tilde{C}_{q\sigma}^{(i)}(\nu)\sin q\nu}{d\varepsilon_q^{(i)}/dq}t\,\tau_{q\sigma}^{(i)}\right]^2 \frac{2}{N}\sum_k\left(k - q - \frac{\pi}{N}\Theta_{q\sigma}^{(i)}\right)^{-2} + $$
$$+\mathrm{O}\left(\frac{1}{N}\right) = 2N(t\,\tau_{q\sigma}^{(i)})^2\left[\frac{\tilde{C}_{q\sigma}^{(i)}(\nu)\sin q\nu}{(d\varepsilon_q^{(i)}/dq)\sin\pi\Theta_{q\sigma}^{(i)}}t\,\tau_{q\sigma}^{(i)}\right]^2 = 1. \qquad (232)$$

Substituting $\tau_{q\sigma}^{(i)}$ from (232) into (231) one obtains (197)–(198).

It follows from (232) that

$$(t\,\tau_{q\sigma}^{(i)})^2 = \sum_{k,j}\left(\frac{C_{k\sigma}^{(j)}(\nu)}{\varepsilon_k^{(j)} - z_{q\sigma}^{(i)}}\right)^2 =$$
$$= \left(\frac{d\,z_{q\sigma}^{(i)}}{dt}\right)^{-1}\frac{d}{dt}\sum_{k,j}\frac{[C_{k\sigma}^{(j)}(\nu)]^2}{\varepsilon_k^{(j)} - z_{q\sigma}^{(i)}} = -\frac{1}{t^2}\left(\frac{d\,z_{q\sigma}^{(i)}}{dt}\right)^{-1}. \qquad (233)$$

Taking also into account that according with (231) and (232) $\varphi_{q\sigma}^{(i)}(\nu) = \tau_{q\sigma}^{(i)}$, one obtains (201).

Now let us consider functions $G_{0\sigma}(\nu,\mu;z)$, where

$$\frac{|z|}{2|\beta|} \notin (d, \sqrt{1+d^2}),$$

i. e., for states splitting off zones. Using (184)–(186) one obtains

$$G_{0\sigma}(\nu,\nu;z) = -\sum_{k,j}\frac{[C_{k\sigma}^{(j)}(\nu)]^2}{\varepsilon_k^{(j)} - z} =$$
$$= \frac{\tilde{z} + (-1)^{\nu}d\,\tau_{\sigma}}{\pi|\beta|}\int_0^{\pi}dk\,(1 - \cos\nu k)/(\alpha + \cos k), \qquad (234)$$

where

$$\tilde{z} = z/2|\beta|, \quad d = a/2|\beta|, \quad \alpha = 1 + 2(d^2 - \tilde{z}^2).$$

The integral in (234) is calculated as the integral (227) except the poles of the integrand are in the complex plane k on the lines $\mathrm{Re}\,k = 0$ $(\tilde{z}^2 > 1 + d^2)$ and $\mathrm{Re}\,k = \pi$ $(|\tilde{z}| < d)$. Having carried out the calculations one obtains

$$\int_0^{\pi}dk\frac{\cos\nu k}{\alpha + \cos k} = \begin{cases}(-1)^{\nu}\pi e^{-\nu q_0}/\mathrm{sh}\,q_0, & (\alpha > 0)\\ \pi e^{-\nu Q_0}/\mathrm{sh}\,Q_0, & (\alpha < 0)\end{cases} \qquad (235)$$

where

$$\mathrm{ch}\,q_0 = 1 + 2(d^2 - \tilde{z}^2), \quad (\tilde{z}^2 < d^2)$$
$$\mathrm{ch}\,Q_0 = 2(\tilde{z}^2 - d^2) - 1. \quad (\tilde{z}^2 > 1 + d^2)$$

Using (235) one can calculate all functions $G_{0\sigma}(\nu,\mu;z)$ with $\tilde{z}^2 > 1 + d^2$ or $\tilde{z}^2 < d^2$. In particular, one can obtain equations for local energies

$$1 - t\,G_{0\sigma}(\nu,\nu;z_{pz}) = 0 \qquad (236)$$

and for corresponding functions

$$\varphi_{p\sigma}(\mu) = t\,\tau_{p\sigma}G_{0\sigma}(\mu,\nu;z_{pz}). \qquad (237)$$

The relations (212), (215), (217)–(222) results from (236) and (237). If $|\lambda| \gg 1$, then it follows from (235) and (236) that $q_0Q_0 \gg 1$. Using (212) and (199) one can see that if $|\lambda| \ll 1$ then

$$\tau_{p\sigma}^2 \sim t^{-2}(1-e^{-2q})\,\mathrm{sh}^2 q, \quad (q = q_0, Q_0)$$
$$\text{hence } |\varphi_{p\sigma}(\mu)|^2 \sim \lambda^2. \qquad (238)$$

Finally in part 2 of the review we turn to cumulenes which have two orthogonal π-systems, as compared with polyenes, and will end with the thorough discussion of the physical nature of the forbidden zone in quasi-one-dimensional electron systems including the summary of the review with conclusions and perspectives.

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