MINISTRY OF EDUCATION AND SCIENCE OF UKRAINE ODESSA STATE ENVIRONMENTAL UNIVERSITY

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Calculational Methods in Quantum Geometry and Chaos Theory, P. 4.

Odessa - 2015

ББК 22.193 G55 УДК 539.184:539.27

Друкується за рішенням Вченої ради Одеського державного екологічного університету (протокол № 11 від 27.11.2014 р.).

Kruglyak Yu.A., Glushkov A.V., Prepelitsa G.P., Buyadzhi V.V., Calculational Methods in Quantum Geometry and Chaos theory, P. 4. Lecture's Notes - Odessa: TEC.-2015.

There are presented the key elements of modern quantum geometry and quantum mechanics methods, namely, elements of Hartree-Fock calculation method of energy spectra (eigenvalues, eigenfunctions) for some multielectronic systems, crystalline compounds, quasi-1-dimensional electronic systems etc. For M.Sc. and PhD students of the specialities: "Calculational Mathematics", "Mathematical Physics", "Optics and Laser Physics".

Изложены элементы современной квантовой геометрии и квантовой механики, в т.ч., методы типа Хартри-Фока вычисления энергетических спектров (собственных значений, собственных финкций) для ряда многоэлектронных систем, кристаллических соединений, квази-1-мерных электронных систем и др. Для магистров и аспирантов специальностей «Вычислительная математика», «Оптика и лазерная физика» «Математическая физика».

Викладені елементи сучасної квантової геометрії і квантової механіки, у т.ч., методи типу Хартрі-Фока обчислення енергетичних спектрів (власних значень, власних фінкцій) для ряда багатоелектронних систем, кристалічних сполук, квазіодномірних електронних систем тощо. Для магістрів та аспірантів спеціальностей «Обчислювальна математика», «Оптика та лазерна фізика» «Математична фізика».

Навчальне видання

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Introducing Remarks

Numerical methods in quantum geometry and a chaos theory are central to modern computing mathematics and quantum physics and chemistry. It reflects new requirements that relate to modern mathematics and physics training.

It is well known that the methods of applied mathematics – Quantum geometry and Quantum mechanics give a powerful and and efficient tool researchers in various fields of science and engineering for mathematical modeling of the most difficult tasks. Especially this fact applies to address a wide range of problems of modern applied mathematics and computational physics. Implementation of new mathematical models on the computer is using methods of applied mathematics, which, of course, constantly being improved with advances in computer technology. Construction of mathematical model of any problem, which is to ensure efficiency and optimality criterion, can be obtained quickly through an appropriate effective algorithm. Any reduction of problems of mathematical physics or engineering course often reduces to the solution of algebraic equations with one or other structure. As a result, most of the methods applied mathematics related to reducing the problem to a system of algebraic equations and their subsequent resolution.

In this book we present the key elements of modern quantum geometry and quantum mechanics methods, in particular, the elements of Hartree-Fock calculation method of energy spectra (eigenvalues and eigenfunctions) for much of some electronic systems, crystalline compounds, quasi-one-dimensional electronic systems (polyenes and cumulenes) and others. For MSc and PhD students of the the specialities: "Applied Mathematics", "Mathematical Physics" *etc.*

Chapter 1. QUANTUM-MECHANICAL STUDIES OF QUASI-ONE-DIMENSIONAL ELECTRON SYSTEMS

1.1 Introduction

This chapter 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 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 we 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 electronic 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, the summary with conclusions and perspectives is given [13].

1.2 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 1d-metal 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.

1.2.1 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 :

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

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)

$$g_{mn}(E) = \sum_{i} \frac{\varphi_{i}^{*}(m) \varphi_{i}(n)}{E - E_{i}},$$
(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:

$$U_{l} = -\sum_{p,s} g_{lp}(E) V_{ps} U_{s}.$$
 (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])

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

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

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

For the corresponding Green function (2) one has

$$g_{mn}^{0}(E) = \frac{2}{N+1} \sum_{k} \frac{\sin kn \cdot \sin km}{E - E_0 - 2\beta \cos k}.$$
 (5')

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

$$g_{mn}^{0}(E) = \frac{\sinh n\kappa \, e^{-m\kappa}}{\beta \, \mathrm{sh}\kappa} \left[(-1)^{m-n} Q(E) - Q(-E) \right], \tag{5}$$

where a step-function

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

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 $m \ge n$.

Let us consider the polyene chain with 2*N* 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

$$\begin{split} \psi_{k}^{(1)} &= \frac{1}{\sqrt{N}} \sum_{n=1}^{N} \left[\chi_{2n} \sin kn - \chi_{2n-1} \frac{\beta_{1} \sin kn + \beta_{2} \sin k(n-1)}{\sqrt{\beta_{1}^{2} + \beta_{2}^{2} + 2\beta_{1}\beta_{2} \cos k}} \right], \quad (6') \\ E_{1}(k) &= E_{0} - \sqrt{\beta_{1}^{2} + \beta_{2}^{2} + 2\beta_{1}\beta_{2} \cos k}, \\ \psi_{k}^{(2)} &= \frac{1}{\sqrt{N}} \sum_{n=1}^{N} \left[\chi_{2n} \sin kn + \chi_{2n-1} \frac{\beta_{1} \sin kn + \beta_{2} \sin k(n-1)}{\sqrt{\beta_{1}^{2} + \beta_{2}^{2} + 2\beta_{1}\beta_{2} \cos k}} \right], \quad (6'') \\ E_{2}(k) &= E_{0} + \sqrt{\beta_{1}^{2} + \beta_{2}^{2} + 2\beta_{1}\beta_{2} \cos k}. \end{split}$$

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

$$\sin kN + \frac{\beta_1}{\beta_2} \sin k(N+1) = 0.$$
 (7)

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

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

Inserting the corresponding coefficients $\varphi_k(m)$ from (6') and (6") 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:

$$g_{2m,2n}(E) = (-1)^{n-m} \frac{E' \operatorname{sh} m \kappa e^{-\kappa n}}{\beta_1 \beta_2 \operatorname{sh} \kappa}, \qquad (8a)$$

$$g_{2m-1,2n}(E) = (-1)^{n-m+1} [\beta_1 \operatorname{sh} m\kappa - \beta_2 \operatorname{sh}(m-1)\kappa] \frac{e^{-\kappa n}}{\beta_1 \beta_2 \operatorname{sh} \kappa}, \qquad (8b)$$

$$g_{2n+1,2n}(E) = \frac{\beta_2 - \beta_1 e^{-\kappa}}{2\beta_1 \beta_2 \operatorname{sh} \kappa},$$
(8c)

$$g_{2m-1,2m-1}(E) = \frac{E'}{2\beta_1\beta_2 \operatorname{sh}\kappa} \left[1 - \frac{e^{-(2m-1)\kappa}}{E'^2} \left(\beta_2 e^{\kappa/2} - \beta_1 e^{-\kappa/2}\right)^2 \right],$$
(8d)

where

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

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.

1.2.2 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

$$1 + \Delta \alpha g_{nn}(E) = 0 \tag{9}$$

determines the energies of the local states.

We first consider the chain without bond alternation. Substituting the function $g_{nn}^{0}(E)$ from (5) into (9), one obtains

$$1 + \Delta \alpha \frac{1 - e^{-2n\kappa}}{2\beta \operatorname{sh}\kappa} [Q(E) - Q(-E)] = 0.$$
 (10)

Equation (10) can be solved analytically for two limiting cases: 1) when $n \rightarrow \infty$ that is the substitution is made far away from the edge of the chain, and 2) when n=1 (surface state). When $n \rightarrow \infty$, neglecting in Eq. (10) the term $\Box e^{-n\kappa}$ and solving the corresponding equation, one obtains the known expression for the energy of the state localized in the middle of the chain [24]

$$E = E_0 + \operatorname{sign}(\Delta \alpha) \sqrt{(\Delta \alpha)^2 + 4\beta^2} \,. \tag{11}$$

Putting n=1 into (10) one also obtains the known expression for the energy of the surface state

$$E = E_0 + \operatorname{sign}(\beta / \Delta \alpha) (\Delta \alpha + \beta^2 / \Delta \alpha).$$
(12)

It is easy to show that the state with an energy given by (12) exists only when

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

whereas in the case of the removal of the local level in the middle of the chain, as it follows from (11), the perturbation $\Delta \alpha$ might be infinitely small.

For $n \neq 1$ and $n \neq \infty$ Eq. (10) 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 (5) that the minimal distance of the local level from the band edge corresponds to $\kappa \rightarrow 0$ (or $|E - E_0| \rightarrow |2\beta|$). Substituting $\kappa \rightarrow 0$ into (10) one concludes that perturbation of the *n*-th atom leads to the appearance of the local level only when

$$|\frac{\Delta\alpha}{\beta}| > \frac{1}{n}.$$
 (13)

Now we shall consider the chain with alternating bonds. It follows from (8a) and (8d) that the results should be different for even and odd perturbed atoms. However, for $n \rightarrow \infty$ these differences are exponentially small and equations of the type (9) should be the same for the states localized in the middle of the chain. Substituting $n \rightarrow \infty$ into (8a) and (8d) and putting a corresponding expression into (9), 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:

$$E_{\infty} = \pm \operatorname{sign}(\Delta \alpha) \sqrt{\beta_1^2 + \beta_2^2 + \frac{(\Delta \alpha)^2}{2}} \pm \left[(\beta_1^2 + \beta_2^2) (\Delta \alpha)^2 + \frac{(\Delta \alpha)^4}{4} + 4\beta_1^2 \beta_2^2 \right]^{1/2} . \quad (14)$$

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 (14) 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 (8a) for the even atoms into (9), one obtains

$$1 + \Delta \alpha \frac{E' \operatorname{sh} m \kappa e^{-m\kappa}}{\beta_1 \beta_2 \operatorname{sh} \kappa} = 0, \qquad (15)$$

where $2m \equiv l$ is the number of the perturbed atom. Approaching $E \rightarrow \pm |\beta_1 - \beta_2|$ in Eq. (15), one concludes that the minimal perturbation by its absolute value needed for removing the level in the forbidden zone is

$$\Delta \alpha_{\min}^{in}(l) = -\operatorname{sign}(E) \left| \frac{2\beta_1 \beta_2}{\beta_1 - \beta_2} \right| \frac{1}{l}, \qquad (16)$$

and for the out-of-band levels

$$\Delta \alpha_{\min}^{out}(l) = \operatorname{sign}(E) \left| \frac{2\beta_1 \beta_2}{\beta_1 + \beta_2} \right| \frac{1}{l}.$$
 (17)

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

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

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

$$\Delta \alpha_{\min}^{in}(l) = -\operatorname{sign}(E) \left| \frac{\beta_1 - \beta_2}{2\beta_1 \beta_2} l + \frac{\beta_1 + \beta_2}{2\beta_1 \beta_2} \right|^{-1},$$
(18)

and for the out-of-band level

$$\Delta \alpha_{\min}^{out}(l) = \operatorname{sign}(E) \left| \frac{\beta_1 + \beta_2}{2\beta_1 \beta_2} l + \frac{\beta_1 - \beta_2}{2\beta_1 \beta_2} \right|^{-1}.$$
 (19)

Comparing (18) and (19) with (16) and (17) 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 (18) and (19) that the appearance conditions for the surface level (l = 1) outside the bands and in the forbidden zone are the same, namely:

$$|\Delta \alpha_{\min}^{in}(1)| = |\Delta \alpha_{\min}^{out}(1)| = |\beta_2|, \qquad (20)$$

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 (6') and (6") 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

$$\psi^{(3)} = \sum_{l} \varphi_{3}(l) \chi_{l}, \quad \varphi_{3}(l) = \begin{cases} \sqrt{\beta_{2}^{2} - \beta_{1}^{2}} (\beta_{1} / \beta_{2})^{l-1} / \beta_{2} & \text{if} \quad l = 2m + 1, \\ 0 & \text{if} \quad l = 2m, \end{cases}$$

and Eq. (9) leads to the following equation for the energy of the local states

$$\frac{2 \cdot \Delta \alpha \cdot E}{\pi} \int_{0}^{\pi} \frac{|\varphi_{1}(k,l)|^{2}}{E^{2} - E_{1}^{2}(k)} dk + \frac{\Delta \alpha}{E} |\varphi_{3}(l)|^{2} = 1, \qquad (21)$$

where *l* is the number of the perturbed atom, and $\varphi_1(k,l)$ are the coefficients of AOs in (6'). For even values of *l*: $\varphi_3(l) = 0$. This means that the formulae (15) – (17) remain valid. For l = 2m+1 the condition for removing the local level outside of the bands coincides with (19). However, for the existence of the level near the edge of the forbidden zone it is now necessary to have

$$\Delta \alpha = \operatorname{sign}(E) \left(\frac{\beta_2 - \beta_1}{2\beta_1 \beta_2} l - \frac{\beta_1 + \beta_2}{2\beta_1 \beta_2} \right)^{-1}$$
(22)

instead of (18).

Equation (22) 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 (21) for l = 1 (perturbed surface level). The energy of the level in the forbidden zone

$$E = \operatorname{sign}(\Delta \alpha) \sqrt{\beta_1^2 + \beta_2^2 - 2\beta_1 \beta_2 \operatorname{ch} \kappa} , \qquad (23')$$

where

$$\kappa = \ln\left\{\frac{1}{2}\left[\frac{\beta_2}{\beta_1} - \frac{(\Delta\alpha)^2}{\beta_1\beta_2}\right] + \sqrt{\frac{1}{4}\left[\frac{\beta_2}{\beta_1} - \frac{(\Delta\alpha)^2}{\beta_1\beta_2}\right]^2 + \frac{(\Delta\alpha)^2}{\beta_2^2}}\right\}.$$
 (23")

It is seen from (23) 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 $|\Delta \alpha| \rightarrow |\beta_2|$, then $|E| \rightarrow |\beta_2 - \beta_1|$ which is in agreement with the criteria (22). Further increase of $|\Delta \alpha| > |\beta_2|$ leads to the infusion of the local level into the allowed band. It follows from (19), the surface level appears with an energy $|E| \ge |\beta_1 + \beta_2|$, 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 (22), 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.

1.2.3 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

$$U_{l} + \Delta \alpha [g_{lm}(E)U_{m} + g_{ln}(E)U_{n}] = 0.$$
(24)

Substituting consequently l = m and l = n into (24), one obtains a system of two homogeneous linear equations, the solvability condition of which

$$[1 + \Delta \alpha g_{mn}(E)][1 + \Delta \alpha g_{nn}(E)] - (\Delta \alpha)^2 g_{mn}^2(E) = 0$$
⁽²⁵⁾

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 (25), one obtains

$$\left(1 + \frac{\Delta\alpha}{\beta} e^{-m\kappa} \frac{\mathrm{sh}m\kappa}{\mathrm{sh}\kappa}\right) \left(1 + \frac{\Delta\alpha}{\beta} e^{-n\kappa} \frac{\mathrm{sh}n\kappa}{\mathrm{sh}\kappa}\right) = \left(\frac{\Delta\alpha}{\beta} e^{-m\kappa} \frac{\mathrm{sh}n\kappa}{\mathrm{sh}\kappa}\right)^2.$$
(26)

When |n-m| increases, the right-hand side of (26) decreases approximately as $\exp[-(m-n)\kappa]$. So for a large distance between defects it might be assumed equal to zero. Then Eq. (26) is transformed to Eq. (10) for the energy of the local state in the case of single substitution, and for $m,n \square$ 1 there are two degenerate local states with an energy

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

For $m,n \square 1$, but $|m-n \square 1$, then neglecting terms like $\square \exp(-m\kappa)$, $\exp(-n\kappa)$, one obtains from (26)

$$\left|\frac{\Delta\alpha}{\beta}\right|\frac{1\pm e^{-|m-n|\kappa}}{\mathrm{sh}\kappa} = 1.$$
(27)

The solution of (27) with the positive sign exists for any value of $|\Delta \alpha / \beta|$ and $\kappa \rightarrow 0$, that is an appearance of the local level corresponds to $|\Delta \alpha / \beta| \rightarrow 0$. If one considers the negative sign in (27), then a solution does not always exist. An appearance of solution ($\kappa \rightarrow 0$) 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

$$\left|\frac{\Delta\alpha}{\beta}\right| > \frac{1}{m-n} \,. \tag{28}$$

If condition (28) is fulfilled and the splitting of two local states is small, then Eq. (27) can be solved by the iteration method. For the zero approximation one can take the solution when $|m-n| \rightarrow \infty$, namely:

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

The corresponding value of κ_0 is substituted into (27), then κ_1 is found, *etc*. After the first iteration the solution is as follows:

$$E = E_0 + \sqrt{4\beta^2 + (\Delta\alpha)^2} \left\{ 1 \pm \frac{1}{2} \frac{(\Delta\alpha)^2}{4\beta^2 + (\Delta\alpha)^2} \left[\sqrt{1 + \left(\frac{\Delta\alpha}{2\beta}\right)^2} - \left|\frac{\Delta\alpha}{2\beta}\right| \right]^{m-n} \right\} \operatorname{sign}(\Delta\alpha) . \quad (29)$$

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 (26). Letting $\kappa \rightarrow 0$, one obtains the following appearance conditions for one

$$\left|\frac{\Delta\alpha}{\beta}\right| \ge \frac{m+n-\sqrt{(m+n)^2-4n(m-n)}}{2n(m-n)} \tag{30'}$$

and for two local levels

$$\left|\frac{\Delta\alpha}{\beta}\right| \ge \frac{m+n+\sqrt{(m+n)^2-4n(m-n)}}{2n(m-n)}.$$
(30")

It is easy to see that the right-hand side of (30') is smaller than 1/m but that of (30'') 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 (8a) into (25) one obtains an equation for the determination of local state energies, namely:

$$\left(1 + \frac{\Delta \alpha E'}{\beta_1 \beta_2} e^{-m\kappa} \frac{\mathrm{sh}m\kappa}{\mathrm{sh}\kappa}\right) \left(1 + \frac{\Delta \alpha E'}{\beta_1 \beta_2} e^{-n\kappa} \frac{\mathrm{sh}n\kappa}{\mathrm{sh}\kappa}\right) = \left(\frac{\Delta \alpha E'}{\beta_1 \beta_2} e^{-m\kappa} \frac{\mathrm{sh}n\kappa}{\mathrm{sh}\kappa}\right)^2.$$
(31)

Analysis of the appearance conditions having one or two solutions of (31) is analogous to the analysis of Eqs. (26) and (27). In fact, this analysis was based on the consideration of these equations in the limiting case where $\kappa \rightarrow 0$ which in the present case corresponds to an approach up to the edges of the allowed bands, that is $|E| \rightarrow |\beta_1 - \beta_2|$. Comparing asymptotic expressions for (26) and (27) 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 (28) – (30) 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

$$|\Delta \alpha_{1}| \geq \left| \frac{\beta_{1}\beta_{2}}{\beta_{1} - \beta_{2}} \right| \frac{m + n - \sqrt{(m + n)^{2} - 4n(m - n)}}{2n(m - n)},$$
(32)

and for a perturbation which leads to the two local states

$$|\Delta \alpha_{2}| \ge \left| \frac{\beta_{1}\beta_{2}}{\beta_{1} - \beta_{2}} \right| \frac{m + n + \sqrt{(m + n)^{2} - 4n(m - n)}}{2n(m - n)}.$$
(33)

In the case when $m,n \square 1$, but $|m-n \square 1$, Eqs (32) and (33) give

$$|\Delta \alpha_1| \ge 0, \quad |\Delta \alpha_2| \ge \left| \frac{\beta_1 \beta_2}{\beta_1 - \beta_2} \right| \frac{1}{m - n}.$$
(34)

In the latter case Eq. (31) is simplified to

$$\frac{\Delta\alpha}{2\beta_1\beta_2} \frac{E'}{\mathrm{sh}\kappa} (1 \pm e^{-|m-n|\kappa}) = -1$$
(35)

and can be solved by the iteration method if the second term of the left-hand side of (35) is small enough. As a zero approximation, we may take the values of E' and κ_0 for infinitely distant impurities given by (14). The solution after the first iteration is

$$E = -\operatorname{sign}(\Delta \alpha) \sqrt{\beta_1^2 + \beta_2^2 + \frac{(\Delta \alpha')^2}{2} - \sqrt{\frac{(\Delta \alpha')^4}{4} + (\beta_1^2 + \beta_2^2)(\Delta \alpha')^2 + 4\beta_1^2\beta_2^2}}, \quad (36)$$

where

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

It should be noted that perturbed atoms in the formulae (31) - (36) have numbers 2m and 2n.

Finally considering the interaction of two even defects we note, as is seen from (31), 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 (8c) - (8d) into (25), one obtains the following equation for the energies of the local states:

$$\left(1 + \frac{\Delta \alpha E'}{\beta_1 \beta_2} e^{-m\kappa} \frac{\mathrm{sh}m\kappa}{\mathrm{sh}\kappa}\right) \left\{1 + \frac{\Delta \alpha E'}{2\beta_1 \beta_2} \left[1 - \frac{e^{-(2m-1)\kappa}}{E'^2} (\beta_2 e^{-\kappa/2} - \beta_1 e^{\kappa/2})^2\right]\right\} = \left(\frac{\Delta \alpha}{\beta_1 \beta_2}\right)^2 \frac{[\beta_1 \mathrm{sh}m\kappa - \beta_2 \mathrm{sh}(m-1)\kappa]^2}{\mathrm{sh}^2 \kappa} e^{-2n\kappa}.$$
(37)

It is seen from (37) 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 (37) when $\kappa \rightarrow 0$ 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 $(E' \rightarrow -(\beta_1 - \beta_2))$ 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 $\kappa \rightarrow 0$ and $E \rightarrow (\beta_1 - \beta_2)$ into (37), one obtains a quadratic equation with respect to $\Delta \alpha$, namely:

$$\left(\frac{\Delta\alpha}{\beta_1\beta_2}\right)^2 [m(\beta_1 - \beta_2) + \beta_2][(\beta_1 - \beta_2)(n - m) - \beta_2] + \frac{\Delta\alpha}{\beta_1\beta_2}[(n + m)(\beta_1 - \beta_2) + \beta_2] - 1 = 0.$$
(38)

As it is seen from (38), 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 $\Delta \alpha \ge \alpha_1$ and $\Delta \alpha \ge \alpha_2$, where α_1 and α_2 are the larger and smaller roots of (38) in the absolute sense.

If $|m-n| < \beta_2/(\beta_1 - \beta_2)$, then one solution of (38) is positive, and the other which is larger in the absolute sense is negative. The value $\Delta \alpha \ge \alpha_1$ 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 $\Delta \alpha \rightarrow \alpha_2$. 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

$$|n-m| < \frac{\beta_2}{\beta_1 - \beta_2},\tag{39}$$

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 (39), 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.

1.2.4 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

$$U_{l} = -\Delta\beta [g_{ln}(E)U_{n+1} + g_{l,n+1}(E)U_{n}].$$
(40)

Following the same procedure used for the derivation of Eq. (25), one obtains from (40) an equation determining the energy of the local states

$$[1 + \Delta\beta g_{n,n+1}(E)]^2 - (\Delta\beta)^2 g_{n,n}(E) g_{n+1,n+1}(E) = 0.$$
(41)

It follows from (5) and (8a) - (8d) that Eq. (41) 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 (41), one obtains

$$\left[1 - \frac{\Delta\beta}{\beta} \frac{\mathrm{sh}\kappa}{\mathrm{sh}\kappa} e^{-(n+1)\kappa}\right]^2 - \left(\frac{\Delta\beta}{\beta}\right)^2 \frac{\mathrm{sh}\kappa \cdot \mathrm{sh}(n+1)\kappa}{\mathrm{sh}^2\kappa} e^{-(2n+1)\kappa} = 0.$$
(42)

If the perturbation is localized in the middle of the chain, then neglecting terms like $exp(-n\kappa)$ in (42) and solving the corresponding equation, one obtains

$$E = E_0 \pm \left(\beta' + \frac{\beta^2}{\beta'}\right), \quad \beta' = \beta e^{\kappa}.$$
(43)

It follows from (43) 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 (42) and solving the corresponding equation, one obtains

$$E = E_0 \pm \frac{\left(1 + \frac{\Delta\beta}{\beta}\right)^2}{\sqrt{\left(\frac{\Delta\beta}{\beta}\right)^2 + 2\frac{\Delta\beta}{\beta}}}, \quad e^{\kappa} = \sqrt{\left(\frac{\Delta\beta}{\beta}\right)^2 + 2\frac{\Delta\beta}{\beta}}.$$
 (44)

It follows from (44) 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

$$V_{ps} = \Delta \alpha \,\delta_{p1} \delta_{s2} + \Delta \beta (\delta_{p1} \delta_{s2} + \delta_{p2} \delta_{s1}) \,. \tag{45}$$

Substituting (45) into (3) and following the same standard procedure as before, one obtains

$$E_{\pm} = E_0 \pm 2\beta \mathrm{ch}\kappa\,,\tag{46}$$

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 (46) 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. (42) 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 $\kappa \rightarrow 0$ in (42) we see that the local states appear only if

$$\left|\frac{\beta'}{\beta}\right| \ge \sqrt{1 + \frac{1}{n}} \,. \tag{47}$$

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 (8a) - (8d) into (41), the following equation is obtained for the local levels appearing under the perturbation of the weaker bond

$$\left[1 + \frac{\Delta\beta}{\beta_1\beta_2}(\beta_2 - \beta_1 e^{-\kappa})\frac{\mathrm{shn}\kappa e^{-n\kappa}}{\mathrm{sh}\kappa}\right]^2 = \frac{(\Delta\beta)^2 E'^2 \mathrm{shn}\kappa}{2\beta_1^2\beta_2^2 \mathrm{sh}^2\kappa} e^{-n\kappa} \left[1 - \frac{e^{-(2n+1)\kappa}}{E'^2}(\beta_2 e^{\kappa/2} - \beta_1 e^{-\kappa/2})^2\right], \quad (48)$$

where 2n is the number of the perturbed bond. This equation can be solved exactly for the limiting case $n \square 1$. Letting $n \to \infty$ in (48) and solving the corresponding equation, one obtain the energies of the two states localized far away from the chain edge

$$E' = \pm \sqrt{\beta_1^2 + \beta_2^2 - 2\beta_1\beta_2 \mathrm{ch}\kappa}, \qquad (49)$$

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 (49) 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 (48) 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 $\kappa \rightarrow 0$ in (48), the following condition for their appearance is obtained

$$\left|\frac{\beta_2'}{\beta_2}\right| > \sqrt{1 + \frac{2\beta_1}{l(\beta_1 - \beta_2)}},\tag{50}$$

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

$$\left\{1+\frac{\Delta\beta}{\beta_1\beta_2}\frac{e^{-m\kappa}}{\mathrm{sh}\kappa}[\beta_1\,\mathrm{sh}m\kappa-\beta_2\,\mathrm{sh}(m-1)\kappa]\right\}^2 = \frac{1}{2}\left(\frac{\Delta\beta}{\beta_1\,\beta_2\,\mathrm{sh}\,\kappa}\right)^2 e^{-m\kappa}\mathrm{sh}m\kappa[E^2-e^{-2m\kappa}(\beta_2e^{-\kappa}-\beta_1)^2],(51)$$

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

$$E_{\pm} = \pm \sqrt{\beta_1^2 + \beta_2^2 - 2\beta_1 \beta_2 \mathrm{ch}\kappa} , \qquad (52)$$

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 (52) 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 (51) one obtains for the surface state

$$E_{surf} = \pm \sqrt{\beta_1^2 + \beta_2^2 - 2\beta_1 \beta_2 \mathrm{ch}\kappa} , \qquad (53)$$

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 (53) as well as the surface state exists only when the first bond is sufficiently relaxed, namely, when

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

From Eq. (51) 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 (51) that the local states appear only if

$$\left|\frac{\beta'}{\beta_1}\right| < \sqrt{1 - \frac{2\beta_2}{\beta_1 + \beta_2 + m(\beta_1 - \beta_2)}}.$$
(54)

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).



Figure 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 (52) with $\beta' = \beta_2$. The picture of the energy levels is given in Fig. 2a.



Figure 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. 2b) 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.

Chapter 2. The Generalized Hartree – Fock Method and Its Versions

2.1 Introduction

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}_2 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 $[\lambda] = [\lambda_1, \lambda_2, \lambda_3, ..., \lambda_n]$ of corresponding Young schemes [43], where λ_i is the length of the *i*-th row of the Young scheme under condition that $\lambda_{i+1} \leq \lambda_i$. 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]

$$f^{[\lambda]} = \frac{N! \prod_{i < j} (h_i - h_j)}{h_1! h_2! h_3! \dots h_m!},$$
(55)

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

$$\Psi = \hat{G}\Phi X, \qquad (56)$$

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]

$$\hat{G} \equiv \hat{G}_{i}^{\mu} = \sum_{r} \xi_{\hat{\sigma}_{ri}} \hat{O}_{ri}^{\mu} \hat{\omega}_{\bar{r}\bar{i}}^{\bar{\mu}} , \qquad (57)$$

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 , $\xi_{\hat{\sigma}_n}$ is the parity of the permutation $\hat{\sigma}_n$, and the Young operators \hat{O}_n^{μ} and $\hat{\omega}_{r\bar{t}}^{\bar{\mu}}$ are given by [43 – 45]:

$$\hat{O}_{rs}^{\mu} = \frac{f^{\mu}}{N!} \sum_{\hat{\tau}} U_{rs}^{\mu}(\hat{\tau})\hat{\tau},$$

$$\hat{\omega}_{\bar{r}\bar{s}}^{\bar{\mu}} = \frac{f^{\bar{\mu}}}{N!} \sum_{\hat{\tau}} U_{\bar{r}\bar{s}}^{\bar{\mu}}(\hat{\tau})\hat{\tau},$$
(58)

where $U_{rs}^{\mu}(\hat{\tau})$ are matrix elements of the matrix of the standard orthogonal Young – Yamanouchi representation, and summation in (58) 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}^{μ} 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: $\mu = [2^m, 1^{n-m}], \ \overline{\mu} = [n,m]$ with $n \ge m, n+m = N$. The dimensionality of this representation according to (55) is equal to:

$$f^{[2^{m},1^{n-m}]} = f^{[n,m]} \equiv f = \frac{N!(2S+1)}{\left(\frac{N}{2} + S + 1\right)! \left(\frac{N}{2} - S\right)!},$$
(59)

where 2S = n - m.

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

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$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

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 S_N for any $\hat{\tau}_a, \hat{\tau}_b, \hat{\tau}_r$ can be written as

$$\hat{\tau} = \hat{\tau}_a \hat{\tau}_b \hat{\tau}_r \,. \tag{60}$$

The corresponding matrix elements are given by [46]

$$U_{ff}^{[2^{m},1^{n-m}]}(\hat{\tau}_{a}\hat{\tau}_{b}\hat{\tau}_{r}) = \xi_{\hat{\tau}_{a}}\xi_{\hat{\tau}_{b}}\binom{n}{r}^{-1}, \qquad (61)$$

$$U_{11}^{[n,m]}(\hat{\tau}_a \hat{\tau}_b \hat{\tau}_r) = (-1)^r \binom{n}{r}^{-1}, \qquad (62)$$

where $\binom{n}{r} = \frac{n!}{(n-r)!r!}$ - binomial coefficients.

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

$$\hat{ au}\hat{G}_{i}^{\mu}\Phi ext{X}=\!\xi_{\hat{ au}}\hat{G}_{i}^{\mu}\Phi ext{X}$$

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

$$\hat{S}^{2}\hat{G}_{i}^{\mu}\Phi X = S(S+1)\hat{G}_{i}^{\mu}\Phi X$$

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

$$\Psi^{(GI)} = \hat{G}_i^{\mu} \Phi X \tag{63}$$

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^{μ} satisfy [46] the following relation

$$\sum_{\mu} \frac{1}{f^{\mu}} \sum_{i} \hat{G}_{i}^{\mu} = \hat{\Omega}_{11}^{[1^{N}]} \equiv \frac{1}{N!} \sum_{\hat{\tau}} \hat{\xi}_{\hat{\tau}} \hat{\tau} , \qquad (64)$$

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]

$$E = \left\langle \hat{G}_{i}^{\mu} \Phi \mathbf{X} \middle| \hat{H} \middle| \hat{G}_{i}^{\mu} \Phi \mathbf{X} \right\rangle / \left\langle \Psi^{(GI)} \middle| \Psi^{(GI)} \right\rangle = \left\langle \Phi \middle| \hat{H} \middle| \hat{O}_{ii}^{\mu} \Phi \right\rangle / \left\langle \Phi \middle| \hat{O}_{ii}^{\mu} \Phi \right\rangle.$$
(65)

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

$$\Phi = \varphi_1(\vec{r}_1) \varphi_2(\vec{r}_2) \cdots \varphi_N(\vec{r}_N),$$

$$X = \chi_1(s_1) \chi_2(s_2) \cdots \chi_N(s_N),$$
(66)

where

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

Substituting (66) into (65) 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 (65), namely:

$$\hat{H}_{k}(\vec{r})\varphi_{k}(\vec{r}) = \varepsilon_{k}\varphi_{k}(\vec{r}), \quad (k = 1, 2, ..., N)$$
(67)

where $\hat{H}_k(\vec{r})$ is rather complicated effective Hamiltonian, which depends on the functions φ_k . Equations (67) is a set of nonlinear integro-differential SCF equations for variation function (56). 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 (63) and variational Fock function [42] in the form of Slater determinant [53, 54]. Let us select Φ and X in the form

$$\Phi_{0} = \hat{\tau}_{1i} \varphi_{1}(\vec{r}_{1}) \varphi_{1}(\vec{r}_{2}) \cdots \varphi_{m}(\vec{r}_{2m-1}) \varphi_{m}(\vec{r}_{2m}) \varphi_{m+1}(\vec{r}_{2m+1}) \cdots \varphi_{n}(\vec{r}_{N}),$$

$$X_{0} = \hat{\tau}_{fi} \alpha(1) \beta(2) \cdots \alpha(2m-1) \beta(2m) \alpha(2m+1) \cdots \alpha(n+m),$$
(68)

where $\hat{\tau}_{ji}$ is a permutation by which one obtains table *j* from table *i*. The function $\hat{G}_i^{\mu} \Phi_0 X_0$ coincides up to a phase factor with the Slater determinant. Thus, equations (67) are a generalization of the Hartree – Fock approximation, since during transition from (66) to (68) we superimpose additional constraints on the form of the variation function. This implies that

$$E^{(GI)} = \frac{\left\langle \hat{G}_{i}^{\mu} \Phi \mathbf{X} \middle| \hat{H} \middle| \hat{G}_{i}^{\mu} \Phi \mathbf{X} \right\rangle}{\left\langle \hat{G}_{i}^{\mu} \Phi \mathbf{X} \middle| \hat{G}_{i}^{\mu} \Phi \mathbf{X} \right\rangle} \leq \frac{\left\langle \Psi^{(HF)} \middle| \hat{H} \middle| \Psi^{(HF)} \right\rangle}{\left\langle \Psi^{(HF)} \middle| \Psi^{(HF)} \right\rangle}.$$
(69)

When solving equations (67) it is convenient to use the Roothaan's method [56]. Let us expand the orbitals φ_k over a certain basis functions χ_v :

$$\varphi_k = \sum_{\nu=1}^M C_{\nu k} \chi_{\nu} \quad (M \ge N) \,. \tag{70}$$

Then from (67) one obtains the equations for the expansion coefficients $C_{\nu k}$ of the form

$$\sum_{\nu=1}^{M} H_{\mu\nu}^{(k)} C_{\nu k} = \sum_{\nu=1}^{M} \varepsilon_k S_{\mu\nu} C_{\nu k} , \qquad (71)$$

where $S_{\mu\nu}$ are overlap integrals of the basis functions. Equation (71) is solved by the method of successive approximations [55]. It should be noted that in the general case (for any *i* in the formula (63)) the matrices $H_{\mu\nu}^{(k)}$ depend on *k* [47], which considerably complicates the solution of the equations (71) in comparison with the analogous equations for the Fock variational function. However, if *i* = *f*, thus a variation function $\hat{G}_{f}^{\mu}\Phi X$ is used, equations (71) take the form [48]

$$\sum_{\nu=1}^{M} H_{\mu\nu}^{(a)} C_{\nu k}^{(a)} = \sum_{\nu=1}^{M} \varepsilon_{k}^{(a)} S_{\mu\nu} C_{\nu k}^{(a)} , \qquad (72)$$

$$\sum_{\nu=1}^{M} H_{\mu\nu}^{(b)} C_{\nu k}^{(b)} = \sum_{\nu=1}^{M} \varepsilon_{k}^{(b)} S_{\mu\nu} C_{\nu k}^{(b)} .$$
(73)

Thus, if one uses the operator \hat{G}_{f}^{μ} for the construction of the wave function (9), then one obtains only two sets of equations for the expansion coefficients $C_{\nu k}$. Solving the system of equations (72) – (73), 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

$$\Psi^{(GF)} = \hat{G}_{f}^{\mu} \Phi_{1} X_{1}, \qquad (74)$$

where

$$\Phi_1 = \varphi_{1a}(1) \cdots \varphi_{na}(n) \varphi_{1b}(n+1) \cdots \varphi_{mb}(N) , \qquad (75)$$

$$X_1 = \alpha(1) \cdots \alpha(n) \beta(n+1) \cdots \beta(n+m), \qquad (76)$$

$$\varphi_{ia} = \sum_{\nu} C_{\nu i}^{(a)} \chi_{\nu}, \quad \varphi_{ib} = \sum_{\nu} C_{\nu i}^{(b)} \chi_{\nu} .$$
(77)

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

$$\langle \varphi_{ia} | \varphi_{jb} \rangle \neq 0 \quad (i, j = 1, 2, ..., M).$$
 (78)

Amos and Hall have shown [56] that it is always possible to make such a unitary transformation of the functions in (75):

$$\varphi_{ia}' = \sum_{l=1}^{n} \varphi_{la} V_{li} \quad (\hat{V}\hat{V}^{+} = \hat{I}),$$
(79)

$$\varphi'_{jb} = \sum_{l=1}^{m} \varphi_{lb} U_{lj} \quad (\hat{U}\hat{U}^{+} = \hat{I}),$$
(80)

that

$$\left\langle \varphi_{ia}^{\prime} \mid \varphi_{jb}^{\prime} \right\rangle = \lambda_{i} \delta_{ij}, \quad \lambda_{i} \leq 1 \quad \begin{pmatrix} i = 1, 2, \dots, n \\ j = 1, 2, \dots, m \end{pmatrix}.$$

$$(81)$$

A method to obtain matrices \hat{V} and \hat{U} is explicitly described in [56, 57]. Functions that satisfy equations (81), are usually referred to as the *corresponding orbitals* [58].

Goddard [48] has shown that the function (74) and the matrices of the operators $\hat{H}^{(a)}$ and $\hat{H}^{(b)}$ appearing in the equations (72) and (73) are invariant under the transformation (79) – (80). However, if you require that the self-consistent solutions of the equations (72) and (73) satisfy (81), 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]:

$$H_{\mu\nu}^{(a)} \equiv \left\langle \mu | \hat{h} | \nu \right\rangle \wp_{a}^{a} + \sum_{i,\nu} \left[\left\langle \mu | \hat{h} | i \right\rangle \left\langle \nu b | \nu \right\rangle \wp_{i,a}^{a,\nu b} + \left\langle \mu | \nu b \right\rangle \left\langle i | \hat{h} | \nu \right\rangle \wp_{\nu b,a}^{a,i} \right] \right. \\ \left. + \sum_{u,\nu} \left\langle \mu | ub \right\rangle \left\langle \nu b | \nu \right\rangle \sum_{i,j} \left\langle i | \hat{h} | j \right\rangle \wp_{ub,a,j}^{a,\nu b,i} + \sum_{i,j} \left[\left\langle \mu, i | \hat{g} | \nu, j \right\rangle \wp_{a,j}^{a,i} + \left\langle \mu, i | \hat{g} | j, \nu \right\rangle \wp_{j,a}^{a,i} \right] \right. \\ \left. + \sum_{i,j,t;\nu} \left[\left\langle \mu, i | \hat{g} | j, t \right\rangle \left\langle \nu b | \nu \right\rangle \wp_{j,a,t}^{a,\nu b,i} + \left\langle \mu | \nu b \right\rangle \left\langle j, t | \hat{g} | \nu, i \right\rangle \wp_{\nu b,a,i}^{a,j,t} \right] \right. \\ \left. + \sum_{u,\nu} \left\langle \mu | ub \right\rangle \left\langle \nu b | \nu \right\rangle \sum_{i < j; s, t} \left\langle i, j | \hat{g} | s, t \right\rangle \wp_{ub,a,s,t}^{a,\nu b,i,j} - E \sum_{u,\nu} \left\langle \mu | ub \right\rangle \left\langle \nu b | \nu \right\rangle \wp_{ub,a}^{a,\nu b} \right] \right\}$$

$$(82)$$

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

$$\begin{split} \left\langle \mu \left| \hat{A} \right| vb \right\rangle &= \int d\vec{r} \,\chi_{\mu}^{*}(\vec{r}) \hat{A}(\vec{r}) \varphi_{vb}(\vec{r}) \,, \\ \hat{h}(r) &= -\frac{1}{2} \Delta + \hat{V}(r) \,, \\ \left\langle i, j \left| \hat{g} \right| t, s \right\rangle &= \int d\vec{r}_{1} \, d\vec{r}_{2} \,\varphi_{i}^{*}(\vec{r}_{1}) \varphi_{t}(\vec{r}_{1}) \frac{1}{\left| \vec{r}_{1} - \vec{r}_{2} \right|} \varphi_{j}^{*}(\vec{r}_{2}) \varphi_{s}(\vec{r}_{2}) \,. \end{split}$$

The quantities \wp are quite complicated functions of overlap integrals λ_i defined by (81), for example:

$$\wp_{a}^{a} = \sum_{p=0}^{m-1} {\binom{n}{p}}^{-1} A_{p} \equiv T00,$$
$$A_{p} = \sum_{\substack{\{k_{1}, k_{2}, \dots, k_{p}\}\\(k_{i} \neq k_{j})}} x_{k_{1}} x_{k_{2}} \cdots x_{k_{p}}, \quad x_{k} = \lambda_{k}^{2}.$$

It follows from (82) 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 (81).

Normalization integral for the function (74)

$$\left\langle \Psi^{(GF)} \mid \Psi^{(GF)} \right\rangle = T00.$$
(83)

With the assumption that the unitary transformations (79) and (80) were performed and $\varphi_i^* = \varphi_i$ the average energy value over the function $\Psi^{(GF)}$ is the following [5]:

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

$$\tag{84}$$

where

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

$$TIJ = \sum_{p=0}^{m-J} {\binom{n}{p+I}}^{-1} A_p,$$

$$TIJ(i) = \sum_{p=0}^{m-J} {\binom{n}{p+I}}^{-1} A_p(i),$$

$$TIJ(i, j) = \sum_{p=0}^{m-J} {\binom{n}{p+I}}^{-1} A_p(i, j),$$

$$(85)$$

$$A_{p}(i) = A_{p} - x_{i}A_{p-1}(i) = A_{p}|_{x_{i}=0},$$

$$A_{p}(i, j) = A_{p}(i) - x_{j}A_{p-1}(i, j) = A_{p}|_{x_{i}=x_{j}=0},$$

$$A_{0} = A_{0}(i) = A_{0}(i, j) = 1.$$
(86)

Iterative procedure for solving equations (72) and (73) is as following. Compute the eigenvectors $C_k^{(a)}(i)$ and $C_k^{(b)}(i)$ of the equations (72) and (73) on the *i*-th iteration. Then, being performed the transformations (79) and (80) and defined the corresponding vectors $C_k^{\prime(a)}(i)$ and $C_k^{\prime(b)}(i)$, 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 $C_k^{(a)}$ μ $C_k^{(b)}$ are obtained. Thus, the procedure for solving the equations (72) and (73) 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 (72) and (73) and to perform the transformations (79) and (80) 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 (84). According to (69) 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 (74) built on corresponding orbitals since the function (74) is invariant under transformations (79) and (80) [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

$$\Psi^{(UHF)} = \hat{\Omega}_{11}^{[1^{N}]} \psi_{1\alpha}(1) \cdots \psi_{n\alpha}(n) \psi_{1\beta}(n+1) \cdots \psi_{m\beta}(N) = \frac{1}{N!} \sum_{i=1}^{N!} \xi_{\hat{\tau}_{i}}[\hat{\tau}_{i} \varphi_{1a}(\vec{r}_{1}) \cdots \varphi_{na}(\vec{r}_{n}) \varphi_{1b}(\vec{r}_{n+1}) \cdots \varphi_{mb}(\vec{r}_{N})], \qquad (87) \times [\hat{\sigma}_{i} \alpha(s_{1}) \cdots \alpha(s_{n}) \beta(s_{n+1}) \cdots \beta(s_{n+m})] = \hat{\Omega}_{11}^{[1^{N}]} \Phi_{1} X_{1}$$

where

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

 $\hat{\tau}_i$ – 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 (87), 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 (64), the wave function (87) 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 (87) 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 (87) by projection operators \hat{O}_i :

$$\Psi_l = \hat{\mathbf{O}}_l \Psi^{(UHF)}, \qquad (88)$$

where

$$\hat{O}_{l} = \prod_{k \neq l} \frac{\hat{S}^{2} - k(k+1)}{l(l+1) - k(k+1)} \,. \tag{89}$$

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

$$E^{(EHF)} = \left\langle \Psi_l | \hat{H} | \Psi_l \right\rangle / \left\langle \Psi_l | \Psi_l \right\rangle.$$
(90)

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

The wave function (88) can be represented [62] as

$$\Psi_{l}^{(EHF)} = \hat{\Omega}_{11}^{[1^{N}]} \Phi_{1} \hat{O}_{l} \chi_{1} = \hat{\Omega}_{11}^{[1^{N}]} \Phi_{1} \sum_{p=0}^{m} C_{p}(l, M_{s}) \chi_{1}^{(p)}, \qquad (91)$$

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

$$\chi_1^{(p)} = \sum_{\sigma_p} \hat{\sigma}_p \chi_1 , \qquad (92)$$

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 (60). 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]:

$$C_{p}(S,M_{s}) = (2S+1)\frac{(m+S-M_{s}-p)!(S+M_{s})!}{(S-M_{s})!}\sum_{t}\frac{(-1)^{t}}{t!}\frac{\left[(S-M_{s}+t)!\right]^{2}}{(S-M_{s}+t-p)!(m-t)!(2S+1)!}.$$

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

$$C_p(M_s, M_s) \equiv C_p(S) = (-1)^p \frac{2S+1}{n+1} {\binom{n}{p}}^{-1}.$$
 (93)

Calculation of average values of operators over wave functions of the form (88) 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 (90) 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 (91) for the case $S = M_s$ can be represented as

$$\Psi^{(EHF)} = \hat{O}_{s} \hat{\Omega}_{11}^{[1^{N}]} \Phi_{1} X_{1} = \hat{\Omega}_{11}^{[1^{N}]} \Phi_{1} \hat{\omega}_{11}^{[n,m]} X_{1} = \frac{1}{f} \hat{G}_{f}^{[2^{m}, 1^{n-m}]} \Phi_{1} X_{1} = \frac{1}{f} \Psi^{(GF)}.$$
(94)

This is easily seen by comparing the expressions (58) and (62) for the operators $\hat{\omega}_{ri}^{\mu}$ and matrix elements $U_{11}^{[n,m]}$ with the expression (93) for the coefficients $C_p(S)$ in (91). Thus, the EHF wave function is equivalent to the Goddard GF wave

function if $S = M_s$. However, taken into account the expression (65), 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 (65) 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 (72) – (73) [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 [71, 72, 28] 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 $a_{k+1}, ..., a_n$. 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 $a_k(k \ge m)$ and thus two orthonormal AMO sets are constructed:

$$\varphi_{ka} = \cos \theta_k a_k + \sin \theta_k a_{\overline{k}}, \quad (k = 1, 2, 3, ..., m)$$

$$\varphi_{kb} = \cos \theta_k a_k - \sin \theta_k a_{\overline{k}}, \quad (k = 1, 2, 3, ..., m)$$

$$\varphi_{ka} = a_k. \qquad (k = m + 1, ..., n)$$

$$(95)$$

Substituting Φ_1 in (91) 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 (95) satisfy (81) due to orthogonality of orbitals a_k , the average energy value

$$E^{(AMO)} = \left\langle \Psi^{(AMO)} | \hat{H} | \Psi^{(AMO)} \right\rangle / \left\langle \Psi^{(AMO)} | \Psi^{(AMO)} \right\rangle$$
(96)

will be determined by the expression (84). Varying $E^{(AMO)}$ over θ_k , one obtains optimal AMO of the form (95). 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 (41) complementary orbitals a_k and $a_{\bar{k}}$ are pairing in the following way [74]:

$$a_{k} = \sum_{\nu} C_{\nu k} \chi_{\nu} + \sum_{\nu} C_{\nu k} \chi_{\nu},$$

$$a_{\bar{k}} = \sum_{\nu} C_{\nu k} \chi_{\nu} - \sum_{\nu} C_{\nu k} \chi_{\nu},$$
(97)

where \sum_{v^*} means that the summation is taken over the atoms of a one subset, and $\sum_{v^{**}}$ – 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 (96) 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 (37) can always be transformed in a way as to hold the relation (81). Orbitals that satisfying (81) can be represented in a form of (95) [56] if

where

$$\lambda_{k} = \left\langle \varphi_{ka} \middle| \varphi_{kb} \right\rangle = \cos 2\theta_{k}. \tag{99}$$

Minimization of the expression (96) 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.

2.2 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 (74). Equations (67) or (72) – (73) for orbitals φ_{ka} and φ_{kb} can be transformed [50] to

$$(\hat{h} + \hat{V}_{ka}^{GF}) \varphi_{ka} = \varepsilon_k^{(a)} \varphi_{ka},$$

$$(\hat{h} + \hat{V}_{kb}^{GF}) \varphi_{kb} = \varepsilon_k^{(b)} \varphi_{kb},$$

$$(100)$$

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-1electrons. It follows from (100) 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 3Ndimensional 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 (100) in order their solutions obey a singleparticle 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 (100), 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 (100) 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 (74) 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-1electrons. 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 (84) of N-electron system can be represented as a sum of two terms:

$$E^{(GF)} = E(N) = E(N-1) + e_k, \quad e_k = \varepsilon_k / D_k^k, \quad (101)$$

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 (72) and (73) will have $M \ge N$ 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 (74), 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

$$\left\langle \Psi^{(EHF)}(k,k') \,|\, \hat{H} \,|\, \Psi^{(EHF)} \right\rangle = 0 \,. \tag{102}$$

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

$$\left\langle \Psi^{(EHF)}(k,k') | \Psi^{(EHF)} \right\rangle \neq 0.$$
 (103)

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 { φ_{ka} } and { φ_{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 (72) and (73) 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 (72) and (73) 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 ($I \neq F$)[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 (56) 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

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

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 H₂ molecule in the framework of GF approach and compare results with similar calculations by the Hartree – Fock – Roothaan method [47]. Function (63) of the ground state of the hydrogen molecule is (m = n = 1)

$$\Psi^{(G1)} = \hat{G}_{1}^{[2]} \varphi_{a}(1) \varphi_{b}(2) \alpha(1) \beta(2) .$$
(104)

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 $2p\sigma$ 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 (104) 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.

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 selfconsistent 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 H₂ molecule

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

Table 1

EHF orbitals for the hydrogen molecule

AO	Exponents	$arphi_a$	$arphi_b$		
	$R = 1.4 \ a.u.$				
A1s	1.3129	0.775023	0.121577		
A2s	1.1566	0.111130	0.042025		
A2po	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		
	$R = 6.0 \ a.u.$				
Als	1.0045	0.993720	0.002525		
A2s	0.850	0.007571	0.002730		
A2po	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		

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

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		

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

As follows from Table 2, the GF method in contrast to the Hartree – Fock approximation shows the correct asymptotic behavior of the H₂ 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]:

$$\rho_{z}(\vec{R}) = \left\langle \Psi \right| \sum_{i=1}^{N} \hat{s}_{z}(i) \,\delta(\vec{r}_{i} - \vec{R}) \left| \Psi \right\rangle / S \left\langle \Psi \right| \Psi \right\rangle, \tag{105}$$

where $\hat{s}_z(i)$ – spin projection operator of the *i*-th electron, $\delta(\vec{r})$ – threedimensional 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.

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 (87), 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.

Table 3

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

Energy and spin density at the nucleus of a lithium atom

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

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

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 (63) for constructing the function Ψ of N electrons one can choose f different operators \hat{G}_i^{μ} (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 (59). Selecting ivalue 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 (63) for the wave function instead of using just one particular operator \hat{G}_i^{μ} 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 (105).

Table 4 shows the energies and spin and electron densities for the ground state ${}^{2}S$ of the lithium atom.

Table 4

Method	$\rho_z(0)$	ρ (0)	Energy, <i>a.u.</i>
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

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

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

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

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 (63) is connected with the fact that the equations for optimal orbitals (67) 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 (87) 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 $\rho_z^{\pi}(C)$ and $\rho_z(H)$ 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.

As many calculations in the π -electron approximation [102 – 104], *ab initio* calculations have led to similar values of π -spin density $\rho_z^{\pi}(C)$ 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 $\rho_z(H)$ 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 $N \rightarrow \infty$ [6, 10, 105].

Table 5

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

Atom	$\rho_z^{\pi}(C)$	$a^{\scriptscriptstyle \mathrm{H}}$, Oe			$\rho_z(\mathrm{H})$	Atom		
		Calc.*	Experiment		Calc.**			
			[96]	[97]	[98]			
C_o	0.2760	-7.45	5.14	5.15	5.08	-5.88	-0.011 ₆	H _o
\mathbf{C}_m	-0.1916	5.17	1.79	1.75	1.7	3.95	0.0078	H_m
\mathbf{C}_p	0.2757	-7.44	6.14	6.18	6.18	-6.18	-0.0122	H_p
C_{α}	0.7671	-18.72	16.35	16.35	15.7	-17.74	-0.0350	Ηα

* Calculated according to the McConnell equation [99, 100] with the constants $Q_{CH}^{H} = -27$ and $Q_{CH_{2}}^{H} = -24.4$ *Oe* [101].

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

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 ($N \square 1$). It was found [10] that the self-consistent equations for the orbitals in the EHF method asymptotically $(N \rightarrow \infty)$ coincide with the similar equations in the UHF methods:

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

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.

Chapter 3. 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 [114, 14, 34]. 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.

3.1 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

$$\hat{H}_0 = \sum_{i\sigma} \varepsilon^0(i) \hat{A}^+_{i\sigma} \hat{A}^-_{i\sigma} , \qquad (106)$$

where $\hat{A}_{i\sigma}^{\dagger}$ 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

$$\left|\Psi_{0}\right\rangle = \prod_{i=1}^{n} \hat{A}_{i\uparrow}^{+} \hat{A}_{i\downarrow}^{+} \left|0\right\rangle.$$

$$(107)$$

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

$$\left|\Psi^{(0)}\right\rangle = \hat{A}_{p\uparrow}^{+} \left|\Psi_{0}\right\rangle. \tag{108}$$

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

$$\hat{H} = \hat{H}_0 + \hat{V} = \sum_{i\sigma} \varepsilon^0(i) \hat{A}^+_{i\sigma} \hat{A}_{i\sigma} + \sum_{ij\sigma} V_\sigma(i,j) \hat{A}^+_{i\sigma} \hat{A}_{j\sigma}, \qquad (109)$$

where, using standard notations for the integrals,

$$V_{\sigma}(i,j) = \langle ip | jp \rangle - \delta_{\sigma\uparrow} \langle ip | pj \rangle.$$
(110)

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

$$\rho^{(1)}(\vec{r}) = R^{(1)}_{\uparrow}(\vec{r},\vec{r}) - R^{(1)}_{\downarrow}(\vec{r},\vec{r}), \qquad (111)$$

$$\rho^{(1)}(\vec{r}) = \varphi_p^2(\vec{r}) - \sum_{ij} \langle ip | pj \rangle \frac{\varphi_i(\vec{r})\varphi_j(\vec{r})}{\varepsilon^0(i) - \varepsilon^0(j)} (n_i - n_j), \qquad (112)$$

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

$$R_{\sigma}^{(1)}(\vec{r},\vec{r}') = \sum_{ij} \left\langle \Psi^{(1)} | \hat{A}_{i\sigma}^{+} \hat{A}_{j\sigma} | \Psi^{(1)} \right\rangle \varphi_{i}(\vec{r}') \varphi_{j}(\vec{r}) , \qquad (113)$$

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

Using a representation of orthogonal AOs

$$\varphi_i(\vec{r}) = \sum_{\mu} C_{\mu i} \chi_{\mu}(\vec{r}), \qquad (114)$$

one obtains from (112) the familiar McLachlan expression for the elements of the spin density matrix

$$\rho_{\mu\nu}^{(1)} = \rho_{\mu\nu}^{(0)} - \sum_{ij\kappa\lambda} \gamma_{\kappa\lambda} \frac{C_{\kappa i} C_{\lambda j} C_{\mu i} C_{\nu j}}{\varepsilon^{0}(i) - \varepsilon^{0}(j)} (n_{i} - n_{j}) C_{\kappa p} C_{\lambda p}, \qquad (115)$$

$$\rho_{\mu\nu}^{(0)} = C_{\mu p} C_{\nu p}, \qquad (116)$$

$$\gamma_{\kappa\lambda} = \left\langle \kappa \lambda \right| \kappa \lambda \right\rangle. \tag{117}$$

Expressions (12) and (115) are valid if the applicability conditions of perturbation theory

$$|\varepsilon^{0}(i) - \varepsilon^{0}(j)| \square V_{\sigma}(i,j) \quad (i \neq j)$$
(118)

are satisfied. To eliminate conditions (118) 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 $(N \square 1)$ for which conditions (118) break down. For these systems Hamiltonian (109), neglecting terms of order N^{-2} , can be written as

$$\hat{H} = \sum_{\substack{i\sigma\\(1 \le i \le (N+1)/2)}} \left[\varepsilon_{\sigma}'(i) (\hat{A}_{i\sigma}^{+} \hat{A}_{i\sigma} + \hat{A}_{\bar{i}\sigma}^{+} \hat{A}_{\bar{i}\sigma}) + a_{\sigma}(i) (\hat{A}_{i\sigma}^{+} \hat{A}_{\bar{i}\sigma} + \hat{A}_{\bar{i}\sigma}^{+} \hat{A}_{i\sigma}) \right],$$
(119)

where

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

and we suppose in the following that the unpaired electron occupies the non-bonding orbital p = (N+1)/2 with $\varepsilon^0(p) = 0$.

The Hamiltonian (119) can be diagonalized by the following canonical transformation of the annihilation operators

$$\hat{A}_{i\sigma} = [\hat{B}_{i\sigma} + \xi_{\sigma}(i)\tilde{B}_{i\sigma}]\mathfrak{I}_{\sigma}^{-1/2}(i), \qquad (120a)$$

$$\hat{A}_{i\sigma} = [\tilde{\hat{B}}_{i\sigma} - \xi_{\sigma}(i)\hat{B}_{i\sigma}]\mathfrak{T}_{\sigma}^{-1/2}(i), \qquad (120a')$$

$$\hat{B}_{i\sigma} = [\hat{A}_{i\sigma} - \xi_{\sigma}(i)\hat{A}_{\bar{i}\sigma}]\mathfrak{T}_{\sigma}^{-1/2}(i), \qquad (120b)$$

$$\tilde{\hat{B}}_{i\sigma} = [\hat{A}_{\bar{i}\sigma} + \xi_{\sigma}(i)\hat{A}_{i\sigma}]\mathfrak{T}_{\sigma}^{-1/2}(i), \qquad (120b')$$

and similar expressions for the creation operators, where

$$\mathfrak{I}_{\sigma}(i) = 1 + \xi_{\sigma}^{2}(i), \qquad (120c)$$

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 (120) 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 (120) which may depend on spin.

Substituting (120) into (119) one obtains

$$\hat{H} = \sum_{\substack{i\sigma\\(1,2,\dots,n+1)}} \{\varepsilon_{\sigma}(i)\hat{B}_{i\sigma}^{\dagger}\hat{B}_{i\sigma} + \tilde{\varepsilon}_{\sigma}(i)\hat{B}_{i\sigma}^{\dagger}\hat{B}_{i\sigma} + [2\xi_{\sigma}(i)\varepsilon^{0}(i) + a_{\sigma}(i)(1 - \xi_{\sigma}^{2}(i))]\mathfrak{I}_{\sigma}^{-1}(i)(\hat{B}_{i\sigma}^{\dagger}\hat{B}_{i\sigma} + \tilde{B}_{i\sigma}^{\dagger}\hat{B}_{i\sigma}^{\dagger})\},$$
(121)

where

$$\varepsilon_{\sigma}(i) = \{\varepsilon^{0}(i)[1 - \xi_{\sigma}^{2}(i)] - 2\xi_{\sigma}(i)a_{\sigma}(i)\}\mathfrak{I}_{\sigma}^{-1}(i) + \Delta\varepsilon_{\sigma}(i), \qquad (122a)$$

$$\tilde{\varepsilon}_{\sigma}(i) = \{-\varepsilon^{0}(i)[1-\xi_{\sigma}^{2}(i)] + 2\xi_{\sigma}(i)a_{\sigma}(i)\}\mathfrak{T}_{\sigma}^{-1}(i) + \Delta\varepsilon_{\sigma}(i).$$
(122b)

Adjusting the coefficients of the non-diagonal terms in (121) to zero an equation for $\xi_{\sigma}(i)$ is obtained

$$\xi_{\sigma}^{2}(i) - 2\xi_{\sigma}(i)\varepsilon^{0}(i) / a_{\sigma}(i) = 1, \quad (a_{\sigma}(i) \neq 0)$$
(123a)

$$\xi_{\sigma}(i) = 0.$$
 $(a_{\sigma}(i) = 0)$ (123b)

Equation (123a) has always a root not exceeding 1 by module (i=1,2,3,...,n), which will be used in the following. The non-bonding orbital $\varphi_p(\vec{r})$ is not affected by the transformation (120). Nevertheless the energy levels $\varepsilon_{\sigma}(p)$ may be displaced. It can be shown from (119) – (123) that the results are not changed if one formally says that the orbital $\varphi_p(\vec{r})$ mixes with itself. It follows from (123) that $|\xi_{\sigma}(p)|=1$.

For the values $\xi_{\sigma}(i)$ satisfying the Equations (123) the Hamiltonian \hat{H} has a diagonal form and the ground state wave function is

$$\left|\Psi\right\rangle = \prod_{\substack{i\sigma\\(i=1,2,\dots,n)}} \hat{B}_{i\sigma}^{+} \hat{B}_{p\uparrow}^{+} \left|0\right\rangle.$$
(124)

In the state (124) the first order density matrix and the spin density are

$$R_{\sigma}(\vec{r},\vec{r}') = \sum_{ij} \left\langle \Psi \mid \hat{A}_{i\sigma}^{+} \hat{A}_{j\sigma} \mid \Psi \right\rangle \varphi_{i}(\vec{r}) \varphi_{j}(\vec{r}') = \delta_{\sigma\uparrow} \varphi_{p}(\vec{r}) \varphi_{p}(\vec{r}') + \sum_{k=1}^{n} \mathfrak{T}_{\sigma}^{-1}(k) \{ \varphi_{k}(\vec{r}) \varphi_{k}(\vec{r}') + \xi_{\sigma}^{2}(k) \varphi_{\bar{k}}(\vec{r}) \varphi_{\bar{k}}(\vec{r}') - \xi_{\sigma}(k) [\varphi_{k}(\vec{r}) \varphi_{\bar{k}}(\vec{r}') + \varphi_{\bar{k}}(\vec{r}) \varphi_{k}(\vec{r}')] \},$$

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

$$(125)$$

Substituting (114) into (126) and using the pairing relation

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

one obtains for the spin density on atom μ

$$\rho_{\mu} = C_{\mu p}^{2} + (-1)^{\mu} 2 \sum_{k=1}^{n} C_{\mu k}^{2} \left[\frac{\xi_{\uparrow}(k)}{\Im_{\uparrow}(k)} - \frac{\xi_{\downarrow}(k)}{\Im_{\downarrow}(k)} \right].$$
(127)

It should be noted that in the general case the Hamiltonian (119) and the wave function (124) are not self-consistent. In other words, the Hamiltonian in the Hartree – Fock approximation built on function (124) does not coincide in the general case with (119). 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 (119).

3.2 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 (106) are taken as

$$\varepsilon^{0}(i) = -2 |\beta| \cos(i\theta), \qquad (128a)$$

$$\varphi_i(\vec{r}) = \sqrt{\frac{2}{N+1}} \sum_{\mu=1}^N \sin(\mu i \theta) \,\chi_\mu(\vec{r}) \,, \qquad (128b)$$

where $\theta = \pi/(N+1)$, *N* is the number of atoms in the polyene chain. In the following we will consider a case when $N \square 1$ and omit all terms $\square 1/N^2$. For large *N* the solution (128) are close to the self-consistent ones. The matrix elements $V_{\sigma}(i, j)$ in (109) 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: $\gamma_{\mu\mu} \equiv \gamma_1$, $\gamma_{\mu,\mu\pm 1} \equiv \gamma_2$. The last approximation is based on [117 – 119].

The first case to be considered is that when $\gamma_2 = 0$. Substituting (128) into (109) the following parameters of the Hamiltonian (119) are obtained

$$a_{\sigma}(k) = \Delta \varepsilon_{\sigma}(k) = \frac{\gamma_1}{N} \delta_{\sigma \downarrow}. \quad \left(0 < k \le \frac{\pi}{2}\right).$$
(129)

The Hamiltonian (119) with the parameters (129) is not self-consistent since it is built on the zero order wave function (108) 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

$$\hat{H}^{(r)} = \sum_{\substack{k\sigma\\(0 < k \le \pi/2)}} [\varepsilon^{0}(k)(\hat{n}_{k\sigma} - \hat{n}_{\bar{k}\sigma}) + \Delta \varepsilon_{\sigma}(k)(\hat{n}_{k\sigma} - \hat{n}_{\bar{k}\sigma}) + a_{\sigma}^{(r)}(k)(\hat{A}^{+}_{k\sigma}\hat{A}_{\bar{k}\sigma} + \hat{A}^{+}_{\bar{k}\sigma}\hat{A}_{k\sigma})] + \hat{W}^{(r)}, \quad (130)$$

where

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

$$a_{\sigma}^{(r+1)}(k) = -\frac{\gamma_{1}}{2N} \sum_{k'} (1 + \frac{1}{2} \delta_{kk'}) \frac{a_{-\sigma}^{(r)}(k') n_{-\sigma}^{(1)}(k')}{\sqrt{4\beta^{2} \cos^{2} k' + [a_{-\sigma}^{(r)}(k')]^{2}}},$$
(131)

and $n_{\sigma}^{(1)}(k')$ are the occupation numbers in the state (108),

$$\hat{W}^{(r)} = \frac{\gamma_1}{N} \sum_{\lambda=1}^{4} \sum_{ks} f^{(r)}(s,k) \hat{A}^+_{k\sigma} \hat{A}^-_{s_\lambda\sigma}, \quad f^{(0)}(s,k) \equiv 0, \quad |f^{(r)}(s,k)| < 1,$$

$$s_1 = 2k - s, \quad s_2 = 2k + s, \quad s_3 = 2\pi - 2k - s, \quad s_4 = 2\pi - 2k + s.$$
(132)

The final solution will be found in the following way. Taking $\hat{W}^{(r)} = 0$ and using Equations (131) the self-consistent values of $a_{\sigma}(k)$ are determined. Diagonalizing the Hamiltonian (119) with the self-consistent parameters $a_{\sigma}(k)$ the ground state wave function is obtained in the form (124). 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 (119). This means that (123) 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 (131) terms $\Box 1/N$ one obtains

$$a_{\sigma}^{(r+1)} = -\frac{\gamma_1}{2\pi} a_{-\sigma}^{(r)} \int_{0}^{\pi/2} \frac{dx}{\sqrt{4\beta^2 \cos^2 x + [a_{-\sigma}^{(r)}]^2}} \,.$$
(133)

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 (130)

r	$a^{(r)}_{\uparrow}$	$a_{\downarrow}^{(r)}$
0	0	$rac{\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 (133) has a logarithmic singularity at $a_{\sigma}^{(r)} \rightarrow 0$. 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

$$xK(x) = \frac{4\pi |\beta|}{\gamma_1} , \qquad (134)$$

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

Equation (134) has a root for a certain a > 0 [122]. For reasonable choices of parameters ($\gamma_1 / |\beta| < 5$) the value of *a* satisfying Equation (134) is limited by $2|\beta|/3 > a > 0$. Thus, certain self-consistent values of the parameters of the Hamiltonian (130) exist:

$$a_{\downarrow}(k) = -a_{\uparrow}(k) = a. \tag{135}$$

Substituting (135) into (122) the following expressions for the energy levels correct to $\Box 1/N$ are obtained

$$\varepsilon_{\sigma}(k) = \varepsilon(k) = -\sqrt{4\beta^2 \cos^2 k + a^2}, \qquad (136a)$$

$$\tilde{\varepsilon}_{\sigma}(k) = \tilde{\varepsilon}(k) = \sqrt{4\beta^2 \cos^2 k + a^2}$$
(136b)

since according to (123a) and (135)

$$\xi_{\downarrow}(k) = -\xi_{\uparrow}(k) = \xi(k) = -\frac{2|\beta|}{a}\cos k + \sqrt{1 + \frac{4\beta^2\cos^2 k}{a^2}}.$$
 (137)

It follows from (136) 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 (120b) and (137).

One sees from (136) and (137) that self-consistency leads to a splitting of the energy spectrum with 2N levels into to bands, each with N levels. The wave function (124) 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 (136) $\varepsilon_{\uparrow}(k) = \varepsilon_{\downarrow}(k) = \varepsilon(k)$ 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 2*a*. 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 (128). 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 (132) in the first and second orders changes the elements of the density matrix $\hat{B}_{k\sigma}^+ \hat{B}_{k\sigma}$ by values $\Box 1/N$ and that the contribution to the energy equals $\Delta E_0^{(1)} = \Delta E_0^{(2)} = Const$. Thus, the effect of the perturbation (132) can be neglected. On the other hand, as follows from Table 6, perturbation theory is not applicable to the Hamiltonian (130). The reason is that the interaction between levels with $k \Box \pi/2$ 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 (130) 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 (131) becomes

$$a_{\sigma}(k) = -\frac{1}{2N} \sum_{k'} \left[\gamma_1 (1 + \frac{1}{2} \delta_{kk'}) - \gamma_2 (1 + \frac{1}{2} \delta_{kk'} \cos 2k') \frac{a_{-\sigma}(k') n_{-\sigma}^{(1)}(k')}{\sqrt{4\beta^2 \cos^2 k' + a_{-\sigma}^2(k')}} + \frac{\gamma_2}{2N} \sum_{k} (1 + \sin k \sin k') \frac{a_{\sigma}(k') n_{\sigma}^{(1)}(k')}{\sqrt{4\beta^2 \cos^2 k' + a_{\sigma}^2(k')}} \right].$$
(138)

Supposing $a_{\downarrow}(k) = -a_{\uparrow}(k) = a(k)$ and neglecting in (138) all terms $\Box 1/N$ one obtains for a(k) the equation

$$a(k) = \frac{1}{2\pi} \int_{0}^{\pi/2} (\gamma_1 + \gamma_2 \sin k \sin k') \frac{a(k')dk'}{\sqrt{4\beta^2 \cos^2 k' + a^2(k')}}.$$
 (139)

The solution of (139) can be found in a form

$$a(k) = c_1 + c_2 \sin k , \qquad (140)$$

where

$$c_1 = \frac{\gamma_1}{2\pi} \int_0^{\pi/2} \frac{a(x)dx}{\sqrt{4\beta^2 \cos^2 x + a^2(x)}},$$
 (141a)

$$c_2 = \frac{\gamma_2}{2\pi} \int_0^{\pi/2} \frac{a(x)\sin x \, dx}{\sqrt{4\beta^2 \cos^2 x + a^2(x)}}.$$
 (141b)

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

$$\varepsilon_{\sigma}(k) = \{2\beta \cos k [1 - \xi_{\sigma}^{2}(k)](1 + \Re_{\sigma}) - 2\xi_{\sigma}(k)a_{\sigma}(k)\}\Im_{\sigma}^{-1}(k) + \Delta\varepsilon_{\sigma}$$
(142a)

with

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

and

$$\tilde{\varepsilon}_{\sigma}(k) = \{-2\beta \cos k[1 - \xi_{\sigma}^{2}(k)](1 + \Re_{\sigma}) + 2\xi_{\sigma}(k)a_{\sigma}(k)\}\Im_{\sigma}^{-1}(k) + \Delta\varepsilon_{\sigma}$$
(142b)

with

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

where

$$\Delta \varepsilon_{\uparrow} = \gamma_2 / N, \quad \Delta \varepsilon_{\downarrow} = (\gamma_1 + \gamma_2) / N,$$
$$\Re_{\sigma} = \frac{\gamma_2}{N |\beta|} \sum_k n_{\sigma}^{(1)}(k) \cos k \frac{\xi_{\sigma}^2(k)}{\Im_{\sigma}(k)}.$$

In this case, as follows from (142) and (140), the energy spectrum with 2*N* 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 (127) through $a_{\sigma}(k)$ one obtains for the spin density

$$\rho_{\mu} = \frac{2}{N} \sin \frac{\mu \pi}{2} + (-1)^{\mu+1} \frac{4}{N} \sum_{k=0}^{(\pi/2)-\theta} \frac{a(k) \sin^2 \mu k}{\sqrt{4\beta^2 \cos^2 k + a^2(k)}} \,. \tag{143}$$

We note that for $N \to \infty$ the spin density ρ_{μ} according to (139) and (133) 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 (128) into (115) and accounting only for $\gamma_1(\gamma_2 = 0)$ one obtains

$$\rho_{\mu}^{(1)} = \frac{2}{N+1} \sin \frac{\mu \pi}{2} + \frac{2\lambda}{(N+1)^2} (-1)^{\mu+1} \sum_{k=\theta}^{(\pi/2)-\theta} \frac{\sin^2 \mu k}{\cos k}, \qquad (144)$$

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

For $N \rightarrow \infty$ the second term in (144) is estimated as

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

Thus, McLachlan's method gives incorrect asymptotic behaviour for the spin density in a polyene chain with $N \rightarrow \infty$. The reason is that McLachlan's formula was obtained in the first order of the perturbation over non-diagonal terms in the Hamiltonian (130). As we already know, perturbation theory is not applicable to the operator (130). Contribution to ρ_{μ} in the second order is equal to $[(\ln N)^2/N]$ ($N \rightarrow \infty$) which supports our conclusion.

Results obtained so far indicate that in systems like long polyene radicals the Hartree – Fock solution (128) 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].

3.3. Projection on Pure Spin State

It follows from (120), (124), and (137) 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

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

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

$$[\hat{S}^{2}, \hat{H}_{1}] = \sum_{lkj} [h_{\uparrow}(l,k) - h_{\downarrow}(l,k)] (\hat{A}_{l\downarrow}^{+} \hat{A}_{j\uparrow}^{+} \hat{A}_{j\downarrow} \hat{A}_{k\uparrow} - \hat{A}_{l\uparrow}^{+} \hat{A}_{j\downarrow}^{+} \hat{A}_{j\uparrow} \hat{A}_{k\downarrow}).$$
(145)

Expression (145) proves our statement. For the Hamiltonian (119) with parameters (135) and (139) conditions (1) and (2) above are not satisfied because

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

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

$$\langle \Psi | \hat{S}^2 | \Psi \rangle = m_s^2 + \frac{N}{2} - Sp(R_{\uparrow}R_{\downarrow}) = m_s^2 + \frac{1}{2}\sum_{kl} \rho^2(k,l),$$
 (146)

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 (146) is valid for any state described by a single-determinant real function. Taking the function (124) with parameters $\xi_{\sigma}(k)$ from (137) one obtains the following expressions correct to $\Box 1/N$

$$\rho(k,l) = \frac{a\,\delta_{kl}}{\sqrt{4\beta^2\cos^2 k + a^2}} + \delta_{kl}\,,\tag{147a}$$

$$\left\langle \Psi \left| \hat{S}^2 \right| \Psi \right\rangle = \frac{3}{4} + \frac{dN}{2\sqrt{1+d^2}}$$
(147b)

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

It is seen from (147) that the average value of \hat{S}^2 in the states described by (123), (124), and (133) – (143) 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 (133) or (134) then the operators $\hat{B}_{k\sigma}$ correspond to the states described in the coordinate representation by orbitals like AMO

$$\Re_{k\uparrow}(\vec{r}) = \cos x_k \cdot \varphi_k(\vec{r}) + \sin x_k \cdot \varphi_{\bar{k}}(\vec{r}), \qquad (148a)$$

$$\Re_{k\downarrow}(\vec{r}) = \cos x_k \cdot \varphi_k(\vec{r}) - \sin x_k \cdot \varphi_{\bar{k}}(\vec{r}) \,. \tag{148b}$$

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

$$\sin 2x_k = \frac{a(k)}{\sqrt{4\beta^2 \cos^2 k + a^2(k)}}.$$
 (149)

Projection on the lowest doublet state of the wave function (124) with parameters $a_{\sigma}(k)$ satisfying Equations (134) and (139) by the method due to Harriman [] leads to the following expression for the spin density

$$\rho_{\mu} = \frac{2}{N} \sin \frac{\mu \pi}{2} \left\{ 1 + \frac{2}{3} \sum_{i=1}^{n} \left[1 - \frac{\omega_{1/2}(i)}{\omega_{1/2}} \right] \right\} + \frac{4}{3N} \sum_{i=1}^{n} \left[\frac{\omega_{1/2}(i)}{\omega_{1/2}} - 1 \right] \sin^{2}(\mu i \theta) + \frac{4}{3N} (-1)^{\mu+1} \sum_{i=1}^{n} \frac{\omega_{1/2}(i) a(i\theta) \sin^{2}(\mu i \theta)}{\omega_{1/2} \cdot \sqrt{4\beta^{2} \cos^{2}(i\theta) + a^{2}(i\theta)}},$$
(150)

where according to [124]

$$\omega_s = \sum_{k=0}^n (-1)^k {\binom{2s+k+1}{k}}^{-1} B_k, \qquad (151a)$$

$$\omega_{s}(i) = \sum_{k=0}^{n-1} (-1)^{k} {\binom{2s+k+1}{k}}^{-1} B_{k}(i), \qquad (151b)$$

$$B_{k} = \sum_{\{m_{1}, m_{2}, \dots, m_{k}\}}^{\binom{n}{k}} \prod_{m=m_{1}}^{m_{k}} \left[\frac{a^{2}(m\theta)}{4\beta^{2}\cos^{2}(m\theta) + a^{2}(m\theta)} \right],$$
 (152a)

$$B_{k}(i) = \sum_{\substack{\{m_{1}, m_{2}, \dots, m_{k}\} \\ (m_{j} \neq m_{i})}}^{\binom{n-1}{k}} \prod_{m=m_{1}}^{m_{k}} \left[\frac{a^{2}(m\theta)}{4\beta^{2}\cos^{2}(m\theta) + a^{2}(m\theta)} \right],$$
 (152b)

2s+1 is the state multiplicity required, $\binom{n}{k} = \frac{n!}{k!(n-k)!}$, summation in (152) is

carried out over all possible choices of *k* numbers from $\{1, 2, ..., n\}$. It can be shown that for $N \rightarrow \infty$ (n = N/2) the values of B_k from (152) may be represented as

$$B_{k} = \left(\frac{N}{\pi}\right)^{k} \int_{0}^{\pi} f(x_{k}) dx_{k} \int_{0}^{x_{k}} f(x_{k-1}) dx_{k-1} \cdots \int_{0}^{x_{2}} f(x_{1}) dx_{1} = \left(\frac{N}{\pi}\right)^{k} \frac{F^{k}(\pi)}{k!} = \frac{(N\alpha)^{k}}{k!}, \quad (153)$$

where

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

and according to [125]

$$F(y) = \int_{0}^{y} f(x) dx = 2\alpha \operatorname{arctg}\left(2\alpha \operatorname{tg} \frac{y}{2}\right)$$

with

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

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

$$B_{k}(i) = \frac{(N\alpha)^{k}}{k!} - 2f(i\theta)\frac{(N\alpha)^{k-1}}{(k-1)!}.$$
(154)

Thus, the expression (151) for s = 1/2 become

$$\omega_{1/2} = 2\sum_{k=0}^{n} (-1)^k \frac{(N\alpha)^k}{(k+2)!},$$
(155)

$$\omega_{1/2}(i) = \omega_{1/2} + 2(-1)^{n+1} \frac{(N\alpha)^n}{(n+2)!} - 4f(i\theta) \sum_{k=1}^{n-1} (-1)^k \frac{k(N\alpha)^{k-1}}{(k+2)!} .$$
(156)

A general term in (155) and (156) $(N\alpha)^k / (k+2)!$ has a maximum for $k \square N\alpha = x$

$$\frac{x^{x}}{(x+2)!} \square \frac{e^{x}}{x^{5/2}}.$$
 (157)

For k = n = N/2 one obtains

$$\frac{(N\alpha)^{N/2}}{\left(\frac{N}{2}+2\right)!} \square (2e\alpha)^{N/2} N^{-5/2} < N^{-5/2}$$
(158)

Since it follows from (133) that for reasonable choices of the parameters $2\alpha < 1/3$.

From the theory of alternating series [125, 126] increasing the upper limit of summation *n* in (155) and (156) to infinity leads to an error less than $N^{-5/2}$. Thus, the following equation is valid within this accuracy

$$\omega_{1/2}(x) = 2\sum_{k=0}^{\infty} (-1)^k \frac{x^k}{(k+2)!} = 2\frac{e^{-x}}{x^2} - \frac{2}{x^2} + \frac{2}{x}.$$
 (159)

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

Noting that according to (156)

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

one obtains

$$\omega_{1/2}(x) - \omega_{1/2}(x,i) = -4f(i\theta) \left(\frac{2}{x^3} - \frac{1}{x^2} - \frac{2e^{-x}}{x^3} - \frac{e^{-x}}{x^2}\right).$$
 (160)

It follows from (160) and (159) that

$$\frac{\omega_{1/2}(i)}{\omega_{1/2}} \Box 1 + \frac{Const}{N\alpha}. \quad (N \to \infty).$$
(161)

Substituting (161) into (150) one obtains

$$\rho_{\mu} = (-1)^{\mu+1} \frac{4}{3\pi} \int_{0}^{\pi/2} \frac{a(x)\sin^{2}\mu x \, dx}{\sqrt{4\beta^{2}\cos^{2}x + a^{2}(x)}} \,. \tag{162}$$

Comparing (162) and (143) one sees that the projection lowers the amplitude of alternation of the spin densities on chain atoms by a factor of three. Nevertheless, for $N \rightarrow \infty$ 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 (128). The state corresponding to the latter is unstable with respect to a perturbation polarizing the closed shells of a radical. Comparing expressions (134), (136), and (143) 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 (162) 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 nonprojected DODS method describes incorrectly the spin properties, for any nonrelativistic Hamiltonian must commute with the operator \hat{S}^2 . After projection the wave function (124) 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 (136) and (142) that a finite forbidden zone appears in the spectra of one-particle eigenvalues of the antiferromagnetic state (124) of the polyene radical, and this state is separated from the usual state (128). Extrapolation to $N \rightarrow \infty$ 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 2a 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.

Chapter 4. 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 [16, 17, 107, 109 – 111, 108, 6]. 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.

4.1 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]

$$\begin{pmatrix} \alpha_0 + \frac{\gamma}{2} + \varepsilon_k^{(j)} \end{pmatrix} C_{k\sigma}^{(j)}(\mu) = \sum_{\nu=1}^N \hat{H}_{\sigma}(\mu, \nu)$$

$$\equiv [\alpha_0 + \gamma n_{\mu\sigma}^{(0)}] C_{k\sigma}^{(j)}(\mu) + \beta [(1 - \delta_{\mu,1}) C_{k\sigma}^{(j)}(\mu - 1) + (1 - \delta_{\mu,N}) C_{k\sigma}^{(j)}(\mu + 1)],$$
(163)

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 (163) is defined by the relations

$$C_{k\sigma}^{(1)}(\mu) = \sqrt{\frac{2}{N}} [1 + (-1)^{\mu+1} \xi_k \tau_\sigma] \sin \mu k / \sqrt{1 + \xi_k^2}, \qquad (164a)$$

$$C_{k\sigma}^{(2)}(\mu) = \sqrt{\frac{2}{N}} [(-1)^{\mu+1} - \xi_k \tau_\sigma] \sin \mu k / \sqrt{1 + \xi_k^2} , \qquad (164b)$$

$$\varepsilon_k^{(1)} = -\varepsilon_k^{(2)} = -\sqrt{4\beta^2 \cos^2 k + a^2} , \qquad (165)$$

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

$$\frac{\gamma}{\pi} \int_{0}^{\pi/2} dk (4\beta^2 \cos^2 k + a^2) = 1, \qquad (166)$$

$$\xi_{k} = \left[2\beta\cos k + \sqrt{4\beta^{2}\cos^{2}k + a^{2}}\right]/a, \quad \tau_{\sigma} = \begin{cases} 1, & (\sigma = \uparrow) \\ -1, & (\sigma = \downarrow) \end{cases}.$$
(167)

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 (164) – (167) that

$$n_{\mu\sigma}^{(0)} = \frac{1}{2} + (-1)^{\mu+1} \frac{2\gamma\tau_{\sigma}}{\pi} \int_{0}^{\pi/2} dk \, \frac{\sin^{2}\mu k}{\varepsilon_{k}^{(2)}} = \frac{1}{2} + (-1)^{\mu+1} \delta_{\mu} \,. \tag{168}$$

As seen from (168), the values of δ_{μ} depend on an atom number μ . The analysis of (168) shows that this dependence occurs near the chain boundary:

$$\delta_{\mu} \approx \delta + \left(\frac{1}{2}\right)^{\mu - 1} \Delta \delta , \qquad (169)$$

where $\delta = a / \gamma = 0.21$, $\Delta \delta = 0.06$ with $\beta = -2.4 \text{ eV}$ and $\gamma = 5.4 \text{ eV} [16]$.

Using the UHF method we now consider the electronic structure of a long polyene chain with the *v*-th atom substituted. We make an assumption that such a substitution can be approximated by changing an appropriate Coulomb integral as $\alpha_v = \alpha_0 + t$. As seen from (163), 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 CH₃, C \rightarrow N.

The UHF Hamiltonian for polyenes (163) is a non-linear operator since it contains $n_{\mu\sigma}^{(0)}$ (168). 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]

$$(\hat{H}_{\sigma} + t\hat{\Lambda} - z_{\sigma})\varphi_{\sigma} = 0, \qquad (170)$$

where \hat{H}_{σ} is given by (163), and operator $\hat{\Lambda}$ is defined by

$$(g, \hat{\Lambda} \varphi) \equiv \sum_{\mu, \mu'} g^*(\mu) \Lambda(\mu, \mu') \varphi(\mu') = g^*(\nu) \varphi(\nu).$$
(171)

Let us present some general results which follow from [20,21]. Eigenvalues $z_{q\sigma}^{(i)}$ of the Equation (170) are determined by

$$1 + t \sum_{k,j} \frac{[C_{k\sigma}^{(j)}(\nu)]^2}{\varepsilon_k^{(j)} - z_{q\sigma}^{(i)}} = 0.$$
(172)

It follows from (172) that a perturbation of type (171) gives rise to the infinitesimal shifts of zone levels

$$z_{k\sigma}^{(i)} = \varepsilon_k^{(i)} + \frac{\pi}{N} \frac{d\varepsilon_k^{(i)}}{dk} \Theta_{k\sigma}^{(i)}.$$
(173)

The perturbation of the type (171) 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 $(v \square N)$. Then the shifts in a quasi-continuous spectrum are determined by the equation (see Appendix below in § 5.3)

$$\operatorname{ctg}\pi\,\Theta_{k\sigma}^{(i)} = -\frac{\sin 2k}{2\lambda L_{k\sigma}^{(i)}(\nu)\sin^2\nu k} \left[1 - \lambda L_{k\sigma}^{(i)}(\nu)\frac{\sin 2\nu k}{\sin 2k}\right],\tag{174}$$

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

$$L_{k\sigma}^{(i)}(\nu) = \frac{1}{2|\beta|} [\mathcal{E}_{k}^{(i)} + (-1)^{\nu} a \tau_{\sigma}].$$
(175)

The eigenfunctions corresponding to the eigenvalues (173) can be written as (see Appendix below in § 5.3)

$$\varphi_{k\sigma}^{(i)}(\mu) = \sqrt{\frac{2}{N}} C_{k\sigma}^{(i)}(\mu) \sin(k * \mu - \pi \Theta_{k\sigma}^{(i)}), \qquad (\mu > \nu), \qquad (176)$$

$$\varphi_{k\sigma}^{(i)}(\mu) = \sqrt{\frac{2}{N}} C_{k\sigma}^{(i)}(\mu) \sin(k\nu - \pi \,\Theta_{k\sigma}^{(i)}) \frac{\sin \mu k}{\sin \nu k}, \quad (\mu < \nu), \quad (177)$$

$$\varphi_{k\sigma}^{(i)}(\nu) = \sqrt{\frac{1}{2N}} \frac{d\varepsilon_k^{(i)}}{dk} \sin \Theta_{k\sigma}^{(i)} / (tC_{k\sigma}^{(i)}(\nu)\sin k\nu), \qquad (178)$$

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 (176) that the perturbation results in the phase shift of the eigenfunctions for $\mu > \nu$. In order to define under what conditions the relations

(172) – (178) correspond to the self-consistent solution of Eq. (170) we evaluate $n_{\mu\sigma}$. Transforming (176) yields for the zone-state density at the μ -th atom

$$[n_{\mu\sigma}^{(1)}]_{zone} = \sum_{k} [\varphi_{k\sigma}^{(1)}(\mu)]^{2} = \frac{1}{2} + (-1)^{\mu+1} \delta_{\mu} \tau_{\sigma} + \frac{a}{\pi} \int_{0}^{\pi/2} dk [\cos(2\mu k - 2\pi \Theta_{k\sigma}^{(i)})] / \varepsilon_{k}^{(2)}. \quad (\mu > \nu) \quad (179)$$

Comparing (179) with (168) 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 $\mu-\nu \Box = 1$ then (179) leads to $n_{\mu\sigma}^{(1)} = n_{\mu\sigma}^{(0)}$. 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 (179) one can obtain for the electron density at the impurity atom (see Appendix below in § 5.3)

$$n_{\nu\sigma}^{(1)} = \frac{d}{dt} \sum_{k} (z_{k\sigma}^{(1)} - \varepsilon_{k}^{(1)}) \,. \tag{180}$$

Taking into consideration Coulson's and Lonquet-Higgins' relation [73], we reduce the expression (180) to the form

$$n_{\nu\sigma}^{(1)} = \frac{d}{dt} \frac{1}{2\pi i} \prod_{C} z \, d \ln[M_{\sigma}(z) / M_{\sigma}^{(0)}(z)], \qquad (181)$$

where the integration is in the positive direction along the infinite half-circle (Re z < 0) and imaginary axis in the complex plane z; $M_{\sigma}(z)$ and $M_{\sigma}^{(0)}(z)$ are determinants which vanish at the points $z = z_{k\sigma}^{(i)}$ and $z = \varepsilon_{k}^{(1)}$, respectively. The expression (181) can be written as [133]

$$n_{v\sigma}^{(1)} = \frac{d}{dt} \frac{1}{2\pi i} \iint_{C} z \, d \ln[1 - t \, G_{0\sigma}(v, v; z)] = -\frac{1}{2\pi i} \iint_{C} dz \, \frac{d}{dt} \ln[1 - t \, G_{0\sigma}(v, v; z)], \quad (182)$$

where the function

$$G_{0\sigma}(\nu,\mu;z) = \sum_{kj} \frac{C_{k\sigma}^{(j)}(\nu)C_{k\sigma}^{(j)}(\mu)}{z - \varepsilon_k^{(j)}}$$
(183)

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 (181) and (182) results from the fact that in accordance with (172) the functions in brackets in (181) and (182) have simple poles and zeros at the same points. Having failed to obtain general analytical expressions for (179) or (181) we now discuss some limiting cases. Let $|\lambda| = 1$. Then the integrand in(182) can be expanded in the series of λ

$$n_{\nu\sigma}^{(1)} = \frac{1}{2\pi i} \prod_{C} dz G_{0\sigma}(\nu,\nu;z) \sum_{n=0}^{\infty} [\lambda \mid \beta \mid G_{0\sigma}(\nu,\nu;z)]^{n} .$$
(184)

According to (183) $|\beta G_{0\sigma}(v,v;z)| < 1$ if $z \in C$. Therefore, the series in (184) converges regularly if $|\lambda| < 1$ and $z \in C$. As a consequence, integrating (184) term by term yields

$$n_{\nu\sigma}^{(1)} = \sum_{k} [C_{k\sigma}^{(1)}(\nu)]^2 \sum_{n=0}^{\infty} [\lambda L_{k\sigma}^{(1)}(\nu) \sin 2\nu k / \sin 2k]^n .$$
(185)

It follows from (185) that

$$n_{\nu\sigma}^{(1)} = n_{\nu\sigma}^{(0)} + \mathcal{O}(\lambda). \quad |\lambda| \square 1.$$
(186)

Thus, if $|\lambda|$ is small, the solution of (170) given by (172) – (180) 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

$$\sum_{\mu'=1}^{N} \{ \hat{H}_{\sigma}(\mu,\mu') + t\Lambda(\mu,\mu') + \lambda [n_{\mu\sigma}^{(1)} - n_{\mu\sigma}^{(0)}] \delta_{\mu\mu'} - z\delta_{\mu\mu'} \} \varphi_{\sigma}(\mu') = 0.$$
(187)

Let us consider this equation for the case v=1, *i.e.* when the perturbation is localized at the first atom of the chain. It follows from (185) that

$$n_{1\sigma}^{(1)} - n_{1\sigma}^{(0)} = \sum_{n=1}^{\infty} \lambda^n (-1)^n f_{n\sigma} = -\lambda \Delta^{(1)} / \gamma , \qquad (188)$$

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 (188), 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 (185) that this result is also valid if $\nu \neq 1$.

In order to evaluate differences $n_{\mu\sigma}^{(1)} - n_{\mu\sigma}^{(0)}$ for $\mu > \nu$ we now consider another limiting case: $|\lambda| \rightarrow \infty$. Then it follows from (174) that $\pi \Theta_{k\sigma}^{(i)} \rightarrow \nu k$. Hence, the relations (176) – (178) take the form

$$\lim_{|\lambda| \to \infty} \varphi_{k\sigma}^{(i)}(\mu) = \begin{cases} C_{k\sigma}^{(i)}(\mu - \nu), & (\mu > \nu) \\ 0. & (\mu \le \nu) \end{cases}.$$
 (189)

It follows from (189) that a strong perturbation tears the link consisting of v atoms of the chain. It is obvious that the functions (189) are self-consistent for the chain consisting of $N-v \approx N$ atoms because they coincide with the self-consistent zone functions of an ideal polyene chain. Substituting (189) into (179) and using (168) and (169) one obtains

$$|n_{\mu\sigma}^{(1)} - n_{\mu\sigma}^{(0)}| = |\delta_{\mu\nu} - \delta_{\mu}| \le |\delta_1 - \delta_2| = 0.09.$$
(190)

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 $\varphi_{k\sigma}^{(i)}(\mu)$ of a long polyene chain with the *v*-th atom substituted $(\nu \square N)$ as $\mu > \nu$, it is quite sufficient to restrict oneself to the first iteration of the selfconsistency procedure for any value of the perturbation parameter λ . In particular, if $\nu = 1$ one can suppose that $n_{\mu\sigma}^{(1)} - n_{\mu\sigma}^{(0)} = \delta_{\mu 1}(-\lambda \Delta^{(1)}/\gamma)$. It means that the non-linearity of Eq. (170) 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 $|\lambda| \square 1$ then functions $\varphi_{\sigma}(\mu) \quad (\mu < \nu)$ 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 $n_{\mu\sigma}^{(1)}$ -values, we neglect the contribution of local-state functions, which have the amplitude (see Appendix below in § 5.3)

$$|\varphi_{p\sigma}(\mu)| = Const(e^{-|\mu-\nu|q_0/2} + e^{-|\mu+\nu|q_0/2}), \qquad (191)$$

where $q_0 > 0$. Hence it is clear that the functions are localized near the substituted atom. If $|\lambda| = 1$ then $q_0 = 1$, *i.e.* $\varphi_{p\sigma}(\mu) = \delta_{\mu\nu}$; if $|\lambda| = 1$ then $\varphi_{p\sigma}(\mu) = \lambda$ (see Appendix below in § 5.3). Thus, we are taking into account that the local-state functions does not affect the relations (186) and (190).

4.2. 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

$$\varphi_{\sigma}(\nu) = -\sum_{\mu,\mu'} G_{0\sigma}(\nu,\mu';z) t_{\mu',\mu} \varphi_{\sigma}(\mu) .$$
(192)

Here $t_{\mu\nu}$ is the matrix elements of perturbation produced by substitution. If, for example, only one of the Coulomb integrals changes $\alpha_{\nu} \rightarrow \alpha_{\nu 0} + t\Delta \alpha_{\nu 0}$, then $t_{\mu\mu'} = t\delta_{\mu\mu'}\delta_{\mu\nu_0}$. To solve (192) the following relation should be satisfied

$$Det[G_{0\sigma}(\mu,\mu';z)t_{\mu\mu'}+\delta_{\mu\mu'}]=0.$$
(193)

The relation (193) gives the equation for evaluating the energies of local states. Substituting $\varepsilon_k^{(j)}$ and $C_{k\sigma}^{(j)}(\mu)$ from (164) – (165) into (183) one can obtain expressions for $G_{0\sigma}(\mu, v; z)$ for the most interesting case of local states in the forbidden zone:

$$\begin{array}{l}
G_{0\sigma}(2\mu,2\nu;z_{\sigma}) = (z_{\sigma} - a\tau_{\sigma})(2\beta^{2}\mathrm{sh}\Theta)^{-1}(-1)^{\mu-\nu}[e^{-|\mu-\nu|\Theta} - e^{-|\mu+\nu|\Theta}],\\
G_{0\sigma}(2\mu - 1,2\nu - 1;z_{\sigma}) = (z_{\sigma} + a\tau_{\sigma})(2\beta^{2}\mathrm{sh}\Theta)^{-1}(-1)^{\mu-\nu}[e^{-|\mu-\nu|\Theta} + e^{-|\mu+\nu|\Theta}],\\
G_{0\sigma}(2\mu - 1,2\nu;z_{\sigma}) = (-1)^{\mu-\nu}(\beta\,\mathrm{sh}\Theta)^{-1}[\mathrm{sh}\mu\,\Theta - \mathrm{sh}(\mu - 1)\,\Theta], \quad (\nu \ge \mu)\\
G_{0\sigma}(2\mu - 1,2\nu;z_{\sigma}) = (-1)^{\mu-\nu}(\beta\,\mathrm{sh}\Theta)^{-1}[1 - e^{\Theta}]e^{-\mu|\Theta}\mathrm{sh}\mu\,\Theta, \quad (\nu < \mu)
\end{array}\right\}$$
(194)

where Θ is given by the relation

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

The Green functions determined by (194) are identical with those for a diatomic (...-A-B-A-B-...) chain with equal bonds in tight binding approximation (see the expressions (8a) – (8d) in paragraph 2 above and (9) – (10) in [4] for $\beta_1 = \beta_2$ and $z = a\tau_{\sigma}$). If the values of $n_{v\sigma}$ were independent of v this fact would be considered as trivial because the Hamiltonian (163) and that which is used in paragraph 2 above and in [4] are identical. However, as follows from (168), $n_{v\sigma}$ depends on v and the self-consistent field near the end of a chain differs from the one in the middle of a chain. Thus, the Hamiltonian (163) differs from 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 (194) and (8a) – (8d) 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

$$|\Delta \alpha| > 2\beta^{2} (\sqrt{a^{2} + 4\beta^{2}} \pm a)^{-1} \frac{1}{l}.$$
 (195)

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 v=1 and $t_{\mu\nu} = t \,\delta_{\mu\nu} \,\delta_{\mu 1}$ into (193) one can obtain

$$1 + \lambda (\tilde{z}_{\nu\sigma} - d\tau_{\sigma}) (1 + e^{-q_0}) / \operatorname{sh} q_0 = 0$$
(196)

with

$$\operatorname{ch} q_0 = 1 + 2(d^2 - \tilde{z}_{p\sigma}^2), \quad \tilde{z}_{p\sigma} = \frac{z_{p\sigma}}{|2\beta|} < d, \quad (197)$$

and

$$1 - \lambda (\tilde{z}_{p\sigma} - d\tau_{\sigma}) (1 - e^{-Q_0}) / \operatorname{sh} Q_0 = 0$$
(198)

with

$$\operatorname{ch} Q_0 = 2(\tilde{z}_{p\sigma}^2 - d^2) - 1, \quad |\tilde{z}_{p\sigma}| > \sqrt{1 + d^2}.$$
 (199)

As seen from (196), 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. (198) gives for the energy of local state

$$\tilde{z}_{p\sigma} \rightarrow \pm \infty$$
.

Using the general equation (192) one can obtain the wave function of a local state, the first atom being perturbed

$$\varphi_{p\sigma}(\mu) = \tau_{p\sigma}(-1)^{\frac{\mu-1}{2}} e^{-\frac{\mu-1}{2}q_0}, \quad (\mu \text{ is odd})$$
 (200a)

$$\varphi_{p\sigma}(\mu) = \tau_{p\sigma} \lambda(-1)^{\frac{\mu}{2}} e^{-\frac{\mu}{2}q_0}, \quad (\mu \text{ is even})$$
(200b)

where

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

and q_0 are determined by (197). In accordance with (198) 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 $v \neq 1$.

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 $\Box 1/l$, (*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.

4.3 Appendix

We first deal with the derivation of main relations used in § 5.1, namely, will consider the sum in (172):

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

$$\equiv [\varepsilon_q^{(i)} + a \tau_\sigma (-1)^v] S^{(i)}(q,\sigma),$$
(A1)

where we have used (173). To calculate $S^{(i)}(q,\sigma)$ we shall use the method developed by Lifshits [20, 21]. Let us denote

$$S^{(i)}(q,\sigma) = S_1^{(i)}(q,\sigma) + S_2^{(i)}(q,\sigma)$$
(A2)

and evaluate each sum separately, namely:

$$S_{1}^{(i)}(q,\sigma) = \frac{4}{N^{2}} \sum_{k \neq q} \frac{2\pi \Theta_{q\sigma}^{(i)}(d\varepsilon_{q}^{(i)}/dq) \varepsilon_{q}^{(i)} \sin^{2}kv}{(\varepsilon_{k}^{2} - \varepsilon_{q}^{2}) \left(\varepsilon_{k}^{2} - \varepsilon_{q}^{2} - \frac{2\pi}{N} \Theta_{q\sigma}^{(i)} \frac{d\varepsilon_{q}^{(i)}}{dq}\right)} - \frac{2}{\pi} \frac{\sin^{2}qv}{\Theta_{q\sigma}^{(i)} \varepsilon_{q}^{(i)} \frac{d\varepsilon_{q}^{(i)}}{dq}}$$

$$= \frac{2\sin^{2}qv}{\varepsilon_{q}^{(i)}(d\varepsilon_{q}^{(i)}/dq)} \left[\frac{2}{N^{2}} \sum_{k \neq q} \frac{\pi \Theta_{q\sigma}^{(i)}}{(k - q) \left(k - q - \frac{\pi}{N} \Theta_{q\sigma}^{(i)}\right)} - \frac{1}{\pi \Theta_{q\sigma}^{(i)}} \right] + O\left(\frac{1}{N}\right) \quad (A3)$$

$$\approx \frac{2\sin^{2}qv}{\varepsilon_{q}^{(i)}(d\varepsilon_{q}^{(i)}/dq)} \left[\sum_{n \neq 0} \frac{\pi \Theta_{q\sigma}^{(i)}}{n\pi(n\pi - \pi \Theta_{q\sigma}^{(i)})} - \frac{1}{\pi \Theta_{q\sigma}^{(i)}} \right] = -2\sin^{2}qv \operatorname{ctg}\left[\frac{\pi \Theta_{q\sigma}^{(i)}}{\varepsilon_{q}^{(i)}(d\varepsilon_{q}^{(i)}/dq)} \right],$$

$$S_{2}^{(i)}(q,\sigma) = \frac{4}{N} \sum_{k \neq q} \frac{\sin^{2}kv}{\varepsilon_{k}^{2} - \varepsilon_{q}^{2}} = \frac{1}{2\pi\beta^{2}} \int_{C} \frac{1 - \cos kv}{\cos k - \cos 2q} dk + O\left(\frac{1}{N}\right), \quad (A4)$$

where \int_{c}^{c} denotes the principal value of a corresponding contour integral taken from 0 to π . In order to evaluate (A4) we need to calculate

$$I = \int_{C} \frac{\cos kv}{\cos k - \cos 2q} dk = I_1 + I_2, \tag{A5}$$

$$I_1 = \frac{1}{2} \int_C dx \frac{e^{ivx}}{\cos x - \cos q},$$

$$I_2 = \frac{1}{2} \int_C dx \frac{e^{-ivx}}{\cos x - \cos q}.$$
(A6)

The integrals (A6) can be evaluated by the residue theory. The integral I_1 is taken along the contour C₁, and I_2 – along contour C₂ (fig. 4). Calculations give



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

The substitution of (A7) into (A5) and (A4) results in the relation

$$S_{2}^{(i)}(q,\sigma) = -\frac{1}{2\beta^{2}} \frac{\sin 2vq}{\sin 2q}.$$
 (A8)

Equation (174) can be obtained from (A3), (A8), (A1), and (172). The eigenfunctions of (170) are defined as [20, 21]

$$\varphi_{q\sigma}^{(i)}(\mu) = -t \tau_{q\sigma}^{(i)} \sum_{k,j} \frac{C_{k\sigma}^{(j)}(\mu) C_{k\sigma}^{(j)}(\nu)}{\varepsilon_k^{(j)} - z_{q\sigma}^{(i)}}.$$
 (A9)

The sum in (A9) is calculated just like as $S_1^{(i)}(q,\sigma)$.

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

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

$$= 2N (t\tau_{q\sigma}^{(i)})^{2} \left[\frac{\tilde{C}_{q\sigma}^{(i)}(\nu)\sin q\nu}{(d\varepsilon_{q}^{(i)}/dq)\sin \pi \Theta_{q\sigma}^{(i)}} t\tau_{q\sigma}^{(i)} \right]^{2} = 1.$$
(A10)

Substituting $\tau_{q\sigma}^{(i)}$ from (A10) into (A9) one obtains (176 – 178).

It follows from (A10) that

$$(t\tau_{q\sigma}^{(i)})^{2} = \sum_{k,j} \left(\frac{C_{k\sigma}^{(j)}(\nu)}{\varepsilon_{k}^{(j)} - z_{q\sigma}^{(i)}}\right)^{2} = \left(\frac{dz_{q\sigma}^{(i)}}{dt}\right)^{-1} \frac{d}{dt} \sum_{k,j} \frac{[C_{k\sigma}^{(j)}(\nu)]^{2}}{\varepsilon_{k}^{(j)} - z_{q\sigma}^{(i)}} = -\frac{1}{t^{2}} \left(\frac{dz_{q\sigma}^{(i)}}{dt}\right)^{-1}.$$
 (A11)

Taking also into account that according with (A9) and (A10) $\varphi_{q\sigma}^{(i)}(\nu) = \tau_{q\sigma}^{(i)}$, one obtains (180).

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

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

i.e., for states splitting off zones. Using (164) and (165) one obtains

$$G_{0\sigma}(v,v;z) = -\sum_{k,j} \frac{[C_{k\sigma}^{(j)}(v)]^2}{\varepsilon_k^{(j)} - z} = \frac{\tilde{z} + (-1)^v d\tau_\sigma}{\pi |\beta|} \int_0^{\pi} dk \, (1 - \cos vk) / (\alpha + \cos k)$$
(A12)

where

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

The integral in (A12) is calculated as the integral (A5) except the poles of the integrand are in the complex plane *k* on the lines $\operatorname{Re} k = 0$ $(\tilde{z}^2 > 1 + d^2)$ and $\operatorname{Re} k = \pi$ $(|\tilde{z}| < d)$. Having carried out the calculations one obtains

$$\int_{0}^{\pi} dk \frac{\cos \nu k}{\alpha + \cos k} = \begin{cases} (-1)^{\nu} \pi e^{-\nu q_{0}} / \operatorname{sh} q_{0}, & (\alpha > 0) \\ \pi e^{-\nu Q_{0}} / \operatorname{sh} Q_{0}, & (\alpha < 0) \end{cases}$$
(A13)

where

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

Using (A13) one can calculate all functions $G_{0\sigma}(v,\mu;z)$ with $\tilde{z}^2 > 1 + d^2$ or $\tilde{z}^2 < d^2$. In particular, one can obtain equations for local energies

$$1 - t G_{0\sigma}(v, v; z_{pz}) = 0$$
 (A14)

and for corresponding functions

$$\varphi_{p\sigma}(\mu) = t\tau_{p\sigma}G_{0\sigma}(\mu, \nu; z_{pz}).$$
(A15)

The relations (191), (194), (196) – (200) results from (A14) and (A15). If $|\lambda| = 1$, then it follows from (A13) and (A14) that $q_0Q_0 = 1$. Using (191) and (178) one can see that if $|\lambda| = 1$ then

$$\tau_{p\sigma}^{2} \Box t^{-2} (1 - e^{-2q}) \operatorname{sh}^{2} q, \quad (q = q_{0}, Q_{0})$$
$$|\varphi_{p\sigma}(\mu)|^{2} \Box \lambda^{2}.$$
(A16)

hence

Finally we turn now 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.

Chapter 5. Basics of π -Electron Model of Cumulenes

5.1 Introduction

Cumulene molecules have the general formula $H_2C=(C=)_{N-2}CH_2$ and contain a linear chain of N carbon atoms. The inner N - 2 atoms are characterized by diagonal hybridization *sp* and are in the valence state $didi\pi_x\pi_y$. Hybridization of the end-C-atoms should be close to trigonal sp^2 , and these atoms can be in valence state $trtrtr\pi_x$ or $trtrtr\pi_y$. Properties of cumulenes are discussed in several reviews [139 – 142]. Even cumulenes (EC) with the ethylene as the first member of ECs are known to be planar with symmetry D_{2h} . In odd cumulenes (OC) with the allene [143] as the first member of OCs the two end-groups are perpendicular to one another with symmetry D_{2d} . Both experimental facts are in accordance to valence bond theory.

The ease of *cis-trans* isomerization for the ECs or of stereoisomerization for the OCs is determined by the barrier height of internal rotation of the CH₂ end-groups. Rotation of one of the CH₂ groups by 180° returns the cumulene molecule to its initial state. It is a natural suggestion that the barrier height is determined by the energy of such a molecular conformation in which one of the CH₂ groups is turned by 90° in comparison with the most stable conformation. In the following under barrier height V we shall imply the difference between energies of the lowest singlet states of the molecular conformations with symmetry D_{2h} and D_{2d} .

The barriers V in cumulenes were considered theoretically in [144, 145, 8, 9]. Popov [145] used a simple Huckel method which leads to the conclusion that with an increase of the number of C atoms the barrier tends to zero which is actually simply obvious from physical point of view. σ -Bonds of cumulene chains have cylindrical symmetry and their energy does not depend upon the angle of rotation of the end-groups. Therefore if direct interaction of the end-groups is neglected the barrier height is determined by the energy change of the π -electrons with the change of the molecular conformation.

Cumulenes C_NH_4 have $2N - 2\pi$ -electrons. In accordance with the simple MO theory 2N - 2 levels can contain either N - 1 bonding levels and equally many antibonding levels in ECs or N - 2 bonding and equally many antibonding levels in OCs. In the former $2N - 2\pi$ -electrons occupy all N - 1 bonding levels; in the later – all N - 2 bonding levels and the two remaining electrons occupy the two-fold degenerate nonbonding level. The

first distribution is energetically more favorable than the second one. This is achieved for even N for planar conformations and for odd N for twisted conformations. This may be considered as a simple explanation of the known experimental fact [142] that the stable conformation of the ECs is planar, but that of the OCs is twisted with perpendicular arrangements of planes of the end-groups. This very interesting property of the cumulenes was in fact first explained by van't Hoff [146] in 1877 using the tetrahedral model of the carbon atom.

5.2 Quantum-chemical model

Let us choose the coordinate system in a way so that in the conformation $D_{2h} \pi$ -AOs of the subsystem with *N* AOs are directed along *x*-axis and with *N* – 2 AOs – along *y*-axis. The *z*-axis passes through the C atoms. Conformation D_{2d} is formed by a rotation of one of the end-AO's by 90°. In this case the number of AOs which are directed along the *x*- and *y*-axis equals N - 1 in both cases.

In the conformation $D_{2h} \pi_x$ -states have symmetry b_{2g} and b_{3u} , and π_y -states – b_{2u} and b_{3g} . In the conformation D_{2d} all π -MOs transform according to the irreducible representation e. Therefore in this conformation the frontier MOs (pair of nonbonding orbitals) is degenerated by symmetry. Accidental degeneration of the frontiers MOs in the conformation D_{2h} remains in the Pariser – Parr – Pople (PPP) [147, 148] approximation also, for in this case zero differential overlap approximation is used. It is removed by alternation of the bond lengths.

The lowest electronic configuration of the cumulene molecule in its unstable conformation has a multiplet structure with states ${}^{3}A_{2}$, ${}^{1}B_{1}$, ${}^{1}A_{1}$, and ${}^{1}B_{2}$ for ECs and ${}^{3}A_{u}$, ${}^{1}A_{u}$, ${}^{1}A_{g}$, and ${}^{1}A'_{g}$ for OCs. We shall see later that when electronic interaction is accounted for the lowest states become ${}^{3}A_{2}$, ${}^{1}B_{1}$, resp. ${}^{3}A_{u}$, ${}^{1}A_{u}$. The states ${}^{1}A_{1}$, ${}^{1}B_{2}$, resp. ${}^{1}A_{g}$, ${}^{1}A'_{g}$ correspond to electron transfer between the perpendicular x- and y-subsystems of π -AOs. The molecule in its stable conformation, which is ${}^{1}A_{g}$ for ECs and ${}^{1}A_{1}$ for OCs has a closed shell. The degeneration of the frontier π -MOs is removed for inorganic cumulenes with alternating atoms of different electronegativity. To a smaller degree the same is true if the difference in the hybridization between the parameters of inner and outer C atoms is taken into account. But even in this case the lowest singlet state may be ${}^{1}A_{u}$ if the orbital energy splitting does not exceed the splitting of even and odd states. In the following we shall neglect the difference in hybridization between outer and inner C atoms. This approximation is sufficiently good because the integrals for sp^2 and sp states are almost equal [149].

Let us the *x*- and *y*-MOs in the conformation D_{2h} write down as a linear combination of the π -AOs x_v and y_v with the chain of AOs y_v denoted by primed symbols

$$\varphi_i = \sum_{v} C_{vi} x_v, \quad \varphi'_i = \sum_{v} C'_{vi} y_v$$

The summation is extended over all AOs of the chain. In the same manner it is possible to set up the components of the degenerate pairs of the MOs in the conformation D_{2d} .

Let \hat{A}_i^+ be the creation operator for an electron *i* of orbital state φ_i and spin state α , and \hat{A}_i^+ be the same for spin state β . Degenerate orbital pairs of open shell will be denoted by the symbols *k* and *k'*, and orbitals of closed shell by *j* and *j'*. Then the wave functions of states with closed shell Ψ^e may be written as

$$\Psi^{c}({}^{1}A_{1}, {}^{1}A_{g}) \equiv \Psi^{c},$$

$$\Psi^{c} = \prod_{j} \hat{A}_{j}^{+} \hat{A}_{j}^{+} \prod_{j'} \hat{A}_{j'}^{+} \hat{A}_{j'}^{+} |0\rangle^{2}$$

where $|0\rangle$ is the vacuum state.

Wave functions of states with open shell Ψ^o will be written as follows:

$$\begin{split} \Psi^{o}({}^{3}A_{2}, {}^{3}A_{u}) &= \frac{1}{\sqrt{2}}(\hat{A}_{\bar{k}'}^{+}\hat{A}_{k}^{+} + \hat{A}_{k'}^{+}\hat{A}_{\bar{k}}^{+})\Psi^{c}, \\ \Psi^{o}({}^{1}B_{1}, {}^{1}A_{u}) &= \frac{1}{\sqrt{2}}(\hat{A}_{\bar{k}'}^{+}\hat{A}_{k}^{+} - \hat{A}_{k'}^{+}\hat{A}_{\bar{k}}^{+})\Psi^{c}, \\ \Psi^{o}({}^{1}B_{2}, {}^{1}A_{g}) &= \frac{1}{\sqrt{2}}(\hat{A}_{\bar{k}}^{+}\hat{A}_{k}^{+} - \hat{A}_{\bar{k}'}^{+}\hat{A}_{k'}^{+})\Psi^{c}, \\ \Psi^{o}({}^{1}A_{1}, {}^{1}A_{g}') &= \frac{1}{\sqrt{2}}(\hat{A}_{\bar{k}}^{+}\hat{A}_{k}^{+} + \hat{A}_{\bar{k}'}^{+}\hat{A}_{k'}^{+})\Psi^{c}. \end{split}$$

For these states the *z*-component of the total spin $M_s = 0$. Two other components of the triplet state ${}^{3}A_2$ or ${}^{3}A_u$ with $M_s = \pm 1$ are described by the functions

$$\hat{A}^+_{k'}\hat{A}^+_k\Psi^c$$
 and $\hat{A}^+_{\overline{k}'}\hat{A}^+_{\overline{k}}\Psi^c$.

Let us introduce the standard notations:

$$\begin{split} H_{k} &= \int \varphi_{\bar{k}}^{*} H^{core} \varphi_{\bar{k}} \, d\tau, \\ J_{ij} &= \int \varphi_{i}^{*} \varphi_{\bar{j}}^{*} \frac{1}{r_{12}} \varphi_{i} \varphi_{\bar{j}} d\tau_{1} d\tau_{2}, \\ K_{ij} &= \int \varphi_{\bar{i}}^{*} \varphi_{j}^{*} \frac{1}{r_{12}} \varphi_{i} \varphi_{\bar{j}} d\tau_{1} d\tau_{2}. \end{split}$$

Then the energy of states with closed shell will be:

$$E^{c}({}^{1}A_{1}, {}^{1}A_{g}) = 2\sum_{j}H_{j} + 2\sum_{j'}H_{j'} + \sum_{j_{1}j_{2}}(2J_{j_{1}j_{2}} - K_{j_{1}j_{2}}) + \sum_{j_{1}j_{2}'}(4J_{j_{1}j_{2}'} - 2K_{j_{1}j_{2}'}) + \sum_{j_{1}'j_{2}'}(2J_{j_{1}'j_{2}'} - K_{j_{1}j_{2}'}) + E^{core},$$

where E^{core} is the core total energy. If we denote

$$E_{1} = E^{c} + H_{k} + H_{k'} + \sum_{j} (2J_{jk} - K_{jk} + 2J_{jk'} - K_{jk'}) + \sum_{j'} (2J_{j'k} - K_{j'k} + 2J_{j'k'} - K_{j'k'}),$$

where E^c means an expression which has the same structure as $E^c({}^{1}A_{1}, {}^{1}A_{g})$ above, the sums being taken over the closed shell only, the energy of the states with open shell are:

$$E^{o}({}^{3}A_{2}, {}^{3}A_{u}) = E_{1} + J_{kk'} - K_{kk'},$$

$$E^{o}({}^{1}B_{1}, {}^{1}A_{u}) = E_{1} + J_{kk'} + K_{kk'},$$

$$E^{o}({}^{1}B_{2}, {}^{1}A_{g}) = E_{1} + \frac{1}{2}(J_{kk} + J_{k'k'}) - K_{kk'},$$

$$E^{o}({}^{1}A_{1}, {}^{1}A_{g}') = E_{1} + \frac{1}{2}(J_{kk} + J_{k'k'}) + K_{kk'}.$$

Usually

$$J_{ij} < \frac{1}{2}(J_{ii} + J_{jj})$$

holds. This means that among the lower singlet states the lowest are ${}^{1}B_{1}$ and ${}^{1}A_{u}$.

Reducing the MOs to AOs the integrals over the AOs

$$\left\langle \kappa \lambda \left| \mu \nu \right\rangle = \int x_{\kappa}^{*}(1) x_{\mu}^{*}(2) \frac{1}{r_{12}} x_{\lambda}(1) x_{\nu}(2) d\tau_{1} d\tau_{2} \right\rangle$$

will have to be calculated. Zero differential overlap

 $\left<\kappa\lambda\right|\mu\nu\right> = \left<\kappa\lambda\right|\mu\nu\right> = \delta_{\kappa\lambda}\delta_{\mu\nu}\left<\kappa\kappa\right|\mu\mu\right> = \delta_{\kappa\lambda}\delta_{\mu\nu}\gamma_{\kappa\mu}$

will be used in this context.

Core integrals $H_{\mu\nu}$ with $\mu \neq \nu$ will be accounted for only in case of neighbouring atoms and renamed $\beta_{\mu\nu}(\beta_{\mu\mu} \equiv 0)$. Integrals between AOs π_x and $\pi_y H_{\mu\nu'}$ are zero for symmetry reasons. Integrals $H_{\mu\mu}$ will be calculated in the Goeppert-Mayer and Sklar approximation [150], neglecting penetration integrals

$$\begin{split} H_{\mu\mu} &= -I_{\mu} - \sum_{\nu} \gamma_{\mu\nu} - \sum_{\nu'} \gamma_{\mu\nu'} + \gamma_{\mu\mu}, \\ H_{\mu'\mu'} &= -I_{\mu} - \sum_{\nu} \gamma_{\mu'\nu} - \sum_{\nu'} \gamma_{\mu'\nu'} + \gamma_{\mu\mu}. \end{split}$$

Here I_{μ} is ionization potential of π -electron in the corresponding valence state and in the outer field of neighbouring neutral atoms. It is obvious that $I_{\mu'} = I_{\mu}$ as well as $\gamma_{\mu'\mu'} = \gamma_{\mu\mu}$. The summation runs over all AOs π_x resp. π_y .

Let us introduce the following notations for density matrix elements in AO representation:

$$P_{\mu\nu}^{c} = \sum_{j} C_{\mu j} C_{\nu j}, \quad P_{\mu\nu}^{o} = C_{\mu k} C_{\nu k}, \quad P_{\mu\nu}^{T} = 2 P_{\mu\nu}^{c} + P_{\mu\nu}^{o},$$

and analogous expressions for the primed densities. For the states with closed shell $P^o_{\mu\nu}$ is equal to zero.

Using these notations and under the assumption of the approximations mentioned above we obtain

$$\begin{split} \sum_{j} J_{jk} &= \sum_{\mu\nu} P^{c}_{\mu\mu} P^{o}_{\nu\nu} \gamma_{\mu\nu}, \\ \sum_{j} K_{jk} &= \sum_{\mu\nu} P^{c}_{\mu\nu} P^{o}_{\mu\nu} \gamma_{\mu\nu}, \\ J_{kk'} &= \sum_{\mu'\nu} P^{o}_{\mu'\mu'} P^{o}_{\nu\nu} \gamma_{\mu'\nu}. \end{split}$$

In the zero differential overlap approximation all exchange integrals of the type $K_{ij'}$ are zero. When the necessary substitutions are done we get the following expressions for the energy of states with closed shell:

$$E^{c}({}^{1}A_{1}, {}^{1}A_{g}) = \sum_{\nu} (\gamma_{\nu\nu} - I_{\nu})P_{\nu\nu}^{T} + \sum_{\nu'} (\gamma_{\nu'\nu'} - I_{\nu'})P_{\nu'\nu'}^{T} + \sum_{\mu\nu'} \left\{ \left[\frac{1}{2} P_{\mu\mu}^{T} P_{\nu\nu}^{T} - P_{\nu\nu}^{T} - \frac{1}{4} (P_{\mu\nu}^{T})^{2} \right] \gamma_{\mu\nu} + P_{\mu\nu}^{T} \beta_{\mu\nu} \right\} + \sum_{\mu'\nu'} \left\{ \left[\frac{1}{2} P_{\mu'\mu'}^{T} P_{\nu'\nu'}^{T} - P_{\nu'\nu'}^{T} - \frac{1}{4} (P_{\mu'\nu'}^{T})^{2} \right] \gamma_{\mu'\nu'} + P_{\mu'\nu'}^{T} \beta_{\mu'\nu'} \right\} .$$
(201)
+
$$\sum_{\mu\nu'} (P_{\mu\mu}^{T} P_{\nu'\nu'}^{T} - P_{\nu'\nu'}^{T} - P_{\mu\mu}^{T}) \gamma_{\mu\nu'}$$

Further simplifications will follow if we take into account that for alternant hydrocarbons it holds that $P_{\nu\nu}^T = P_{\nu'\nu'}^T = 1[151]$. This is also true for the SCF method in the PPP approximation, which is assumed, if the ionization potentials and integrals are put equal for all C atoms [148, 152] including the end-atoms:

$$I_{\nu} = I_{\nu'} \equiv I, \quad \gamma_{\nu\nu} = \gamma_{\nu'\nu'} \equiv \gamma.$$

This assumption seems to be not far from the truth for organic cumulenes.

If the alternant properties of cumulenes are taken into account then the energy of the states with closed shell can be divided up as follows:

$$E^{c}({}^{1}A_{1}, {}^{1}A_{g}) = E_{x}^{c} + E_{y}^{c} + E_{int} + E^{core},$$

where

$$E_{x}^{c} = \sum_{\nu} (\gamma_{\nu\nu} - I_{\nu}) + \sum_{\mu\nu} \left[P_{\mu\nu}^{T} \beta_{\mu\nu} - \frac{1}{2} \gamma_{\mu\nu} - \left(\frac{1}{2} P_{\mu\nu}^{T}\right)^{2} \gamma_{\mu\nu} \right],$$
(202a)

$$E_{y}^{c} = \sum_{v'} (\gamma_{v'v'} - I_{v'}) + \sum_{\mu'v'} \left[P_{\mu'v'}^{T} \beta_{\mu'v'} - \frac{1}{2} \gamma_{\mu'v'} - \left(\frac{1}{2} P_{\mu'v'}^{T}\right)^{2} \gamma_{\mu'v'} \right], \quad (202b)$$
$$E_{\text{int}} = -\sum_{\mu v'} \gamma_{\mu v'}.$$

The energy E_x^c represents the π -electron energy of a hypothetical compound with the same space structure as the corresponding cumulene with closed shell but having only one system of AOs of the type π_x . The same is true for the energy E_y^c . E_{int} represents the energy of the static electron interaction of the two chains and does not depend upon the MO coefficients.

Analogous transformations for the states with open shell ${}^{1}B_{1}$ and ${}^{1}A_{u}$ lead to the following result:

$$E^{o}({}^{1}B_{1}, {}^{1}A_{u}) = E_{x}^{o} + E_{y}^{o} + E_{int} + E^{core},$$

where

$$E_{x}^{o} = \sum_{\nu} (\gamma_{\nu\nu} - I_{\nu}) + \sum_{\mu\nu} \left[P_{\mu\nu}^{T} \beta_{\mu\nu} - \frac{1}{2} \gamma_{\mu\nu} - \left(\frac{1}{2} P_{\mu\nu}^{T}\right)^{2} \gamma_{\mu\nu} - \left(\frac{1}{2} P_{\mu\nu}^{o}\right)^{2} \gamma_{\mu\nu} \right], \quad (203a)$$

$$E_{y}^{o} = \sum_{v'} (\gamma_{v'v'} - I_{v'}) + \sum_{\mu'v'} \left[P_{\mu'v'}^{T} \beta_{\mu'v'} - \frac{1}{2} \gamma_{\mu'v'} - \left(\frac{1}{2} P_{\mu'v'}^{T}\right)^{2} \gamma_{\mu'v'} - \left(\frac{1}{2} P_{\mu'v'}^{o}\right)^{2} \gamma_{\mu'v'} \right]. \quad (203b)$$

As we see, division into two chains is possible also in this case, but now each chain is in a doublet state and has an open shell structure as in organic free radicals. However, for the open shell states ${}^{1}A_{1}$, ${}^{1}B_{2}$, ${}^{1}A_{g}$, and ${}^{1}A'_{g}$ division of the π electron system in two subsystems is not possible despite of the fact that rule $P_{VV}^{T} = P_{VV'}^{T}$ is satisfied.

The energy E_{int} is not the same for different cumulene conformations. A simple consideration yields

$$E_{\rm int}(D_{2d}) - E_{\rm int}(D_{2h}) = -\gamma_{\alpha\omega'},$$

where α and ω are the indices of the end-atoms.

Let us note one incorrectness of the Goeppert-Mayer and Sklar approximation [150] when one calculates the interaction energy of positive core charges E_D . In fact, if we try to find E_D in this approximation by the method of Dewar and Gleicher [153]

$$E_D = \sum_{\mu < \nu} \gamma'_{\mu\nu} ,$$

where the summation is taken over all AOs of the two chains, one gets different interaction energies for different conformations:

$$E_D(D_{2d}) - E_D(D_{2h}) = \gamma_{\alpha \omega'} - \gamma_{\alpha \omega}.$$

However on physical grounds the interaction energies of positive charges in different core conformations of cumulenes can not be different. These differences are small, of course, and decrease rapidly with increasing chain length.

If one accepts the differences mentioned then the barrier height V may be found from the relation

$$V = E_x(D_{2d}) + E_y(D_{2d}) - E_x(D_{2h}) - E_y(D_{2h}) - \gamma_{\alpha\omega}.$$
 (204)

The last term will then result from compensations of charges of E_{int} and E^{core} .

If, on the other hand, one takes the same core energies E^{core} for both conformations then

$$V = E_x(D_{2d}) + E_y(D_{2d}) - E_x(D_{2h}) - E_y(D_{2h}) - \gamma_{\alpha\alpha'}.$$
 (205)

Barrier values by (204) and (205) are almost identical especially for large N.

As we see from (204) and (205) the barrier height is determined first of all by SCF energies of the π -electron subsystems which may be calculated from formulae (202a,b) and (203a,b) [9]. It is also of interest to consider the case of Huckel orbitals for a chain with all bond lengths equal. These orbitals are expressed analytically as

$$C_{\mu j} = \sqrt{\frac{2}{m+1}} \sin \frac{\mu j \pi}{m+1} \,.$$

Let us take into account the integrals $\beta_{\mu\nu}$ and $\gamma_{\mu\nu}$ only for neighbouring atoms and use the following relations:

$$\sum_{\mu=1}^{m-1} P_{\mu,\mu+1}^{T} \equiv Q_{m} = \begin{cases} \csc \frac{\pi}{2m+2} - 1, & m \text{ even} \\ \csc \frac{\pi}{2m+2} - 1, & m \text{ odd} \end{cases}$$
$$\sum_{\mu=1}^{m-1} (P_{\mu,\mu+1}^{T})^{2} = \frac{Q_{m}^{2}}{m+1} + \begin{cases} m/(m+1), & m \text{ even} \\ (m-1)/m, & m \text{ odd} \end{cases}$$
$$\sum_{\mu=1}^{m} (P_{\mu\mu}^{o})^{2} = \frac{2}{m+1}, & m \text{ odd} \end{cases}$$
$$\sum_{\mu=1}^{m-1} (P_{\mu,\mu+1}^{o})^{2} = 0.$$

It is possible then to show analytically that barriers calculated by formula (204) tend asymptotically to zero with increasing N in accord with Huckel calculations in [145].

Now we are ready to consider very long cumulene chains using sophisticated EHF as well as UHF approaches.

Chapter 6. Electronic Structure of Long Cumulene Chains in the Extended Hartree – Fock Method Compared with its Unrestricted Version

6.1 Introduction

It is important to note once more that most properties of carbon polymeric chains like polyenes, cumulenes, polyacetylenes, polyacenes, and graphene can be explained in terms of the π -electron approximation. This fact enables methods involving electron correlation to be used for theoretical treatment of such electronic systems, which in turn gives a possibility for studying the main features of electron correlation methods for calculations of molecular electronic structure. It is well known [6, 16, 17, 107 – 111] that electron interaction may give rise to qualitative changes in spectra of systems we are concerned. Thus, if electron correlation are taken into account by the UHF method, then energy spectra of long polyenes with equal bond lengths [6, 16, 109. 110] and long regular cumulenes [17, 111] contain a forbidden zone, the width of which is in good agreement with experimental data. If the Huckel or the RHF methods are used, *i.e.*, when electron correlations are neglected, the molecular systems we consider have spectra of the metallic type unless the further assumptions about the bond length alternation have been made [129].

We begin our consideration of long cumulenes with the UHF equations for long polyene chains.

6.2 The UHF equations for long polyene chains

Here will be now proved that the UHF equations for long neutral polyenes both with even and odd number of carbon atoms are the same. For this purpose let us analyze the results obtained for polyenes with even [16] and odd (§ 4 above) number of C atoms $N \square$ 1 by the UHF method. If the chain boundaries are taken into account, as in the Hubbard's approximation, the Hamiltonian for a long polyene with equal bond lengths can be expressed as [16, 107, 108]

$$\hat{H} = \sum_{k\sigma} (\alpha + 2\beta \cos k) \hat{A}^{+}_{k\sigma} \hat{A}^{-}_{k\sigma} + \frac{\gamma}{2N} \sum_{k,k',k'',\sigma} \hat{A}^{+}_{k\sigma} \hat{A}^{+}_{k'\sigma} \hat{A}^{+}_{k'',\sigma} \hat{A}^{+}_{k''$$

where α and β are the Coulomb and the resonance integrals respectively, γ is the Coulomb integral corresponding to the electron interaction with one of the nearest atoms, $\hat{A}^+_{k\sigma}$ and $\hat{A}_{k\sigma}$ are the operators of π -electron creation and annihilation in the state

$$\varphi_k^{(0)}(\vec{r}) = \sqrt{\frac{2}{N}} \sum_{\nu=1}^N \chi_\nu(\vec{r}) \sin k\nu,$$

involving σ -spin, $\sigma = \uparrow, \downarrow, \chi_{\nu}(\vec{r})$ is the vth AO,

$$f(k,k',k'',k''') = \frac{4}{N} \sum_{\mu=1}^{N} \sin k \,\mu \cdot \sin k' \,\mu \cdot \sin k'' \,\mu \cdot \sin k''' \,\mu$$

is a linear combination of the Kroneker δ -symbols of the type

$$\delta(k \pm k' \pm k'' \pm k''' \pm 2n\pi)$$
. $n = 0, 1, 2, ...$

It is easy to show that functions $\varphi_k^{(0)}$ are the HF solutions for the Hamiltonian (206). In the HF approximation only averages over the ground state of the type $\langle \hat{A}_{k\sigma}^+ \hat{A}_{k\sigma} \rangle$ do not vanish. In case of the UHF method we have also to take as non-zero the averages of the type $\langle \hat{A}_{k\sigma}^+ \hat{A}_{k\sigma} \rangle$, where $\bar{k} = \pi - k$. The case when the chain boundaries are neglected, *i.e.* the cyclic boundary conditions are used, see in [16, 107, 108]. Hence it follows that

$$\varphi_k^{(0)} = \frac{1}{\sqrt{N}} \sum_{\nu=1}^N \chi_\nu e^{ik\nu}, \quad -\pi \le k \le \pi, \quad \overline{k} = k - \pi \cdot \operatorname{sign}(k).$$

The UHF Hamiltonian for a long polyene chain can be written as

$$\hat{H}_{\sigma}^{(UHF)} = \sum_{k \le \pi} (2\beta \hat{A}_{k\sigma}^{\dagger} \hat{A}_{k\sigma} \cos k + \gamma \cdot \Delta \cdot \tau_{-\sigma} \hat{A}_{k\sigma}^{\dagger} \hat{A}_{\bar{k}\sigma}) + C, \qquad (207)$$

$$C = \frac{N}{2} \left(\alpha + \frac{\gamma}{4} + \gamma \Delta^2 \right), \quad \tau_{\sigma} = \begin{cases} 1, & (\sigma = \uparrow) \\ -1. & (\sigma = \downarrow) \end{cases}$$

The self-consistent value of

$$\Delta = \frac{\tau_{\sigma}}{N} \sum_{k} \left\langle \hat{A}_{k\sigma}^{+} \hat{A}_{k\sigma} \right\rangle \tag{208}$$

is defined by the equation

$$\frac{\gamma}{\pi} \int_{0}^{\pi/2} dk (4\beta^2 \cos^2 k + \gamma^2 \Delta^2)^{-1/2} = 1.$$
(209)

Let us transform the operators $\hat{A}^{+}_{k\sigma}$ and $\hat{A}^{-}_{k\sigma}$ using Eqs (120) above as

$$\hat{A}_{k\sigma} = (\hat{A}_{k\sigma}^{(1)} - \xi_k \tau_\sigma \hat{A}_{k\sigma}^{(2)}) \mathfrak{I}_k^{-1/2},$$

$$\hat{A}_{\bar{k}\sigma} = (\hat{A}_{k\sigma}^{(2)} + \xi_k \tau_\sigma \hat{A}_{k\sigma}^{(1)}) \mathfrak{I}_k^{-1/2},$$
(210)

where

$$0 \le k \le \pi / 2, \quad \mathfrak{I}_{k} = 1 + \xi_{k}^{2},$$

$$\xi_{k} = (2\beta \cos k + \sqrt{4\beta^{2} \cos^{2} k + (\gamma \Delta)^{2}}) / (\gamma \Delta). \quad (211)$$

Substituting (210) and (211) into (207) one obtains

$$\hat{H}_{\sigma}^{(UHF)} = \sum_{i,k} \varepsilon_k^{(i)} \hat{A}_{k\sigma}^{(i)+} \hat{A}_{k\sigma}^{(i)} , \qquad (212)$$

where

$$\varepsilon_k^{(1)} = -\varepsilon_k^{(2)} = -\sqrt{4\beta^2 \cos^2 k + \gamma^2 \Delta^2} \,. \tag{213}$$

The operators $\hat{A}_{k\sigma}^{(i)}$ correspond to one-electron wave functions

$$\varphi_{k\sigma}^{(i)}(\vec{r}) = \sum_{\mu=1}^{N} C_{k\sigma}^{(i)}(\mu) \chi_{\mu}(\vec{r}),$$

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

$$C_{k\sigma}^{(2)}(\mu) = \sqrt{\frac{2}{N}} [(-1)^{\mu+1} - \xi_k \tau_\sigma] \mathfrak{I}_k^{-1/2} \sin \mu k.$$
(214)

In the ground state all levels $\varepsilon_k^{(1)}$ are filled and all levels $\varepsilon_k^{(2)}$ are empty whether *N* is even or odd. Thus, the relations (208) – (214) are valid in both cases. Consequently, in the UHF method the self-consistent functions (214) and the energy spectra of long polyene chains with even *N* coincide with those for odd *N*, as it should be expected so far as $N \square 1$. By contrast, the HF solution for long polyene is unstable relative to a small perturbation modeling the addition of an unpaired electron to the system.

Unfortunately, the UHF wave function is not an eigenfunction of the total spin operator \hat{S}^2 . To get rid of this disadvantage one has to use the EHF method. It will be shown below that both the UHF and the EHF methods being applied to large enough systems give identical results except spin density expressions. This means that the projection of the UHF wave function on the state involving the lowest multiplicity does not affect the relations (208) – (214). It should also be noted that the exact solution of the Schrodinger equation with the Hamiltonian (206) and the cyclic boundary conditions is obtained in [112]. The study of the exact solution [112, 154] has shown that there was an energy gap in the spectrum of quasi-ionic excitations active in optical spectra. Hence, it can be concluded that the UHF/EHF method treats correctly this feature of the exact solution.

Now we shall consider the values

$$n_{\mu\sigma} = \sum_{k \le \pi/2} [C_{k\sigma}^{(1)}(\mu)]^2 \,. \tag{215a}$$

Substituting (214) into (215a) one obtains

$$n_{\mu\sigma} = \frac{1}{2} + (-1)^{\mu+1} \tau_{\sigma} \delta_{\mu}, \qquad (215b)$$

$$\delta_{\mu} = \frac{2\gamma \Delta}{\pi} \int_{0}^{\pi/2} dk \, (\varepsilon_{k}^{(2)})^{-1} \sin^{2} \mu k \,.$$
(216)

The chain boundary effect is revealed in the dependence of δ_{μ} on μ . It follows from (216) that

$$\delta_1 = 0.28, \delta_2 = 0.18, \delta_3 = 0.23, \dots, \delta_{\mu} = \Delta = 0.21 \text{ for } \mu \Box \ 1 (\beta = -2.4 \text{ eV}, \gamma = 5.4 \text{ eV}[16]).$$

Thus, the chain boundary effect extends, in fact, to only the first two – three atoms. It also follow s from (215) that $n_{\mu} = \sum_{\sigma} n_{\mu\sigma} = 1$. The values $n_{\mu\sigma}$ are equal to electron populations of the μ th AO with σ -spin in the UHF method, but it is not the case when the EHF method is used as shown below. In the latter case the values (215) can be treated as self-consistent parameters.

6.3. Electronic Structure of Long Cumulene Chains

Now we shall turn to the treatment of long cumulenes $C_N H_4$ ($N \square 1$) using the results obtained just above. As we know the π -electron system of a cumulene molecule consists of the two π -subsystems which have the maxima of the electron density at two mutually perpendicular planes. From now all values corresponding to one of these subsystems will be marked with letter a/A and to another – with letter b/B. There are two possible conformations of a cumulene molecule which differ by mutual orientation of its end-groups CH₂. Let us denote the conformation of symmetry D_{2h} in which the end-groups lie in the same plane as A_{\Box} and the alternative conformation of symmetry D_{2d} – as A_{\perp} .

Let us consider a cumulene molecule neglecting its end-groups. In the short-range interaction approximation [17, 111] one can obtain the following expression for the Hamiltonian of a long chain $=(C=)_N$

$$\hat{H} = \sum_{k\sigma} (\alpha + 2\beta \cos k) \left(\hat{A}_{k\sigma}^{+} \hat{A}_{k\sigma} + \hat{B}_{k\sigma}^{+} \hat{B}_{k\sigma} \right)
+ \frac{1}{2N} \sum_{k,k',k'',k''',\sigma} \left[\frac{\gamma \left(\hat{A}_{k\sigma}^{+} \hat{A}_{k'\sigma} \hat{A}_{k'',-\sigma}^{+} \hat{A}_{k'',-\sigma} + \hat{B}_{k\sigma}^{+} \hat{B}_{k'\sigma} \hat{B}_{k'',-\sigma}^{+} \hat{B}_{k'',-\sigma} \right)
+ \tilde{\gamma} \left(\hat{A}_{k\sigma}^{+} \hat{B}_{k'\sigma} \hat{A}_{k'',-\sigma}^{+} \hat{B}_{k'',-\sigma} + \hat{B}_{k\sigma}^{+} \hat{A}_{k'\sigma} \hat{B}_{k'',-\sigma}^{+} \hat{A}_{k'',-\sigma} \right)
+ 2\sum_{\sigma'} \left(\tilde{\gamma} \hat{B}_{k\sigma}^{+} \hat{B}_{k'\sigma} \hat{A}_{k''\sigma'}^{+} \hat{A}_{k''\sigma'} - \tilde{\gamma} \hat{A}_{k\sigma}^{+} \hat{A}_{k'\sigma'} \hat{B}_{k''\sigma}^{+} \hat{B}_{k'''\sigma} \right) \right],$$
(217)

where $\hat{A}_{k\sigma}^{+}$ and $\hat{B}_{k\sigma}^{+}$ are the operators of electron creation in the states $\varphi_{k,a}^{(0)}$ and $\varphi_{k,b}^{(0)}$ with σ -spin,

$$\varphi_{k,j}^{(0)}(\vec{r}) = \sqrt{\frac{2}{N}} \sum_{\mu=1}^{N} \chi_{\mu}^{(j)}(\vec{r}) \sin \mu k ,$$

$$\tilde{\tilde{\gamma}} = e^2 \int dV_{12} |\chi_{\mu}^{(a)}(\vec{r}_1)|^2 r_{12}^{-1} |\chi_{\mu}^{(b)}(\vec{r}_2)|^2 , \qquad (218a)$$

$$\tilde{\gamma} = e^2 \int dV_{12} \,\chi_{\mu}^{(a)}(\vec{r}_1) \,\chi_{\mu}^{(b)}(\vec{r}_1) \,r_{12}^{-1} \,\chi_{\mu}^{(a)}(\vec{r}_2) \,\chi_{\mu}^{(b)}(\vec{r}_2) \,.$$
(218b)

Taking into account that the orbitals of different subsystems do not mix and assuming that the values $\langle \hat{A}_{k\sigma}^{+} \hat{A}_{k\sigma} \rangle$, $\langle \hat{B}_{k\sigma}^{+} \hat{B}_{k\sigma} \rangle$, $\langle \hat{A}_{k\sigma}^{+} \hat{A}_{\bar{k}\sigma} \rangle$ and $\langle \hat{B}_{k\sigma}^{+} \hat{B}_{\bar{k}\sigma} \rangle$ being averaging over the ground state do not vanish, we obtain the effective UHF Hamiltonian for a long cumulene molecule

$$\hat{H}_{\sigma,a}^{(UHF)} = \sum_{k} [2\beta \hat{A}_{k\sigma}^{+} \hat{A}_{k\sigma} \cos k + (\gamma \Delta_{a} \tau_{-\sigma} - \tilde{\gamma} \Delta_{b} \tau_{\sigma}) \hat{A}_{k\sigma}^{+} \hat{A}_{\bar{k}\sigma}] + C_{1},$$

$$\hat{H}_{\sigma,b}^{(UHF)} = \sum_{k} [2\beta \hat{B}_{k\sigma}^{+} \hat{B}_{k\sigma} \cos k + (\gamma \Delta_{b} \tau_{-\sigma} - \tilde{\gamma} \Delta_{a} \tau_{\sigma}) \hat{B}_{k\sigma}^{+} \hat{B}_{\bar{k}\sigma}] + C_{1},$$
(219)

where

$$\Delta_{a} = \frac{\tau_{\sigma}}{N} \sum_{k} \left\langle \hat{A}_{k\sigma}^{+} \hat{A}_{\bar{k}\sigma} \right\rangle, \quad \Delta_{b} = \frac{\tau_{\sigma}}{N} \sum_{k} \left\langle \hat{B}_{k\sigma}^{+} \hat{B}_{\bar{k}\sigma} \right\rangle,$$
$$C_{1} = \frac{N}{4} \left[2\alpha + \frac{\gamma - \tilde{\gamma}}{2} + \tilde{\tilde{\gamma}} + 2(\gamma + \tilde{\gamma}) \Delta_{1}^{2} \right]. \quad 0 \le k \le \pi$$

According to [17, 111], there are two possible self-consistent solutions:

(1)
$$\Delta_a = \Delta_b = \Delta_1$$
,
(2) $\Delta_a = -\Delta_b = \Delta_2$.

Since the lowest ground state energy is known to correspond to the first case [17, 111], we shall restrict ourselves to the case $\Delta_a = \Delta_b$. Substituting this condition into Eq. (219) one obtains

$$\hat{H}_{\sigma,a}^{(UHF)} = \sum_{k} [2\beta \hat{A}_{k\sigma}^{+} \hat{A}_{k\sigma} \cos k + (\gamma + \tilde{\gamma})\Delta_{1}\tau_{-\sigma} \hat{A}_{k\sigma}^{+} \hat{A}_{\bar{k}\sigma}] + C_{1},$$

$$\hat{H}_{\sigma,b}^{(UHF)} = \sum_{k} [2\beta \hat{B}_{k\sigma}^{+} \hat{B}_{k\sigma} \cos k + (\gamma + \tilde{\gamma})\Delta_{1}\tau_{-\sigma} \hat{B}_{k\sigma}^{+} \hat{B}_{\bar{k}\sigma}] + C_{1}.$$
(220)

The expression (220) have the same form as (203). Because of this the expressions (220) are diagonalized by canonical transformation of the type (205), namely:

$$\hat{H}_{\sigma,a}^{(UHF)} = \sum_{i,k} \varepsilon_{k}^{(i)} \hat{A}_{k\sigma}^{(i)+} \hat{A}_{k\sigma}^{(i)} + C_{1},$$

$$\hat{H}_{\sigma,b}^{(UHF)} = \sum_{i,k} \varepsilon_{k}^{(i)} \hat{B}_{k\sigma}^{(i)+} \hat{B}_{k\sigma}^{(i)} + C_{1},$$
(221a)

where

$$\varepsilon_{k}^{(1)} = -\varepsilon_{k}^{(2)} = -\sqrt{4\beta^{2}\cos^{2}k + (\gamma + \tilde{\gamma})^{2}\Delta_{1}^{2}}, \quad 0 \le k \le \pi/2, \quad (221b)$$

the self-consistent value of Δ_1 is defined by the equation

$$\frac{\gamma + \tilde{\gamma}}{\pi} \int_{0}^{\pi/2} (\varepsilon_k^{(2)})^{-1} dk = 1.$$
(222)

The operators $\hat{A}_{k\sigma}^{(i)}$ and $\hat{B}_{k\sigma}^{(i)}$ correspond to the functions $\varphi_{k\sigma,a}^{(i)}$ and $\varphi_{k\sigma,b}^{(i)}$. Their coefficients of the expansion in terms of the atomic orbitals $\chi_{\mu}^{(a)}$ and $\chi_{\mu}^{(b)}$ are diagonal as to the marking *a* and *b* and have the form

$$C_{k\sigma,a}^{(i)}(\mu) = C_{k\sigma,b}^{(i)}(\mu) = C_{k\sigma}^{(i)}(\mu), \qquad (223)$$

where $C_{k\sigma}^{(i)}$ are determined by (214) if ξ_k is substituted by

$$\xi_{k} = \left[2\beta\cos k + \sqrt{4\beta^{2}\cos^{2}k + (\gamma + \tilde{\gamma})^{2}\Delta_{1}^{2}}\right] / \Delta_{1}(\gamma + \tilde{\gamma}).$$
(224)

In the ground state all levels $\varepsilon_k^{(1)}$ of the two subsystems are filled and all levels $\varepsilon_k^{(2)}$ are empty. Thus, the UHF wave function of the cumulene ground state has the following form

$$\Psi_{0}^{(UHF)} = \prod_{k\sigma} \hat{A}_{k\sigma}^{(1)+} \hat{B}_{k\sigma}^{(1)+} |0\rangle.$$
(225)

Using (217) and (225) one can obtain the expression for the ground state energy

$$E_{0}^{(UHF)} = \left\langle \Psi_{0}^{(UHF)} \middle| \hat{H} \middle| \Psi_{0}^{(UHF)} \right\rangle$$

$$= 4 \sum_{k \le \pi/2} \left(1 - \frac{1}{2} \delta_{k,\pi/2} \right) \varepsilon_{k}^{(1)} + N \left[2\alpha + \tilde{\tilde{\gamma}} + \frac{\gamma - \tilde{\gamma}}{2} + 2\left(\gamma + \tilde{\gamma}\right) \Delta_{1}^{2} \right].$$
(226)

Atomic populations are defined as

$$n_{\mu\sigma}^{(a)} = n_{\mu\sigma}^{(b)} = \frac{1}{2} + (-1)^{\mu+1} \tau_{\sigma} \,\delta_{\mu} \,, \tag{227}$$

where

$$\delta_{\mu} = \frac{2(\gamma + \tilde{\gamma})\Delta_{1}}{\pi} \int_{0}^{\pi/2} dk \left[4\beta^{2}\cos^{2}k + (\gamma + \tilde{\gamma})^{2}\Delta_{1}^{2}\right]^{-1/2} \sin^{2}\mu k .$$
(228)

The analysis of (228) allows to reveal the dependence of δ_{μ} on μ ($\beta = -3.6 eV, \gamma = 5.4 eV, \tilde{\gamma} = 0.5 eV$ [17, 111])

$$\delta_1 = 0.16, \quad \delta_2 = 0.07, \quad \delta_3 = 0.13, \dots \quad \delta_\mu = \Delta_1 = 0.11. \quad (\mu \square \ 1)$$
 (229)

Thus, as with the polyenes, the chain boundary influence on δ_{μ} sharply decreases when the distance from the chain boundary increases.

We shall need further the equations for the coefficients (223), which can be obtained by proper transformation of (221), namely:

$$\left(\varepsilon_{k}^{(i)} + \tilde{\tilde{\gamma}} + \frac{\gamma - \tilde{\gamma}}{2} + \alpha \right) C_{k\sigma,a}^{(i)}(\mu) = \sum_{\nu=1}^{N} \hat{H}_{\sigma,a}^{(UHF)}(\mu,\nu) C_{k\sigma,a}^{(i)}(\nu)$$

$$\equiv \beta [(1 - \delta_{\mu,1}) C_{k\sigma,a}^{(i)}(\mu - 1) + (1 - \delta_{\mu,N}) C_{k\sigma,a}^{(i)}(\mu + 1)] + [\alpha + \gamma n_{\mu,-\sigma}^{(a)} - \tilde{\gamma} n_{\mu,-\sigma}^{(b)} + \tilde{\tilde{\gamma}} n_{\mu}^{(b)}] C_{k\sigma,a}^{(i)}(\mu).$$

$$(230)$$

To obtain the equations for $C_{k\sigma,b}^{(i)}$ it is necessary to permute markings *a* and *b* in (230).

Now let us consider cumulenes taking into account the end-effects. In the conformation A_{\Box} with symmetry D_{2h} the subsystem *a* contains $N \pi$ -electrons and the subsystem *b* contains N - 2 π -electrons. In the conformation A_{\bot} with symmetry D_{2d} both subsystems *a* and *b* contain the same N - 1 π -electrons. In passing from the long ideal no-end-groups cumulene to a real cumulene molecule with the end-groups some alterations in the equation (230) result due to the relative shift of the cumulene π -electron subsystems *a* and *b*. Namely, the effective values of the Coulomb integrals are changed according to

$$\begin{aligned} \alpha_{\nu\sigma}^{(a)} &= \alpha + \gamma n_{\nu,-\sigma}^{(a)} - \tilde{\gamma} n_{\nu\sigma}^{(b)} + \tilde{\tilde{\gamma}} n_{\nu}^{(b)}, \\ \alpha_{\nu\sigma}^{(b)} &= \alpha + \gamma n_{\nu,-\sigma}^{(b)} - \tilde{\gamma} n_{\nu\sigma}^{(a)} + \tilde{\tilde{\gamma}} n_{\nu}^{(a)}. \end{aligned}$$
(231)

It follows from (231) and (229) that the effective Coulomb integrals of the endatoms decrease by the value

$$\Delta_{1\sigma}^{(i)} = \Delta \alpha_{N\sigma}^{(i)} = \tilde{\tilde{\gamma}} n_1^{(i)} - \tilde{\gamma} n_{1\sigma}^{(i)} = \tilde{\tilde{\gamma}} - \tilde{\gamma} n_{1\sigma}^{(i)} \approx 4.7 \, eV$$

without regard for a change in the interaction between σ - and π -electrons in passing from the long ideal no-end-groups cumulene to real cumulene molecule. However, as long as the end carbon atoms of a cumulene molecule have the sp^2 hybridization, one should expect that the absence of the Coulomb interaction between π -electrons at the end-atoms is compensated by an interaction between σ - and π -electrons. This point of view is supported by the fact that the first ionization potential of a carbon atom in the valence sp^2 state coincides with that in the sp state within $10^{-3} eV$ [149]. On the other hand, the exchange interaction

 $\tilde{\gamma}$ does not appear to be compensated for in this case. Thus, we shall assume that the change in the Coulomb integrals (231) at the end-atoms is $|\Delta \alpha_{1\sigma}^{(i)}| = |\Delta \alpha_{N\sigma}^{(i)}| \le 0.66 \tilde{\gamma} \approx 0.3 \, eV$. Let us consider the alteration of $\alpha_{\mu\sigma}^{(i)}$ at the atoms next to the end-atoms. Using (229) and (231) one can obtain for the longer subsystem

$$\Delta \alpha_{2\sigma} = -\tau_{\sigma} \cdot 0.04 \, eV, \\ \Delta \alpha_{3\sigma} = +\tau_{\sigma} \cdot 0.02 \, eV,$$

and for the shorter subsystem

$$\Delta \alpha_{2\sigma} = +\tau_{\sigma} \cdot 0.04 \, eV, \\ \Delta \alpha_{3\sigma} = -\tau_{\sigma} \cdot 0.02 \, eV.$$

Thus, the end-effects in cumulenes are of a local nature and can be considered by means of the local perturbation theory [20], which was applied to long polyenes in the framework of the UHF method in § 5 above.

The ratio $|\Delta \alpha_{\mu\sigma}^{(i)} / \beta| = |\lambda_{\mu\sigma}^{(i)}|$ is a parameter which defines the relative magnitude of a local perturbation [20]. It follows from evaluations given above that Max $|\lambda_{\mu\sigma}^{(i)}| \le 0.08$, *i.e.* the perturbation due to the end-effects in cumulenes is small enough. It was already shown in paragraph 5 above that small local perturbation do not disturb the self-consistency of the UHF Hamiltonian (accurate within $\Box \lambda$). Therefore, let us consider the electronic structure of cumulenes in the conformations A_{\Box} and A_{\perp} neglecting the small alterations of the parameters $\alpha_{\mu\sigma}^{(i)}$. In one of the two conformations, namely A_{\perp} , each π -subsystem *a* and *b* consists of an odd number of electrons, being a long polyene radical. Nevertheless, it follows from the previous section of this paragraph that the energy spectra of long even polyenes and long polyene radicals are the same in the framework of the UHF (or EHF) method. Thus, in both conformations of a cumulene, its excited states are separated from the ground state with the gap $2(\gamma + \tilde{\gamma})\Delta_1$ in accordance with Eq. (221b).

Let us evaluate the difference between the ground state energy of a long cumulene chain in the conformation A_{\Box} and that in the conformation A_{\bot} : $\Delta E = E_{\Box} - E_{\bot}$. The value of ΔE is usually referred to as the torsion barrier of cumulene end-groups. Using the relations (217) and (225), one can obtain

$$\Delta E = \sum_{k\sigma} [\varepsilon_k^{(1)}]_N + \sum_{k\sigma} [\varepsilon_k^{(1)}]_{N-2} - 2\sum_{k\sigma} [\varepsilon_k^{(1)}]_{N-1} + N(\gamma + \tilde{\gamma})[(\Delta_1)_N^2 + (\Delta_1)_{N-2}^2 - 2(\Delta_1)_{N-1}^2], \quad (232)$$

where $\sum_{k} [\varepsilon_{k}^{(1)}]_{N}$ stands for *k* changes from 0 to $\pi/2$ spaced $\pi/(N+1)$ when summing up, $(\Delta_{1})_{N}$ is the root of the equation

$$\frac{\gamma + \tilde{\gamma}}{\pi} \sum_{i=1}^{N/2} \left[4\beta^2 \cos^2 \left(i \frac{\pi}{N+1} \right) + (\gamma + \tilde{\gamma})^2 \Delta_1^2 \right]^{-1/2} = 1.$$
(233)

In order to evaluate Eq. (27) it is important to note that if f(k) is a continuous function of k then

$$f\left(\frac{a}{N+1}\right) + f\left(\frac{a}{N-1}\right) - 2f\left(\frac{a}{N}\right) = O\left(\frac{1}{N^2}\right).$$
 (234)

It follows from Eqs (234), (221b), and (233) that $\Delta E = O(1/N)$, *i.e.*, the torsion barrier tends to zero when the cumulene is lengthened. From the mathematical point of view this result is due to the fact that the intervals between the levels occupied in the ground state are of $\Box 1/N$ whether the cumulene subsystems *a* and *b* consist of the even or odd number of π -electrons.

Let us evaluate the influence of the small perturbations $\Delta \alpha_{\mu\sigma}^{(i)}$ on the π electronic structure of cumulenes. As we already know from paragraph 5 above, small local perturbations can give rise to local states in the forbidden zone of a system like long polyene chains. These local state energies differ from the nearest zone state energy by values $\Box a\lambda^2$, where *a* is the width of the forbidden
zone in the ideal cumulene chain. It means that in our case the forbidden zone width $2(\gamma + \tilde{\gamma}) \Delta_1$ is not affected practically by the end-effects. It was also shown in § 5 above that local perturbations placed at the large distance from one another do not interact. Hence it follows that the end-effects in long cumulenes can not change the value of the torsion barrier. Indeed, the contributions into the ground state energy are additive relative to perturbations of atoms placed at the different ends of a long cumulene chain and, because of this, are the same whether the cumulene is in the conformation A_{\perp} or A_{\perp} .

To study spin properties of cumulenes we should pass from the UHF method to the EHF approach. As it will be shown below, the SCF equations for systems consisting of the large number of electrons are the same whether one uses the UHF or the EHF method. So, the orbitals $\varphi_{k\sigma,a}^{(i)}$ and $\varphi_{k\sigma,b}^{(i)}$ corresponding to the operators $\hat{A}_{k\sigma}^{(i)}$ and $\hat{B}_{k\sigma}^{(i)}$ are also self-consistent ones in the EHF method. To put it another way, the Eqs (230) remain valid in spite of the fact that the values $n_{\mu\sigma}^{(i)}$ given by (227) are not equal to the AO electron populations with σ -spin when the EHF method is used.

Let us now consider the multiplicity of the cumulene grounf state. Suppose the number of cumulene carbon atom to be even, *i.e.* N = 2q. Then both cumulene subsystems *a* and *b* in the conformation A_{\Box} consist of the even number of π -electrons *N* and *N* – 2, respectively. Hence, the total spin projection for each of the two subsystems in the ground state when all levels of both subsystems are filled is equal to zero: $M_a = M_b = 0$. Therefore, the cumulene ground state in the conformation A_{\Box} is a singlet one (S = M = 0) and its EHF wave function, as will be shown below, has the following form

$$\Psi_{A_{\rm U}}^{(EHF)} = \hat{O}_{S=M=0} \hat{A} \phi_{A_{\rm U}} \chi_{A_{\rm U}}, \qquad (235)$$

where A is the antisymmetrization operator be specified later,

$$\phi_{A_{j}} = \prod_{i=1}^{n_{a}} \varphi_{i\uparrow,a}^{(1)}(i) \prod_{i=1}^{n_{b}} \varphi_{i\uparrow,b}^{(1)}(i+n_{a}) \prod_{i=1}^{m_{a}} \varphi_{i\downarrow,a}^{(1)}(i+n) \prod_{i=1}^{m_{b}} \varphi_{i\downarrow,b}^{(1)}(i+n+m_{a}), \qquad (236)$$

$$\varphi_{i\sigma,j}^{(l)} \equiv \varphi_{k_{i},\sigma}^{(l)}, \quad k_{i} = i\pi / (N+1),$$

$$\chi_{A_{j}} = \alpha(1)\alpha(2)\cdots\alpha(n)\beta(n+1)\beta(n+2)\cdots\beta(n+m),$$

$$m = m_{a} + m_{b}, \quad n = n_{a} + n_{b}, \quad n_{a} = m_{a} = N / 2, \quad n_{b} = m_{b} = \frac{N}{2} - 1.$$
(237)

Let us now discuss the conformation A_{\perp} . Each of the cumulene subsystems a and b consists of the odd N – 1 number of π -electrons and, consequently, possesses the total spin projection $|M_a| \models |M_b| \models 1/2$. To determine the total spin projection of the cumulene $M = M_a + M_b$ we shall consider the Eqs (219) taking into account the equivalence of the equations of the UHF and EHF methods for large systems. "Unpaired" electrons in the cumulene subsystems a and b occupy the levels involving $k = \pi/2$ and energies $-(\gamma + \tilde{\gamma})\Delta_1$ in both subsystems according to (219). It follows from the relation $\Delta_a = \Delta_b$ and (219) that one-electron functions of these levels should have the same spin parts in the two different subsystems. Hence, $M_a = M_b$ and the ground state of cumulene in the conformation A_{\perp} is a triplet. Its EHF wave function can be written as

$$\Psi_{A_{\perp}}^{(EHF)} = \hat{O}_{S=M=1}\hat{A}\phi_{A_{\perp}}\chi_{A_{\perp}}$$

where $\phi_{A_{\perp}}$ and $\chi_{A_{\perp}}$ are defined by Eqs (236) and (237) if the following relations are taken into account, namely:

$$n_a = n_b = m_a + 1 = m_b + 1 = N / 2.$$

Let us pass now to the calculation of the AO spin populations in long cumulene chains. Using the Eqs (223) and (224) according to the UHF method one can obtain in the two conformations of cumulenes

$$\rho_{z}^{(UHF)}(\mu) = (-1)^{\mu+1} \frac{2(\gamma + \tilde{\gamma})\Delta_{1}}{\pi} \int_{0}^{\pi/2} dk [\varepsilon_{k}^{2}]^{-1} [\sin^{2}k\mu + \sin^{2}k(\mu - 1)] = (-1)^{\mu+1} 2(\delta_{\mu} + \delta_{\mu-1}).$$
(238)

To obtain spin populations in the framework of the EHF method one should multiply (238) by the factor S/(S+1) in accordance to the relation (252) below. So, the AO spin populations in long cumulene chains C_NH_4 with an even number N vanish identically in the conformation A_{\Box} . But, they differ from zero in the conformation A_{\perp} and are equal to

$$\rho_{z}^{(EHF)}(\mu) = \frac{1}{2} \rho_{z}^{(UHF)}(\mu) = (-1)^{\mu+1} (\delta_{\mu} + \delta_{\mu-1}) \approx 0.22 \times (-1)^{\mu+1}. \quad (\mu \square 1)$$

6.4 EHF and UHF Methods when Applied to Large Electronic Systems

Before to give the final discussion for this paragraph let us compare the UHF and EHF approaches as applied to large systems. The EHF wave function can be written as (see § 3 above)

$$\Psi_{0}^{(EHF)} = \hat{O}_{S,M} \Psi_{0}^{(UHF)} = \hat{O}_{S,M} \hat{A} \phi_{0} \chi_{0}, \qquad (239)$$

where

$$\phi_0 = \varphi_{1\uparrow}(1)\varphi_{2\uparrow}(2)\cdots\varphi_{n\uparrow}(n)\varphi_{1\downarrow}(n+1)\varphi_{2\downarrow}(n+2)\cdots\varphi_{m\downarrow}(N),$$

$$\chi_0 = \alpha(1)\alpha(2)\cdots\alpha(n)\beta(n+1)\beta(n+2)\cdots\beta(n+m).$$
(240)

 $\hat{O}_{S,M}$ is the operator of the projection on the state with the multiplicity 2S + 1, M = (n-m)/2, $\hat{A} = \sum_{\tau} \xi_{\tau} \hat{\tau}$ is the antisymmetrization operator. In the EHF method the ground state energy of a many electron system has the form

$$E_{0}^{(EHF)} = \left\langle \Psi_{0}^{(EHF)} \left| \hat{H} \right| \Psi_{0}^{(EHF)} \right\rangle / \left\langle \Psi_{0}^{(EHF)} \left| \Psi_{0}^{(EHF)} \right\rangle = T00^{-1} \\ \times \left\{ \sum_{i\sigma} \left\langle i\sigma \left| \hat{h}_{i} \right| i\sigma \right\rangle T01(i) + \frac{1}{2} \sum_{ij\sigma} T21(i,j) \left[\sum_{\sigma'} \left\langle i\sigma, j\sigma' \right| \hat{g}_{12} \right| i\sigma, j\sigma' \right\rangle - \sum_{\sigma'} \left\langle i\sigma, j\sigma \right| \hat{g}_{12} \left| j\sigma, i\sigma \right\rangle \right] \\ + \sum_{i\sigma} \left\langle i\sigma \left| \hat{h}_{i} \right| i, -\sigma \right\rangle T11(i) + \frac{1}{2} \sum_{i\sigma} \left\langle i\sigma \right| \hat{h}_{i} \left| i, -\sigma \right\rangle T11(i) + \frac{1}{2} \sum_{ij} \left[T12(i,j)S_{1}(i,j) + T22(i,j)S_{2}(i,j) \right] \right\},$$
(241)

where we have used the standard notations for the electron integrals, $S_1(i, j)$ and $S_2(i, j)$ are the sums of some electron integrals,

$$\left\langle \varphi_{i\sigma} \middle| \varphi_{j\sigma'} \right\rangle \equiv \left\langle i\sigma \middle| j\sigma' \right\rangle = \left[\lambda_i + (1 - \lambda_i) \delta_{\sigma\sigma'} \right] \delta_{ij},$$
 (242)

if S = M, then

$$TIJ = \sum_{p=0}^{m-J} A_p \binom{n}{p+I}^{-1},$$
 (243a)

$$TIJ(i) = TIJ|_{x_i=0}, \qquad (243b)$$

$$TIJ(i, j) = TIJ|_{x_i = x_i = 0},$$
 (243c)

$$A_{p} = \sum_{\substack{(k_{1},k_{2},\dots,k_{p})\\(k_{i}\neq k_{j})}} x_{k_{1}} x_{k_{2}} \cdots x_{k_{p}}, \quad (x_{k} = \lambda_{k}^{2}),$$
(244)

$$\binom{n}{k}$$
 is the binomial coefficient. If the relations

$$\frac{T0J}{T00} = \frac{T0J(i)}{T00} = \frac{T0J(i, j)}{T00} = 1,$$

$$\frac{TIJ}{T00} = \frac{TIJ(i)}{T00} = \frac{TIJ(i, j)}{T00} = 0$$
(245)

are valid with I, J = 1, 2 then the expression (241) coincides with $\langle \Psi_0^{(UHF)} | \hat{H} | \Psi_0^{(UHF)} \rangle$, i.e. $E_0^{(UHF)} = E_0^{(EHF)}$. It is shown [69, 70, 155] that the relations (245) are valid for the limit case $n \approx m \rightarrow \infty$ in the one-parameter AMO method $(x_i = x, 0 < x < 1)$. In that case one may write

$$\tilde{T}0J \approx T00 \approx 1/(1-x),$$

$$\tilde{T}1J \approx \frac{1}{m} \frac{d}{dx}(T00), , \qquad (246)$$

$$\tilde{T}2J \approx \frac{1}{m(m-1)} \frac{d^2}{dx^2}(T00),$$

where $\tilde{T}IJ = \tilde{T}IJ |_{x_i=x}$. Let us evaluate the values of *TIJ* for the many-parameter AMO method and, therefore, for the EHF method. To do this let us reduce the expression (244) to the form

$$A_p = \binom{m}{p} t_p^p, \qquad (247a)$$

where

$$t_{p} = \left[\binom{m}{p}^{-1} \sum_{\substack{(k_{1},k_{2},\dots,k_{p})\\(k_{i}\neq k_{j})}} x_{k_{1}} x_{k_{2}} \cdots x_{k_{p}} \right]^{1/p}, \qquad (247b)$$

Since, according to (242) $0 < x_i < 1$, then [156]

$$t_1 \ge t_2 \ge \dots \ge t_m. \tag{248}$$

Taking into account that all terms in (243) are positive and using (247) and (248) one can obtain

$$\tilde{T}IJ|_{x=t_{m}} \leq \tilde{T}IJ \leq \tilde{T}IJ|_{x=t_{1}}.$$
(249)

It follows from (246), (249), and (243) that the relations (245) are also valid in the framework of the multi-parameter AMO method for the limit case $n \approx m \rightarrow \infty$. Thus, the relation

$$E_0^{(EHF)} = E_0^{(UHF)}$$
(250)

is valid in general if the system under consideration consists of a large number of electrons. Besides, it follows from equation (250) that the SCF equations are the same in the EHF and UHF methods for this case. This can be proved directly through the use of the EHF (or the GF) equations (see § 3 above) obtained by Goddard.

As far as the EHF approximation, the spin density expression has the following form

$$\rho_{z}^{(EHF)}(\vec{R}) \equiv \left\langle \Psi_{0}^{(EHF)} \right| \sum_{i=1}^{N} 2\hat{S}_{z}(i) \,\delta(\vec{r}_{i} - \vec{R}) \left| \Psi_{0}^{(EHF)} \right\rangle / T00
= \frac{S}{S+1} T00^{-1} \sum_{i=1}^{m} \{ [|\varphi_{i\uparrow}(\vec{R})|^{2} - |\varphi_{i\downarrow}(\vec{R})|^{2}] T01(i)
+ [2|\varphi_{i\uparrow}(\vec{R})| - \lambda_{i} \varphi_{i\downarrow}^{*}(\vec{R}) \varphi_{i\uparrow}(\vec{R}) - \lambda_{i}^{*} \varphi_{i\uparrow}^{*}(\vec{R}) \varphi_{i\downarrow}(\vec{R})] T11(i) \}
+ \frac{S}{S+1} T00^{-1} \sum_{i=m+1}^{n} |\varphi_{i\uparrow}(\vec{R})|^{2} (2T10 + T00);$$
(251)

in the analogous spin density expressions [67, 124] there seems to be a mistake in the coefficients in the last term in (251).

Using (245) one can obtain from (251) for the case $N \to \infty$ $(n \approx m \to \infty)$

$$\rho_{z}^{(EHF)}(\vec{R}) = \frac{S}{S+1} \left[\sum_{i=1}^{n} |\varphi_{i\uparrow}(\vec{R})|^{2} - \sum_{i=1}^{m} |\varphi_{i\downarrow}(\vec{R})|^{2} \right] = \frac{S}{S+1} \rho_{z}^{(UHF)}(\vec{R}) \,.$$
(252)

For long polyene chain from (242) and (214) one obtains

$$x_{k} = \lambda_{k}^{2} = \cos^{2}k / (\cos^{2}k + d^{2}), \qquad (253)$$

where $d = \Delta \gamma / 2 |\beta|$. Using (247b) and (253) let us evaluate the values of t_1 and t_m for this case, namely:

$$t_{1} = \frac{1}{m} \sum_{k} x_{k} = \frac{2}{\pi} \int_{0}^{\pi/2} dk \cos^{2}k / (\cos^{2}k + d^{2}) \approx 0.77,$$

$$\ln t_{m} = \frac{1}{m} \sum_{k} \ln x_{k} = \frac{2}{\pi} \int_{0}^{\pi/2} dk \ln[\cos^{2}k / (\cos^{2}k + d^{2})], \qquad (254)$$

hence

$$t_m = [1 + 2d^2 + 2\sqrt{d(1+d)}]^{-1} \approx 0.55.$$
(255)

So far $t_1 \neq 0$ and $t_m \neq 0$, then the relation (250) in case of polyenes immediately follows from (255), (246), and (249). So, the orbitals $\varphi_{k\sigma}^{(i)}$ are selfconsistent ones in the framework of the EHF method as well as in the UHF method. The EHF spin density vanishes identically in long even polyenes (S = 0) and differs from zero in long polyene radicals (paragraph 4 above) according to Eq. (252).

Let us calculate the weight of the lowest multiplicity state with the normalized UHF wave function, namely

$$\omega_{S=M} = \frac{2S+1}{n+1} T00 \approx 2 \frac{2S+1}{N} \frac{1}{1-\tilde{x}},$$
(256)

where $t_1 \ge \tilde{x} \ge t_m$. It is interesting to note that using the Gaussian approximation supposed by van Leuven [157, 158] one can obtain

$$\omega_{S=0} = \int_{0}^{\infty} \exp\left[-\theta \frac{m(1-t_{1})}{4}\right] \sin\theta d\theta = \frac{2}{N} \frac{1}{1-t_{1}}.$$
 (257)

It follows from (257) that the Gaussian approximation gives the same value of ω_s as the approximation used for this purpose in [6]. Comparing (257) with the exact expression (256) one can see that the approximation (257) correctly reflects the asymptotic behaviour of ω_s when $N \rightarrow \infty$ (except for the constant). It should be noted that the relation (250) can be obtained also by means of the rotation group theory [157]. However, using this method we lose some important details, *e.g.* it is impossible to obtain the asymptotic form (252) for the spin density expression (251).

Next let us discuss the excited states of long polyene chains by means of the EHF method. Let us replace an orbital $\varphi_{k\sigma}^{(1)}$ by $\varphi_{k\sigma}^{(2)}$ in (239) and denote this "configuration" as $\Psi_{(k\sigma)}^{(EHF)}$. In general the function $\Psi_{(k\sigma)}^{(EHF)}$ is not orthogonal to $\Psi_{0}^{(EHF)}$:

$$\left\langle \Psi_{0}^{(EHF)} \middle| \Psi_{(k\sigma)}^{(EHF)} \right\rangle = -\tau_{\sigma} \lambda_{k} T 11(k) \sqrt{1 - \lambda_{k}^{2}} .$$
(258)

But, when $N \rightarrow \infty$ it follows from (245) that

$$\frac{\left\langle \Psi_{(k\sigma)}^{(EHF)} \middle| \Psi_{0}^{(EHF)} \right\rangle}{\left\langle \Psi_{0}^{(EHF)} \middle| \Psi_{0}^{(EHF)} \right\rangle} \approx \frac{\left\langle \Psi_{(k\sigma)}^{(EHF)} \middle| \Psi_{0}^{(EHF)} \right\rangle}{\left\langle \Psi_{(k\sigma)}^{(EHF)} \middle| \Psi_{(k\sigma)}^{(EHF)} \right\rangle} \approx \frac{1}{N} \Big|_{N \to \infty} \to 0.$$
(259)

So, the wave function $\Psi_{(k\sigma)}^{(EHF)}$ is asymptotically orthogonal to $\Psi_0^{(EHF)}$ and may be used for a description of the excited state the energy

$$E_{(k\sigma)}^{(EHF)} = \left\langle \Psi_{(k\sigma)}^{(EHF)} \middle| \hat{H} \middle| \Psi_{(k\sigma)}^{(EHF)} \right\rangle / T00 = E_{(k\sigma)}^{(UHF)} = E_0^{(UHF)} + 2\varepsilon_k^{(2)} .$$
(260)

To summarize, the ground state energy, energies of the lowest excitations and the the SCF equations for large systems ($N \square 1$) are the same in the framework of the UHF and the EHF methods. Thus, to calculate the electronic structure of the system, which consists of large number of electrons, by the EHF method one may use the simple single determinant UHF wave function rather than the much more complicated EHF wave function (239).

6.5 Some Conclusions

As already known the appearance of the forbidden gap of about 1 eV width in the optical spectra of long cumulene chains can be explained by means of the RHF method with the alternation of bond lengths being introduced. However, the torsion barrier of the end groups of long cumulene chain does not vanish in this model. This fact seems unnatural as far as the end-groups CH₂ of long cumulene chain C_NH_4 ($N \square 1$) are placed at the large distance from one another. On the other hand, the simple MO methods give $\Delta E \rightarrow 0(N \rightarrow \infty)$ for cumulenes with equal bond length. But in this case the first electronic transition frequency also tends to zero which contradicts the experiment.

To put it another way, the assumption that the energy gap in the spectra of long cumulene chains is due to the bond alternation gives rise to the dependence of the gap value to the torsion barrier. The gap value is shown to be equal to the torsion barrier in this model [159]. From the mathematical point of view this correlation between the gap value and the torsion barrier results from neglecting electron correlation. Indeed, if the long cumulene chain in the conformation $A_{\perp}(D_{2d})$ involving the odd number of π -electrons in each of the two subsystems *a* and *b* is treated by means of the Huckel or the RHF methods, then in the spectrum of such chain there are two levels in the ground state which correspond to the zero values of one-electron energies, whether the bond alternation is introduced or not.

It is shown in this paragraph that the appearance of the forbidden zone in spectra of long cumulene chains is not connected with the value of the torsion barrier in the framework of the EHF method in contrast to the simple models mentioned above. Furthermore, the EHF method gives zero value of the torsion barrier for long cumulenes with equal bond lengths. On the one hand, these results once more suggest the necessity for taking account of electron correlation when large conjugated systems are treated. On the other hand, we think that these results provide some further evidence for the correlation nature of the forbidden zone in spectra of long cumulene chains and, consequently, long polyene chains.

Chapter 7. Coexistence or Contradiction of the Peierls- and Mott-type Instabilities in Quasi-One-Dimensional Systems

7.1 Introduction

It has been first stated by Mott [160 - 168] that the one-dimensional array of atoms with a half-filled valence band should necessarily exhibit metal dielectric transition as a result of increasing the lattice constant. Modern developments of the Mott instability have been reviewed in [106, 168, 169]. In such Mott-type dielectrics the lowest quasi-ionic excitations are separated from the ground state by the energy gap of the order $\Delta \approx I - A(I \text{ and } A \text{ are being the})$ ionization potential and electron affinity correspondingly). The value of this important parameter should be $\sim 10 \ eV$ in the case of isolated small atoms, but some factors in real systems like polarizability of the given elementary unit (CH₂ group in polyenes, TCNQ fragment in charge transfer salts) or of the neighbouring elementary units [170] reduce this gap to $\Delta \approx 3-4eV$ for polyenes and up to $\Delta \approx 1 eV$ in TCNQ chains. Furthermore, electron exchange at the real interatomic distances should be taken into account which results in the broadening of previously highly degenerate ionic excited states to a conductance band of width $\Box 4 |\beta|$, where β being the resonance integral. In the case of $\Delta / |\beta| = 1$, this does not change the spectrum qualitatively and even at real distances one gets the Mott-type dielectric at zero temperature. In the opposite case $\Delta / |\beta| = 1$, the exchange broadening is larger than the energy gap which leads to the metal type structure of the excitation spectrum of the 3dcrystal. However, in the 1d-case such a structure is unstable with respect to nuclear displacements of a special kind and the Peierls transition to the usual semiconducting state takes place [17, 171 - 173]. As a result one gets an initially continuous band of allowed states split in two bands with a forbidden zone of the width $\Box | \beta_1 - \beta_2 |$, where β_1 and β_2 are exchange integrals of the neighbouring bonds; no magnetic structure has to be expected.

As it has been pointed out in [174], a close relationship exists between the so-called metal – insulator transition and the various instabilities of the conventional Hartree – Fock state which is associated with formation of the charge or spin density waves [175 – 186].

The following question naturally arises: what will happen if $|\beta|$ and Δ are of the same order of magnitude? Concerning some similar problems [187, 188] it has been supposed that the gap in the energy spectrum would arise from combined effects of two factors. Nevertheless, the opposite points of view have also been introduced [134, 189]. Let us mention here that the situation seems to be different for 1d- and 3d-systems; in the last case there is a strong evidence, both experimental and theoretical, in favour of coexistence of Peierls and Mott instabilities [169]. In this paragraph the 1d-problem will be treated with generalization to consider finite temperatures.

It should be mentioned that for both types of instabilities the gap should be temperature dependent and should be equal to zero if the temperature raises above some critical temperature T_c . This may be qualitatively understood as follows. In the case of the Peierls transition, the width of the gap is determined by two subtle effects: lowering of the total energy due to the lowering of filled energy levels and raising the energy due to lattice distortion. The energy minimum is reached at the definite distortion which determines the energy gap value. If the temperature is raised, some of the electrons pass to the band of excited states which results in two effects of the same sign: 1) the energy gain due to the energy levels lowering becomes smaller because not all those levels are now filled; 2) from the point of view of the excited electrons, decreasing the gap is preferable as it lowers their energy. Thus, the gap width Δ

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and the lattice distortion depend on the occupation *n* of the one-electron states, which in its turn depends on the temperature: $\Delta = \Delta(n(T))$.

Thus, at a higher temperature the gap becomes smaller, which makes it easier for the electrons to occupy excited states after the temperature rise and so on. It seems likely that the process is fast enough and at some T_c the gap vanishes. The quantitative treatment [172, 173] confirms this explanation.

The situation is formally similar in the case of Mott semiconductors. In this case the creation of ionic excitation makes it easier for the electron at the neighbouring atom to be excited also, *i.e.*, the energy gap depends on the electron distribution at the levels of the ground and excited states which, in turn, is temperature dependent.

The method used below is simple and straightforward: the 1d-chain with lattice displacement Δx of the kind of bond alternation will be considered using the SCF calculations allowing, in principle, to get the correlation gap. The total energy or the free energy in the case of T > 0 will be evaluated to investigate whether its minimum correspond to the nonzero values of both correlation gap and the lattice distortion or whether only one of them may differ from zero for the 1d-system.

7.2. Peierls and Mott Instabilities at $T = 0^{\circ} K$

We start with a Hamiltonian that differs from the Hubbard Hamiltonian in two points: the lattice distortion as the bond alternation is taken into account and the repulsion of electrons when accounted for the neighbouring atoms γ_{12} is included, namely:

$$\hat{H} = \alpha \sum_{n\sigma} \hat{A}^{+}_{n\sigma} \hat{A}_{n\sigma} + \sum_{n\sigma} [\beta - (-1)^{n} \Delta \beta] (\hat{A}^{+}_{n\sigma} \hat{A}_{n-1,\sigma} + \hat{A}^{+}_{n+1,\sigma} \hat{A}_{n\sigma}) + U \sum_{n} \hat{A}^{+}_{n\alpha} \hat{A}_{n\alpha} \hat{A}^{+}_{n\beta} \hat{A}_{n\beta} + \frac{\gamma_{12}}{2} \sum_{n\sigma\sigma'} \hat{A}^{+}_{n\sigma} \hat{A}_{n\sigma} (\hat{A}^{+}_{n+1,\sigma'} \hat{A}_{n+1,\sigma'} + \hat{A}^{+}_{n-1,\sigma'} \hat{A}_{n-1,\sigma'}),$$
(261)

where α is the Coulomb integral, *U* is the Hubbard parameter of the electron repulsion on the same atom, γ_{12} accounts for electron repulsion on the nearest-neighbouring atoms. The second term describes the Peierls doubling of the unit cell. The first term will be omitted in the following treatment bearing in mind that it results only in a trivial equal shift of all energy levels.

The translational invariance of the Hamilton (261) may be used to reduce it to a more nearly diagonal form. Let us introduce the operators $\hat{B}_{k\sigma}^+$ and $\hat{B}_{k\sigma}$ which create and annihilate, respectively, an electron in a state with quasi-momentum *k* and spin σ :

$$\hat{A}_{n\sigma}^{+} = \frac{1}{\sqrt{N}} \sum_{k} \hat{B}_{k\sigma}^{+} e^{-ink} \\
\hat{A}_{n\sigma} = \frac{1}{\sqrt{N}} \sum_{k} \hat{B}_{k\sigma} e^{ink} \\
, \quad k = \frac{n\pi}{N}, \quad n = \pm 1, \pm 2, \dots, \pm N.$$
(262)

The usual anticommutation relations for the operators $\hat{B}_{k\sigma}$ are obeyed

$$[\hat{B}_{k\sigma}^{+}, \hat{B}_{k'\sigma'}^{+}]_{+} = [\hat{B}_{k\sigma}, \hat{B}_{k'\sigma'}]_{+} = 0, \quad [\hat{B}_{k\sigma}^{+}, \hat{B}_{k'\sigma'}]_{+} = \delta_{kk'}\delta_{\sigma\sigma'}.$$
(263)

The inverse relations are

$$\hat{B}_{k\sigma}^{+} = \frac{1}{\sqrt{N}} \sum_{n} \hat{A}_{n\sigma}^{+} e^{ink},$$

$$\hat{B}_{k\sigma} = \frac{1}{\sqrt{N}} \sum_{n} \hat{A}_{n\sigma} e^{-ink}.$$
(264)

Transforming the Hamiltonian (262) to the new operators, one obtains

$$\hat{H} = 2\beta \sum_{k} \hat{B}_{k\sigma}^{+} \hat{B}_{k\sigma} \cos k + 2i \Delta \beta \sum_{k} \hat{B}_{k\sigma}^{+} \hat{B}_{k\sigma\sigma} \sin k + \frac{U}{N} \sum_{kk'q} \hat{B}_{k+q,\alpha}^{+} \hat{B}_{k\alpha} \hat{B}_{k'-q,\beta}^{+} \hat{B}_{k'\beta} + \frac{\gamma_{12}}{N} \sum_{k_{1}+k_{3}=k_{2}+k_{4}} \hat{B}_{k_{1}\sigma}^{+} \hat{B}_{k_{2}\sigma} \hat{B}_{k_{3}\sigma'}^{+} \hat{B}_{k_{4}\sigma} \cos(k_{1}-k_{2}),$$
(265)

The quadratic part of the Hamiltonian is diagonal only for the regular lattice ($\Delta\beta = 0$). In the alternating lattice ($\Delta\beta \neq 0$) there are *N*/2 equivalent pairs of sites rather than *N* equivalent sites. Thus, a linear combination of the

operators (264) is required to diagonalize the quadratic part of the Hamiltonian. The energy spectrum breaks up into two bands, separated by a forbidden zone $4\Delta\beta$ in width. We do not follow this procedure here because it is useless in treating the last two quartic interacting terms in (265).

To treat the full Hamiltonian, we have to simplify it in an appropriate way. We wish to obtain the self-consistent solution of our problem. Thus, we shall reolace some terms in the quartic part of the Hamiltonian by their average values. Bearing this in mind one can reduce (265) leaving only the terms we expect to have as nonzero average values in the ground state we are looking for and omitting all the terms with zero ground state average.

In the Hubbard term of (265) only two terms should be left:

(i) the q = 0 term, namely:

$$\frac{U}{N}\sum_{kk'}\hat{B}^{+}_{k\alpha}\hat{B}^{+}_{k\alpha}\hat{B}^{+}_{k'\beta}\hat{B}^{+}_{k'\beta}.$$
(266)

Assuming that in the ground state the average numbers of electrons with spin α and β are equal ($\langle n_{\alpha} \rangle = \langle n_{\beta} \rangle = N/2$), and remembering that

$$\sum_{k} \hat{B}^{+}_{k\alpha} \hat{B}_{k\alpha} = \sum_{n} \hat{A}^{+}_{n\alpha} \hat{A}_{n\alpha} = \hat{n}_{\alpha},$$

one may replace (266) by the C number UN/4; and

(ii) the $q = \pi$ term, namely:

$$\frac{U}{N}\sum_{kk'}\hat{B}^{+}_{k+\pi,\alpha}\hat{B}_{k\alpha}\hat{B}^{+}_{k'+\pi,\beta}\hat{B}_{k'\beta} \equiv UN\hat{\Delta}_{\alpha}\hat{\Delta}_{\beta}, \qquad (267)$$

where

$$\hat{\Delta}_{\alpha} = \frac{1}{N} \sum_{k} \hat{B}^{+}_{k+\pi,\alpha} \hat{B}^{-}_{k\alpha} , \qquad (268)$$

and analogous expression for $\hat{\Delta}_{\beta}$.

To understand the physical meaning of the operator $\hat{\Delta}_{\sigma}$, let us return to the site operators $\hat{A}_{n\sigma}$ and $\hat{A}_{n\sigma}^{+}$ following Eq. (264). Then one obtains

$$\hat{\Delta}_{\sigma} = \frac{1}{N} \sum_{n} (-1)^n \hat{A}_{n\sigma}^+ \hat{A}_{n\sigma} \,. \tag{269}$$

Equation (269) evidently shows that $\langle \hat{\Delta}_{\sigma} \rangle$ is proportional to the overall difference in the number of electrons with spin σ at the even and odd atoms of the chain and differs from zero only if spin alternation at the neighbouring sites of the chain take place. Retaining this term makes it possible to account for the correlation contribution to the energy gap or, in other words, to treat the Mott-type semiconductors, while, as it has been mentioned, the second term in (265) allows ua to consider the Peierls instability.

In the last term of (265) we preserve the following four terms: (i) $k_1 = k_2$, namely,

$$\frac{\gamma_{12}}{N} \sum_{k_1, k_3, \sigma, \sigma'} \hat{B}^+_{k_1 \sigma} \hat{B}^-_{k_1 \sigma} \hat{B}^+_{k_3 \sigma'} \hat{B}^-_{k_3 \sigma'}, \qquad (270)$$

which is merely a correction to the Hartree-type term discussed above, and in the ground state assumbed to be replacable by the C number $N\gamma_{12}$;

(ii) $k_1 = k_4, k_2 = k_3$, namely,

$$-\frac{\gamma_{12}}{N} \sum_{k_1,k_2,\sigma,\sigma'} \hat{B}^+_{k_1\sigma} \hat{B}^+_{k_2\sigma'} \hat{B}^+_{k_2\sigma'} \cos(k_1 - k_2), \qquad (271)$$

which is the usual exchange term;

(iii) $k_1 = k_2 + \pi$, namely,

$$-\frac{\gamma_{12}}{N}\sum_{k_1,k_3,\sigma,\sigma'}\hat{B}^+_{k_1\sigma}\hat{B}^+_{k_3\sigma'}\hat{B}^+_{k_3\sigma'}\hat{B}^+_{k_3\sigma'}\hat{B}^+_{k_3+\pi,\sigma'},$$
(272)

which is a Coulomb-type term connecting the states with impulses k and $k + \pi$ (these states are already connected in the second term in Eqs (265) and (267), thus we continue to keep the terms of this kind); and finally

(iv) $k_1 = k_4 + \pi$, namely,

$$-\frac{\gamma_{12}}{N}\sum_{k_1,k_3,\sigma,\sigma'}\hat{B}^+_{k_1+\pi,\sigma}\hat{B}^-_{k_1,\sigma'}\hat{B}^+_{k_2+\pi,\sigma'}\hat{B}^-_{k_2,\sigma}\cos(k_1-k_2),$$
(273)

which is an exchange-type term, connecting the k and $k + \pi$ states. Writing $\cos(k_1 - k_2)$ as

 $\sin k_1 \sin k_2 + \cos k_1 \cos k_2$, and reffering to subsequent integration, one can reach further simplification of the Hamiltonian due to the fact that the ground-state everage of some terms appearing vanish, thus,

$$\left\langle \hat{B}_{k\sigma}^{+}\hat{B}_{k\sigma'}\right\rangle \approx \delta_{\sigma\sigma'}, \quad \left\langle \hat{B}_{k\sigma}^{+}\hat{B}_{k\sigma}\sin k\right\rangle = 0, \quad \left\langle \hat{B}_{k\sigma}^{+}\hat{B}_{k+\pi,\sigma}\cos k\right\rangle = 0.$$

Introducing two new operators

$$\hat{\xi}_{\sigma} = \frac{1}{N} \sum_{k} \hat{B}_{k\sigma}^{+} \hat{B}_{k+\pi,\sigma} \sin k,$$

$$\hat{\eta}_{\sigma} = \frac{1}{N} \sum_{k} \hat{B}_{k\sigma}^{+} \hat{B}_{k\sigma} \cos k,$$
(274)

one ia able to rewrite the reduced Hamiltonian in the form

$$\hat{H} = 2\beta \sum_{\sigma} \hat{\eta}_{\sigma} + 2\Delta\beta \sum_{\sigma} \hat{\xi}_{\sigma} + \frac{U - 2\gamma_{12}}{2} \sum_{\sigma} \hat{\Delta}_{\sigma} \hat{\Delta}_{-\sigma} - \gamma_{12} \sum_{\sigma} (\hat{\eta}_{\sigma}^2 + \hat{\Delta}_{\sigma}^2 + \hat{\xi}_{\sigma}^2) \,. \tag{275}$$

This reduced Hamiltonian is formally very similar to the reduced Hamiltonian solved in the Bardeen – Cooper – Schrieffer (BCS) theory of superconductivity. As has been proved by Bogolyubov [120, 121], its SCF solution for a large system $(N \rightarrow \infty)$ asymptotically coinsides with the exact one. Thus, what we have to do now is to solve the wave equation with Hamiltonian

(275) using the SCF method. It seems to be convenient in our case to write the wave equation in the form of equation of motion.

Let us use the standard Bogolyubov transformation

$$\hat{b}_{k\sigma} = U_{k\sigma}\hat{B}_{k\sigma} + V_{k\sigma}\hat{B}_{k+\pi,\sigma}$$
(276)

to define the new operators $\hat{b}^{+}_{k\sigma}$, $\hat{b}^{-}_{k\sigma}$, satisfying the equation of motion

$$[\hat{b}_{k\sigma},\hat{H}] = \lambda_{k\sigma}\hat{b}_{k\sigma}.$$
(277)

If the coefficients $U_{k\sigma}$, $V_{k\sigma}$ in (276) are found to satisfy Eq. (277), then the transformation (277) diaginalize Hamiltonian (275).

Requiring the new operators (276) to be of the Fermi-type

$$[\hat{b}_{k\sigma}^{+}, \hat{b}_{k'\sigma'}]_{+} = \delta_{kk'} \,\delta_{\sigma\sigma'}, \qquad (278)$$

one obtains the following relation for $U_{k\sigma}$, $V_{k\sigma}$:

$$|U_{k\sigma}|^2 + |V_{k\sigma}|^2 = 1.$$
(279)

Substituting Eqs (276) and (275) into (277), and performing the calculations required using (278), one obtains the system of two nonlinear equations with respect to $U_{k\sigma}$, $V_{k\sigma}$. Linearizing these equations, which corresponds to the SCF procedure, and using (279), one obtains the solution in the form

$$\lambda_{k\sigma} = \pm (4\tilde{\beta}^2 \cos^2 k + 4\Delta\tilde{\beta}^2 \sin^2 k + U^2 \left\langle \Delta_{-\sigma} \right\rangle^2)^{1/2}, \qquad (280)$$

$$|U_{k\sigma}|^{2} = \frac{1}{2} \pm \frac{\hat{\beta} \cos k}{(4\tilde{\beta}^{2}\cos^{2}k + 4\Delta\tilde{\beta}^{2}\sin^{2}k + U^{2}\langle\Delta_{-\sigma}\rangle^{2})^{1/2}},$$

$$|V_{k\sigma}|^{2} = \frac{1}{2} \pm \frac{\tilde{\beta} \cos k}{(4\tilde{\beta}^{2}\cos^{2}k + 4\Delta\tilde{\beta}^{2}\sin^{2}k + U^{2}\langle\Delta_{-\sigma}\rangle^{2})^{1/2}},$$
(281)

where

$$-\frac{\pi}{2} < k < \frac{\pi}{2}, \quad \tilde{\beta} = \beta - \gamma_{12} \left\langle \hat{\eta}_{\sigma} \right\rangle, \quad \Delta \tilde{\beta} = \Delta \beta - \gamma_{12} \left\langle \xi_{\sigma} \right\rangle.$$
(282)

To make the solution complete, we have to calculate $\langle \Delta_{\sigma} \rangle$, $\langle \hat{\eta}_{\sigma} \rangle$, and $\langle \xi_{\sigma} \rangle$, where the everaging is implied over the just found ground state, corresponding to all states $\lambda_{k\sigma}$ occupied with the minus sign in Eq. (280), *i.e.* the ground state has the form

$$\psi_{0} = \prod_{i=1}^{N} {}^{(-)} \hat{b}_{k_{i}}^{+} |0\rangle, \qquad (283)$$

where the operators ${}^{(-)}\hat{b}_k^+$ are defined by Eqs (276) and (281) with the lower sign in (281).

To perform the required calculations, one should express $\hat{B}_{k\sigma}$ and $\hat{B}_{k+\pi,\sigma}$ in terms of the operators ${}^{(-)}\hat{b}_{k}^{+}$ and ${}^{(+)}\hat{b}_{k}^{+}$; and after substituting them into (274) to average Δ_{σ} , $\hat{\eta}_{\sigma}$, and ξ_{σ} over the ground state (283). Taking into account that only terms like ${}^{(-)}\hat{b}_{k}$ and ${}^{(+)}\hat{b}_{k}^{+}$ contribute to the ground state average values, one obtains the following system of coupled integral equations with respect to $\langle \Delta_{\sigma} \rangle$, $\langle \hat{\eta}_{\sigma} \rangle$, and $\langle \xi_{\sigma} \rangle$:

$$\frac{U}{\pi} \int_{0}^{\pi/2} \frac{dk}{\sqrt{\tilde{\varepsilon}^{2}(k) + U^{2} \langle \Delta_{\sigma} \rangle^{2}}} = 1,$$

$$\tilde{\beta} = \beta \left(1 - \frac{2\gamma_{12}}{\pi} \int_{0}^{\pi/2} \frac{\cos^{2} k \, dk}{\sqrt{\tilde{\varepsilon}^{2}(k) + U^{2} \langle \Delta_{\sigma} \rangle^{2}}} \right)^{-1}, \quad (284)$$

$$\Delta \tilde{\beta} = \Delta \beta \left(1 + \frac{2\gamma_{12}}{\pi} \int_{0}^{\pi/2} \frac{\sin^{2} k \, dk}{\sqrt{\tilde{\varepsilon}^{2}(k) + U^{2} \langle \Delta_{\sigma} \rangle^{2}}} \right)^{-1},$$

where

$$\tilde{\varepsilon}^2(k) = 4(\tilde{\beta}^2 \cos^2 k + \Delta \tilde{\beta}^2 \sin^2 k).$$

This system of equations may be solved iteratively, but in the usually assumed case of $\gamma_{12} \Box \beta, U$ it breaks into

$$\Delta \tilde{\beta} \approx \Delta \beta, \quad \tilde{\beta} \approx \beta,$$

and

$$\frac{U}{\pi} \int_{0}^{\pi/2} \frac{dk}{\sqrt{\varepsilon^2(k) + U^2 \left\langle \Delta_\sigma \right\rangle^2}} = 1,$$
(285)

where

$$\varepsilon^{2}(k) = \beta_{1}^{2} + \beta_{2}^{2} + 2\beta_{1}\beta_{2}\cos 2k,$$

$$\beta_{1} = \beta + \frac{1}{2}\Delta\beta, \quad \beta_{2} = \beta - \frac{1}{2}\Delta\beta,$$

the last equation being the gap equation that, in the case of the regular chain structure (no bond alternation), transforms to equation for the correlation gap [17, 111]

$$\frac{U}{\pi} \int_{0}^{\pi/2} \frac{dk}{\sqrt{4\beta^2 \cos^2 k + U^2 \left\langle \Delta_{\sigma} \right\rangle^2}} = 1.$$
(286)

As has been stated in [187], Eq. (286) has a nonzero solution $\langle \Delta_{\sigma} \rangle \neq 0$ for all values of the parameters, which we will denote as Δ_0 .

Let us now return to the general case of Eq. (285), assuming that

$$\beta(\delta x) = \beta_0 e^{-\alpha \delta x},$$

where δx denotes displacement from the regular, equal-bond configuration. Thus, Eq. (285) may be rewritten as

$$\frac{U}{\pi} \int_{0}^{\pi/2} \frac{dk}{\sqrt{(\beta_1 - \beta_2)^2 + 4\beta_0^2 \cos^2 k + U^2 \langle \Delta_\sigma \rangle^2}} = 1.$$
(287)

Comparing (287) with (286) one easily concludes that if Δ_0 is the solution of (286) then the solution of (287) is given by

$$2U^{2}\left\langle \Delta_{\sigma}\right\rangle ^{2}+\left(\beta_{1}-\beta_{2}\right)^{2}=U^{2}\left\langle \Delta_{\sigma}\right\rangle _{0}^{2},$$

so that

$$\left\langle \Delta_{\sigma} \right\rangle^{2} = \left\langle \Delta_{\sigma} \right\rangle_{0}^{2} - \frac{1}{2} \left(\frac{\beta_{1} - \beta_{2}}{U} \right)^{2}.$$
 (288)

We are now in a position to turn to the final step of the treatment, namely, calculation of the total energy and minimization of it with respect to δx .

Substituting Eqs (275) and (280) - (283) into the usual expression for the total electronic energy in the ground state

$$\overline{E}_{el} = \langle \psi_0 | \hat{H} | \psi_0 \rangle,$$

one obtains

$$\overline{E}_{el} = \frac{U}{4} + \sum_{k} \lambda_{k} + U\Delta^{2}.$$
(289)

It is important to recognize that according to (280) and (288)

$$\lambda_k (\beta_1 - \beta_2)^2 / U$$

is independent on δx because the only term containing this dependence cancels in the expression for λ_k . Thus, assuming δx to be small, which results in $\beta_1 - \beta_2 \approx \delta x$, one can rewrite (289) in the form

$$\bar{E}_{el} = E_0 - E_1 (\delta x)^2.$$
(290)

Adding the core deformation energy

$$E_{core} = \frac{1}{2}\kappa(\delta x)^2,$$

one obtains the total energy of the chain in the form

$$E = E_0 + \alpha(\delta x)^2. \tag{291}$$

This expression, when minimized with respect to δx , gives us a solution $\delta x = 0$ only in the case

$$\alpha = E_1 - \frac{1}{2}\kappa > 0 ,$$

which obviously corresponds to a vanishing bond correlation and to the energy gap (286) of the pure "correlation" type.

In the opposite case of $\alpha < 0$, the total energy does not exibit a minimum at all, decreasing formally to $-\infty$ when δx increases. Nevertheless, taking into account (288), one can see that for some δx and corresponding $\beta_1 - \beta_2$, value of $\langle \Delta^2 \rangle$ becomes negative, which evidently means that our solution fails completely. Here we should remember that apart from the solution described by Eqs. (284) and (286), which is the non-trivial solution of the UHF SCF equations, we always have the trivial solution $\Delta = 0$, corresponding to the usual HF SCF procedure. We have used the non-trivial solution in the case of the regular chain structure (no alternation) because in this case it corresponds to a lower energy than the trivial solution [174]. However, for $\alpha < 0$ this non-trivial solution does not minimize the total energy, and for some δx in the process of its increasing we get $\Delta = 0$; at this point we should jump to the trivial solution because the non-trivial one ceases to exist. Hence, in this case we have an alternating-bond chain with a vanishing $(\Delta = 0)$ contribution of the Mott-type correlation to the creation of the energy gap; while the gap due to the bond alternation should be calculated in a quite different way [171 - 173]. The results is well known: in the absence of the Mott-type contribution, the Peierls-type transition to a semiconducting state necessarily takes place, and the gap obtained can be approximately calculated as

$$\Delta_{alt} = 8\beta_0 e^{-\kappa/2\beta} \,. \tag{292}$$

Therefore, at least at zero temperature the picture is clear: depending on the numerical values of the parameters involved the quasi-one-dimensional chain represents either a Mott-type or a Peierls-type semiconductor, but not their combination, and the choice should be done by comparison of the total energies of both states. Roughly speaking, it may be stated that the real state is the state with the larger gap calculated neglecting the possibility of the other state available. In fact, in addition to the criterion $U > |\beta|$ mentioned above for the Mott metal – dielectric transition, one more criterion should be formulated determining the value of the gap arised due to Peierls instability. However, it is evident that if we have $U \square |\beta|$, then the correlation gap is large, *ca. U*, very likely larger than the gap due to the lattice distortion, and the situation is reversed for $U < |\beta|$.

7.3 Finite Temperatures

Let us now consider the same question of the possible combined nature of the energy gap in the case of a finite temperature. Only the general method of calculations and the final results will be presented below. For details of calculations see [172].

To get the temperature dependence of all the values we are interested in the following procedure may be proposed: in all equations used the average over the ground state should be replaced by statistical average calculated as

$$\overline{\hat{A}} = Sp\hat{A}e^{-\hat{H}/kT} / Sp e^{-\hat{H}/kT}.$$
(293)

Bearing in mind that the Hamiltonian expressed in terms of the operators \hat{b}_k^+, \hat{b}_k at (276) – (282) is diagonal, standard equation (293) is reduced to

$$\overline{\hat{A}} = \sum_{k,l} \eta_{kl,\sigma}(T) \langle kl\sigma | \hat{A} | kl\sigma \rangle, \qquad (294)$$

where η_{kl} is the average number of particles in the state (k,l) with k stands for the quasi-impulse and l – for the zone number. During all transformations the Fermi character of quasi-particles has been required (see Eq. 278), hence

$$\eta_{kl,\sigma}(T) = \{ \exp[\varepsilon_{kl,\sigma} / kT] + 1 \}^{-1}, \quad \varepsilon_{kl,\sigma} \equiv \lambda_{k\sigma}.$$
(295)

For the temperature dependent energy gap playing a central role in all the treatment using Eqs (278) and (294) one obtains

$$\left\langle \Delta_{\sigma} \right\rangle = \frac{1}{N} \sum_{kl} \eta_{kl} \left\langle \hat{B}^{+}_{k+\pi,\sigma} \hat{B}_{k\sigma} \right\rangle.$$
(296)

Substituting Eqs (295) and (276) – (280) into (296) and performing the calculations required which are very similar to those leading to (285) one obtains the following equation determining

 $\Delta_{\sigma}(T)$, namely:

$$\frac{U}{2\pi} \int_{0}^{\pi} \frac{\operatorname{th} E(k)/2kT}{E(k)} dk = 1, \qquad (297)$$

where

$$E(k) = [(U\Delta)^2 + \varepsilon^2(k)]^{1/2}, \quad \varepsilon^2(k) = (\beta_1 - \beta_2)^2 + 4\beta_0^2 \cos^2 k .$$
 (298)

Introducing the density of states, one can transform (297) into the form

$$\frac{U}{\pi} \int_{\Delta}^{\sqrt{\varepsilon^2 + \Delta^2}} \frac{\operatorname{th} \varepsilon / 2kT}{\sqrt{\varepsilon^2 + \Delta^2} \sqrt{\varepsilon_F^2 + \Delta^2 - \varepsilon^2}} d\varepsilon = 1, \qquad (299)$$

where the same assumption $\beta(\delta x) \approx \beta_0 e^{-\delta x}$ and notation $\varepsilon_F = |\beta_0|$ have been used, but now

$$\Delta^2 = |\beta_1 - \beta_2|^2 + \langle \Delta_\sigma \rangle^2.$$
(300)

Equation (299) may be considered in the same way as it has been done concerning Eq. (287). The one-electron energy levels which are now temperature dependent are also independent on δx and all the discussion following Eq. (291) may be repeated leading to the same conclusions at the finite temperature as were arrived at in the case of zero temperatute.

Let us now note that if our system is a Mott-type semiconductor with $(\beta_1 - \beta_2) = 0$ and $\langle \Delta_{\sigma} \rangle \neq 0$, then Eq. (299) becomes similar to the Peierls gap in the chain with bond alternation, namely, both of them are BCS-type gaps in superconductors. Unfortunately this does not provide us much information on the nature of metal – Mott semiconductor phase transition because low-lying triplet and singlet excitations should be taken into account before one treats the quasi-ionic states with higher energies; but only these later states may be considered using the standard UHF procedure.

Chapter 8. Coexistence of Mott and Peierls Instabilities in Quasi-One-Dimensional Systems

8.1 Introduction

The quasi-one-dimensional conductors have so far being studied are of interest for both theoreticiants and experimentators. This interest, on the one hand, is due to advances in synthesis of polyacetylene (PA), polydiacetylene (PDA), organic crystalline conductors based on molecular donors and acceptors of electrons. On the other hand, 1d-conductors are nontrivial systems. Thus, 1dmetal is unstable to the transition into semiconducting state. As a result the 1dmetal with half-filled conduction band becomes the Mott semiconductor or Peierls semiconductor. The Peierls transition leads to dimerization of the uniform regular 1d lattice (bond alternation) and semiconducting energy gap is proportional to the dimerization amplitude. The Mott transition is a result of electron correlation and energy gap in the Mott semiconductor vanishes with decreasing electron – electron interaction strength. The semiconductor of the Mott and Peierls type possesses some interesting properties. For example, the Mott semiconductors are characterized by antiferromagnetic structures [190], and in the Peierls semiconductors the kink-type excitations are possible [191, 192].

The influence of the Mott and Peierls instabilities on the properties of real quasi-one-dimensional systems have already long story. The main problem in theoretical studies consists in complications related to correct account of electron correlation effects. In ealier papers contradiction of the Mott and Peierls transitions was usually stated. Then it was shown that this contradiction is a result of one-electron approach in the RHF theory. The conclusion that the Mott and Peierls transitions coexist one with another was first made in [193]. This result was obtained due to more correct treatment of pair electron correlations using varying localized geminals (VLG) approach [194 – 196]. It was shown that electron – electron interaction can enhance the Peierls dimerization [193]. This somewhat surprising result initiates several theoretical studies [197 – 202] which conformed the conclusion that even account for a small electron – electron interaction leads to increase in dimerization. This conclusion has been received on the basis of perturbation theory for infinite chains using computations [200] and the Feynman diagram technique [201]. Numerical

calculations of short polyene chains within the same geminals approach conformed this result slightly deformed by boundary conditions [193].

Thus, we can state now that the theory predicts coexistence of the Mott and Peierls instabilities in real systems. So, the experimental data on 1d-systems should not correspond to the simple picture of the Peierls or the Mott semiconductors. One must expore the more complicated theoretical model including the both phenomena. On this way only one can give correct description of real 1d materials. For example, we can now give the correct answer to the question what mechanism of the forbidden gap formation is more essential – the electron correlation or dimerization.

In this paragraph we shall study now the simultaneous effect of the Mott and Peierls instabilities on electronic spectra and lattice distortion in real 1d conductors such as organic donor – acceptor molecular crystals and conjugated polymers of PA type. These studies are based on the VLG approach [193 – 196].

8.2 The Method of Calculations and Qualitative Evaluations

Studying the electronic properties of organic 1d materials the following model of uniform chain with the adiabatic Hamiltonian is used:

$$\hat{H} = \sum_{\sigma,m=1}^{N} \beta_m (\hat{c}_{m\sigma}^+ \hat{c}_{m+1,\sigma} + \hat{c}_{m+1,\sigma}^+ \hat{c}_{m\sigma}) + \gamma \sum_m \hat{c}_{m\uparrow}^+ \hat{c}_{m\uparrow} \hat{c}_{m\downarrow}^+ \hat{c}_{m\downarrow} + \gamma_1 \sum_m n_m n_{m+1} + \frac{K_{\sigma}}{2} \sum_m (x_m - x_{m+1})^2 , (301)$$

where $n_{m\sigma} = \hat{c}_{m\sigma}^{\dagger} \hat{c}_{m\sigma}$, number of sites $N \rightarrow \infty$, x_m is the *m*th site displacement, resonance integrals

$$\beta_m = -[\beta + (x_{m+1} - x_m)\beta'] = -\beta(1 + \Delta_m), \quad \beta, \beta' > 0, \quad (302)$$

 γ and γ' are the electron repulsion parameters, K_{σ} is the lattice elasticity constant.

Treatment below will be restricted by the most interesting case of halffilled conduction band with the number of electrons $N_e = N$. The Peierls deformation in this case reduces to the chain dimerization

$$x_{m+1} - x_m = (-1)^m x_0, \quad \beta_m = -\beta [1 + (-1)^m \Delta].$$
(303)

The experimental values of displacements x_0 are small as compared to the lattice constant *a*. For example, in PA $x_0 = 0.07A$ and a = 1.395 A [190, 203], for [K⁺-TCNQ] complexes $x_0 = 0.18A$ and a = 3.6 A [204]. For small values of x_0 the linear dependence

$$\Delta = \frac{\beta'}{\beta} x_0 \tag{304}$$

is valid. The increase of displacement $x_0 \rightarrow a$ destroys the relation (304) as well as the harmonic adiabatic approach used in (301). Thus, the method used here is valid only for small values of $\Delta \Box$ 1. In this region Hamiltonian (301) is the Frohlich-type Hamiltonian with linear relative to displacements x_m electron – phonon interaction.

Thus, when $\Delta \Box$ 1 the adiabatic approach is good enough and the problem of 1d instabilities is reduced to studying the ground state energy dependence on the value of Δ (304). In other words, we need the Δ -value optimizing the expression

$$\varepsilon_t(\Delta) = \varepsilon_{el}(\Delta) + \frac{1}{2} \frac{\Delta^2}{\kappa}, \qquad (305)$$

where ε_{el} is the electronic contribution into the ground state energy per an electron pair, and

$$\kappa = (\beta')^2 / (2K_{\sigma}\beta). \tag{306}$$

is the constant of electron – phonon interaction.

In order to calculate the electronic contribution into the ground state energy mentioned above the VLG approach will be used. The ground state wave function has the form

$$\Psi_{0} = \prod_{m=1}^{M} \hat{G}_{m}^{+} |0\rangle \equiv \prod_{m=1}^{M} (u \hat{f}_{m\uparrow}^{+} \hat{f}_{m\downarrow}^{+} + v \tilde{f}_{m\uparrow}^{+} \tilde{f}_{m\downarrow}^{+}) |0\rangle, \qquad (307)$$

where

$$\hat{f}_{m\sigma} = \sqrt{\frac{2}{N}} \sum_{|k| < K_F} \hat{A}_{k\sigma} e^{-ikR_m}, \quad \hat{\tilde{f}}_{m\sigma} = \sqrt{\frac{2}{N}} \sum_{|k| < K_F} \hat{\tilde{A}}_{k\sigma} e^{-ikR_m}, \quad (308)$$

$$\hat{A}_{k\sigma} = a_{k\sigma} \cos \theta_k + a_{\bar{k}\sigma} i \sin \theta_k,$$

$$\hat{z} \qquad (309)$$

$$A_{k\sigma} = a_{\bar{k}\sigma} \cos \theta_k + a_{k\sigma} i \sin \theta_k,$$

$$a_{k\sigma} = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} c_{n\sigma} e^{-ikna},$$
 (310)

$$u = \cos \varphi, \quad v = \sin \varphi, \tag{311}$$

$$2\theta_k = \arctan(\lambda tgka), \quad k = 2\pi l / Na, \quad (l = 0, \pm 1, \pm 2, ...)$$
 (312)

 φ and λ are the variational parameters, the Fermi operators $\hat{f}_{m\sigma}$ and $\hat{f}_{m\sigma}$ correspond to the orbitals $f_{m\sigma}$ and $\tilde{f}_{m\sigma}$ which are partially localized near points

$$R_m = (2m + \delta)a. \tag{313}$$

The ground state energy in units of β per electron pair has the form

$$\varepsilon_{el} = 2t\cos 2\varphi - k_0 \sin 2\varphi - v_1 (\frac{2}{N} \sum_{l} |P_l|^2) \cos^2 2\varphi, \qquad (314)$$

where the kinetic energy average

$$t = \sum_{m} [1 + (-1)^{m} \Delta] f_{m}(n) f_{m}(n+1) = \langle 0 | \hat{f}_{m\sigma} \hat{T} f_{m\sigma}^{+} | 0 \rangle, \qquad (315)$$

$$\hat{T} = \sum_{m} (\hat{c}_{m\sigma}^{+} \hat{c}_{m+1,\sigma}^{+} + \hat{c}_{m+1,\sigma}^{+} \hat{c}_{m\sigma}^{-}), \qquad (316)$$

the exchange integral

$$K = \langle 0 | \hat{f}_{m\uparrow} \hat{f}_{m\downarrow} \hat{V}_{ee} f_{m\uparrow}^{+} f_{m\downarrow}^{+} | 0 \rangle = U \sum_{n} |f_{0}(n)|^{4} - U_{1} \sum_{n} |f_{0}(n)|^{2} \cdot |f_{0}(n+1)|^{2}, \quad (317)$$
$$U = \gamma / \beta, \quad U_{1} = \gamma_{1} / \beta,$$

average of non-diagonal density or bond order

$$P_{l} = \left\langle \Psi_{0} \left| \hat{c}_{l\sigma}^{\dagger} \hat{c}_{l+1,\sigma} + \hat{c}_{l+1,\sigma}^{\dagger} \hat{c}_{l\sigma} \right| \Psi_{0} \right\rangle = \sum_{m} f_{m}^{*}(l) f_{m}(l+1) = \left[\frac{1}{\pi} + (-1)^{l} \frac{\lambda}{4\pi} \ln \lambda \right] \cos 2\varphi \,. \quad (318)$$

Now we consider the Hubbard approach $\gamma_1 = 0$ in (301). Then, variation of the energy (314) with respect to φ gives

$$\varepsilon_{el} = -\varepsilon_g + U/2, \tag{319}$$

where

$$\varepsilon_g = \sqrt{4t^2 + K^2}.$$
(320)

The values of t, K, P depend on the value of λ [193, 200], so

$$t(\lambda) = -\frac{4}{\pi} \left[E(1-x^2) + (4-\lambda) \frac{\partial E(1-\lambda^2)}{\partial \lambda} \right],$$
(321)

where the E(x) is the elliptic integral.

The explicit form of λ -dependence of *K*

$$K(\lambda) = \frac{U}{3} - \operatorname{Const} \cdot \lambda \cdot \ln \lambda.$$
 (322)

can be obtained in the limit of small λ . We can see from (322) that when λ and, as a result, U are small the energy dependence (320) on λ is nonanalytic. Thus, we can suppose strong dependence of U on Δ_0 which minimizes the total energy. Results of numerical study of U on λ will be given below. Now the evaluation of asymptotic behaviour in two limiting cases $U \rightarrow 0$ and $U \rightarrow \infty$ will be given.

When $U \rightarrow 0$ the non-interacting-electron model is valid and the energy is defined by the value of (321) and its optimization with respect to λ gives $\lambda = \Delta$. The energy minimum corresponds to

$$\Delta_0 = 4 \exp(-\pi / 8\kappa) |_{U \to 0}$$
(323)

due to the fact that [193]

$$\varepsilon_{t} = 2\left(-\frac{4}{\pi} - \frac{2\Delta^{2}}{\pi}\ln\frac{4}{\Delta}\right) + \frac{\Delta^{2}}{2\kappa}.$$
(324)

When $U \ge 4$ one can use the simpler approach instead of (312), namely:

$$\theta_k = \tilde{\lambda} k. \tag{325}$$

Using (325) one obtains [194, 195]

$$\tilde{t}(\lambda) = -\frac{4}{\pi} \frac{\cos \pi \,\tilde{\lambda}}{1 - 4 \,\tilde{\lambda}^2},\tag{321'}$$

$$\tilde{K}(\lambda) = \frac{U}{3} \left(1 + \frac{1}{2} \sin \pi \, \lambda \right). \tag{322'}$$

Substituting (321') and (322') in (319) and (305) and optimizing Δ one obtains

$$\Delta_0 = \frac{8\kappa}{U} \left(1 - \frac{4}{U^2} \right). \tag{326}$$

We note that Eqs (321'), (322'), and (319) describe well the dependence of the total energy on U for any value of U > 0 [194, 195]. But, the correct description of the Peierls instability near the point U = 0 needs more precise relations due to the fact that the Peierls instability results from a logarithmic term. The latter just lost when passing from (312) to (325) [193].

Now we consider the effect of electron – electron interaction at neighboring sites resulting from the terms with γ_1 in (301). One can conclude from (314) and (318) that γ_1 -term increases the amplitude of dimerization. In the limiting case of weak interactions $U_1 < U \rightarrow 0$ one obtains

$$\Delta_0(U_1) = \Delta_0 |_{U_1=0} \times \exp(\frac{\pi U_1}{24\kappa^2}) = 4\exp(-\frac{\pi}{8\kappa}) \cdot \exp(\frac{\pi U_1}{24\kappa^2})$$
(327)

Thus, we can see an exponential increase of Δ_0 with $U_1 > 0$.

In order to define the optimal value of Δ_0 we have to look for the minimum of the energy (305) taking into account (319) in the space of Δ_0 and λ variables, namely:

$$E(\lambda, \Delta, U) = -[4t^{2}(\lambda, \Delta) + K^{2}(\lambda, U)]^{1/2} + \frac{\Delta^{2}}{2\kappa}, \qquad (328)$$

where *t* and *K* are defined by (315) and (317), respectively. This task is not too complicated, but when $U \square 1$ some difficulties arise with the increase of the chain length due to the logarithmic Δ -dependence of the electronic energies in (319) and (324). As a result we cannot use the standard method of quantum-chemical optimization of the bond lengths. This method is based on the linear

relations between bond length and bond order resulting from the energy expansion

$$\varepsilon(\Delta) = \varepsilon_0 + \varepsilon' \cdot \Delta + \frac{1}{2} \varepsilon'' \cdot \Delta^2,$$

where

$$\varepsilon' \approx \frac{\beta'}{N} \sum_{l} P_l(x_l - x_{l-1}), \quad \varepsilon'' \approx K_{\sigma}$$

and, as a result,

$$\Delta_0 = \frac{\beta'}{N} \frac{P_l}{K_{\sigma}}.$$
(329)

Some calculations of PA chains based on formula (329) were performed. It was found that even for comparatively long chains with N = 70 the difference Δ between t_N and t_{∞} is just a few units of 10⁻⁴. The Peierls contribution into the ground state energy $\Delta^2 \ln \Delta$ when $\Delta \leq 0.01$ is of the same order.

Let us consider now the contribution of dimerization and correlation effects in optical spectra of such organic materials like PA and PDA. For these conjugated polymers one can use the following parameter values:

$$\beta = 2.4 \, eV, \beta' = 4 \, eV/A, K_{\sigma} = 47 \, eV/A^2 \, [205].$$

These values are consistent with the parameters available for small conjugated molecules [106, 205] and with frequencies of vibrations active in IR and Raman spectra of PA [205]. Using these values of parameters one obtains from (306) that $\kappa = 0.07$. It means that we are in the region of strong dependence of U on Δ_0 .

Now let us calculate the dielectric gap ΔE . According to [196] one can write

$$\Delta E = 2[\varepsilon_g - t_0(1 + U^2) + T_k U^2], \qquad (330)$$

where

$$T_{k} = \sum_{m} e^{ikm} \left\langle f_{n} \left| \tilde{T} \right| f_{n+m} \right\rangle.$$

The gap value (330) consists of two contributions: correlation contribution ΔE_{corr} and dimerization contribution ΔE_{dim} . When U is small one can assume

$$\Delta E_{corr} = 2\varepsilon_g - 2t_0, \quad \Delta E_{dim} = 4\beta \Delta_0,$$

where ε_{g} is determined by (320) and t_{0} – by (321').

The dependence of correlation ΔE_{corr} and dimerization contributions ΔE_{dim} on the value of *U* is shown on fig. 5.



Figure 5. The *U*-dependence of the energy gap in electronic spectra of the Mott – Peierls semiconductors like PA or PDA: $\blacksquare - \Delta E_{dim}$, $\bigcirc -\Delta E_{corr}$, $\bullet - \Delta E$.

It follows from fig. 5 that the dimerization contribution ΔE_{dim} to the forbidden zone ΔE exceeds the correlation contribution ΔE_{corr} when U < 2-3. This fact is due to the strong dependence (326) of Δ_0 on U. Using data of Fig. 7 one can now reevaluate the parameters of real organic conductors.

We can conclude from experimental data for trans-PA that $\Delta E = 1.9 \ eV$ [205]. Using the estimation of the electron – phonon interaction constant $\kappa = 0.07$ above one obtains U = 2.5, thus $\kappa = 6.2 \ eV$. It is interesting to note that in this region according to fig. A

 $\gamma = 6.2 \, eV$. It is interesting to note that in this region, according to fig. 4, $\Delta E_{corr} < \Delta E_{dim}$. Nearly the same situation occurs in PDA where $\Delta E = 2.5 \, eV$.

Now using data of Fig. 5 one can also easily understand why there are some differences in evaluation of correlation and dimerization contributions to the gap value. Namely, in the region of intermediate values 1 < U < 4 the ΔE_{corr} sharply increases, exceeding ΔE_{dim} after U = 3. Thus, the values of $U, \kappa < 0.1$ are strongly dependent on small perturbations such as the boundary conditions or chain length.

In such organic materials like [K⁺-TCNQ] we have instead

 $\Delta E = 0.9 \ eV, \ \kappa = 0.05, \ t = 0.15 \ eV,$

which gives U > 6. Thus, the correlation contribution into ΔE is dominant and one can use (326) for the evaluation of Δ_0 .

One can conclude as well that the agreement of the calculated values of Δ_0 or x_0 in (304) can be obtained by different approaches. But it needs different values of parameters $\gamma, \beta, \beta', K_{\sigma}$ which depend on the model used in calculations of short or infinite chains as well as also chains with cyclic boundary conditions. Giving preference to either calculation model one must bare in mind different experimental data, not only the values of Δ_0 .

Conclusions & Perspectives

Advances in physics and chemistry of low-dimensional electron systems have been magnificent in the last few dacades. Hundreds of quasi-1d and quasi-2d systems have been synthesized and studied experimentally and theoretically. The unusual properties of these materials attract attention of physicists, chemists, and engineers.

The most popular representatives of real quasi-1d materials are polyacethylenes [106] and conducting donor – acceptor molecular crystals TTF-TCNQ [206]. One of the promising families of quasi-2d systems are new high temperature superconductors (HTSC) based on cooper oxides La_2CuO_4 , $YBa_2Cu_3O_{6+y}$ [207] and organic superconductors based on BEDT-TTF molecules [208].

Quantum processes in low-dimensional systems are characterized by a number of peculiarities. Thus, special and new theoretical approaches have been developed to study low-dimensional phenomena. We will be concerned further mostly with the 1d-systems. In one-dimensional physics and chemistry there is a number of difficulties and some of them are far from being overcome. On the one hand, equations of motion for 1d-systems are much simpler. This facilitates rigorous solutions of the model problems which are often impeded in case of the larger number of dimensions. On the other hand, manifestations of various interactions in 1d-systems are rather peculiar. This relates, in particular, to electron – electron and electron – phonon interactions. Thus, electron – phonon interaction leads to the field localization of electron excitation in 1d-systems which results in soliton excitations and the Peierls deformations. Calculations of soliton excitation can not be done by decomposition in the series of electron – phonon coupling constants.

Electron – electron interactions, even within the limit of a weak coupling constant, produces an energy gap in the spectrum od 1d-metal which initiate the Mott transition from metal to semiconducting state. In this case the standard perturbation theory is also not applicable.

Similar situation occurs in 1d-systems with respect to electron – impurity interactions. Started by Mott and Twose theoretical studies of this problem show that all one-electron states in 1d disordered system are localized and, as a result, cannot be calculated using the perturbation theory. State localization turns the direct current conductivity into zero.

Inapplycability of the perturbation theory is one of the main difficulties on the way to succeed in the theory of quasi-1d-systems. These difficulties were being partly surpassed in different ways.

Regardling electron – phonon interaction the most fruitful method is to reduce the set of corresponding equations into a completely integrable system like the nonlinear Schrodinger equation, the sine-Gordon equation, and others.

Advances in description of electron – electron interactions turned out to be less pronounced however. The major reason for it lies in the well known complications of the many-electron theory for systems with an infinitely large number of electrons.

Traditional quantum chemistry as one of the many applications of the general theory of many-electron systems is based upon the Hartee - Fock approximation which came first as "the word came first". Then various manyelectron theories being developed where the wave function were not represented by one Slater determinant rather then an infinite series of the determinants. If the number of particles in the system grows as $N \rightarrow \infty$ then the number of terms in this infinite series must increase at least as e^{aN} , where a is a constant ≈ 1 . This particular infinite complication of the theory is the main hindrance in it wide applications in calculations. It is time now to say that these difficulties are often being considerably exaggerated. As a rule, having analyzed the Hamiltonian of the system under study using the many-electron theory one can reduce the problem to a simpler Hamiltonian or without any loss in quality construct multicinfigurational wave function of the system which can be factorized into an antisymmetrized product of one- or two-electron functions. As approximations for a wave function, besides the EHF approximation described in details in paragraph 3 above, the spinless fermion approximation in case of strong interactions [209] and the VLG approximation described in previous paragraph can be mentioned.

In the EHF and spinless fermion approaches a many-electron wave function is finally factorized into the product of one-electron functions (orbitals), but in the VLG approach the factorization into the product of twoelectron functions (geminals) is performed.

Now we draw attention to another aspect of the theory of quasi-1d electron systems. Real systems with one-dimensional anisotropy are, in fact, threedimensional. In case of a theoretical study it is expedient to mentally separate a 1d-system out of the real system using its specific properties. This separation of a quasi-1d-subsystem goes naturally through analysis of the total Hamiltonian represented by the sum

$$\hat{H} = \sum_{n} \hat{H}_{n} + \frac{1}{2} \sum_{n,m} \hat{V}_{nm} , \qquad (331)$$

where \hat{H}_n is the Hamiltonian of a *n*-th quasi-1d subsystem (filaments, needles, chains, stacks, *etc*), and the operators \hat{V}_{nn} describe its interactions with other quasi-1d subsystems.

Further it is usually assumed that the interaction operators do not include terms responsible for electron exchange between separate quasi-1d subsystems. Namely this predetermines the subdivision of the Hamiltonian into the sum (331). This approximation provides satisfactory description of PAs, donor – acceptor molecular conducting crystals as well as many other quasi-1d electron systems.

Before we consider particular expressions for the Hamiltonians for electron – phonon systems under study it is worthwhile to note the following. Most processes in quasi-1d systems are determined by the energy spectrum and the nature of elementary excitations. The low-energy region of the spectrum is mainly related to a small part of the total number of electrons in the system under study. This facilitates a rigorous enough description of electron processes occurring in these systems. As example, most interesting properties of polyenes, cumulenes, and polyacethylenes originate from the π -electron number equals or proportional to the number of carbon atoms and essentially less than the total number of all electrons in the system. Studying the most significant properties of donor – acceptor molecular conducting crystals it is sufficient to consider one electron only per a donor – acceptor pair. In case of TTF-TCNQ crystal it means that only one electron out of 208 is to be considered.

Despite of the simplifications mentioned above we are still have to restrict ourselves with semi-empirical models of quantum chemistry. For example, the well known Huckel – Pople (HP) Hamiltonian

$$\hat{H} = \sum_{m} \alpha \hat{C}_{m\sigma}^{\dagger} \hat{C}_{m\sigma} + \sum_{mm'\sigma} \beta_{mm'} \hat{C}_{m\sigma}^{\dagger} \hat{C}_{m'\sigma} + \frac{1}{2} \sum_{mm'\sigma} \gamma_{mm'} \hat{C}_{m\sigma}^{\dagger} \hat{C}_{m\sigma} \hat{C}_{m'\sigma}^{\dagger} \hat{C}_{m'\sigma}$$
(332)

is very popular and useful to study many properties of molecules with conjugated bonds.

As a rule, it is sufficient in (332) to account for resonance interaction (so called electron hopping) for the adjacent atoms only, namely:

$$\beta_{mm'} = \beta(R_{mm'})\delta_{m',m+1}.$$
(333)

As far as the electron interaction in (332) is conserned only the first several terms are usually accounted for. As an example, in the Hubbard – Anderson (HA) Hamiltonian

$$\gamma_{mn} = \gamma_0 \delta_{mn} \,. \tag{334}$$

Interaction between two neighbouring atoms is only often used:

$$\gamma_{mn} = \begin{cases} \gamma_0 \delta_{mn}, \\ \gamma_1 \delta_{m\pm 1,n}. \end{cases}$$
(335)

Accounting for the bond distance dependence of the resonance integrals it is often sufficient to use only the first term of the β -function expansion in the vicinity of $R_0 = 1.397A$ which corresponds to the C=C bond length in benzene

$$\beta(R) = \beta_0 - (R - R_0)\beta'.$$
(336)

To account for vibrational degrees of freedom the phonon Hamiltonian

$$\hat{H}_{ph} = \sum_{ki} \hbar \omega_{ki} (\hat{B}_{ki}^{+} \hat{B}_{ki} + \frac{1}{2})$$
(337)

is added to (332), where \hat{B}_{ki}^+ is a phonon creation operator for the *i*th mode with a quasimomentum *k*. Starting from (336), the operator of electron – phonon subsystem interactions may be chosen as suggested by Frohlich

$$\hat{H}_{e/ph} = \sum_{kq} \lambda_{qi} (\hat{B}_{q,i}^{+} - \hat{B}_{-q,i}) \hat{A}_{k,\sigma}^{+} \hat{A}_{k+q,\sigma}, \qquad (338)$$

where a constant λ is proportional to the β derivative with respect to R, that is β' in (336). Like in other cases, for quasi-1d systems it is often sufficient to use only the classical form of the phonon part of the Hamiltonian

$$\hat{H}_{ph} = \frac{1}{2} \sum_{mi} M_i \dot{\vec{R}}_{mi}^2 + \frac{1}{2} \sum_{mi} K_i (\vec{R}_{mi} - \vec{R}_{m+1,i})^2, \qquad (339)$$

and

$$\hat{H}_{e/ph} = \sum_{m\sigma} (R_0 - R) \beta' (\hat{C}^+_{m+1,\sigma} \hat{C}_{m\sigma} + h.c.) \,.$$
(340)

The Hamiltonian (332) together with the expressions for the matrix elements (333) - (336) allows us to consider the properties of materials based on conjugated polymers and of donor – acceptor molecular crystals with quasi-1d conductivity such as the crystals based on TTF-TCNQ and their derivatives like TSF, TST, and HTSC [106, 206 – 208].

The greatest interest with respect to newly synthesized quasi-1d and quasi-2d systems is attached to the compounds with high electric conductivity. But on the way to create good organic conductors the investigators encounter difficulties of not only technical but principal nature which relates to an electron
instability of a conducting state. Their most important peculiarity lies in the fact that a metallic state of a quasi-1d crystal is unstable with respect to a transition into a dielectric or semiconductive state. The character of instability and its force strength which determines the metal – insulator transition temperature depends on structural features of the crystal.

Let us consider a system consisting of long needles packed into a 3dcrystal. The Hamiltonian of each needle is supposed to be the first term in the general expression (331)

$$\hat{H} = -\beta_0 \sum_{m\sigma} (\hat{C}^+_{m\sigma} \hat{C}_{m+1,\sigma} + h.c.), \qquad (341)$$

where the same notifications as in (332) are used and let the number of particles $N \rightarrow \infty$. The 1d-system with Hamiltonian (341) is a metal independently on the number of electrons in the conduction band N_e with density

$$\rho = \frac{N_e}{N} = \frac{1}{N} \sum_{m\sigma} \left\langle \hat{C}^+_{m\sigma} \hat{C}_{m\sigma} \right\rangle, \qquad (342)$$

that is, with any filling of the conduction band $0 < \rho < 2$. In case when the number of electrons and sites coincides we have a half-filled conduction band, $N_e = N$ and the Fermi momentum is

 $k_F = \pi / 2a$ where *a* is a 1d-lattice parameter.

A 1d-metal with a half-filled conduction band is unstable with respect to the following metal – insulator transitions:

1) The Mott metal – insulator transition resulting from electron interactions. Instability of a 1d-metal with respect to this transition arises from the fact that electron – electron interactions produce the gap at $T = 0^{\circ} K$ even within a weak coupling constant $U = \gamma / \beta_0$ in the Hamiltonian (332).

2) The Peierls metal – insulator transition is connected with electron – phonon interactions. Alongside with the gap a periodic deformation of the crystal occurs with the period π/k_F .

3) The Anderson metal – insulator transition resulting from structure disordering of the crystal. The instability of a 1d-metal in this case is stimulated by localization of electron states even by a weak random field.

When coupling constant U is large the Wigner ordering of electrons in quasi-1d conductors appears.

Early theories of quasi-1d systems came to the conclusion that various instabilities in a 1d-metal are being competive [106]. However, further analysis

have shown that, in fact, a coexistence of different instabilities is possible. Thus, in [193] it was shown that the Mott and Peierls instabilities coexist both at $\rho = 1$ and at $\rho = 1/2$. In other words, a 1d Mott insulator also undergoes lattice deformation with the period π/k_F .

If we want to obtain a good organic conductor or even superconductoe we should stabilize the system with respect to the above transitions. All history of quasi-1d metal systems is, in fact, the history of fighting the above instabilities.

One of the effective means to fight the metal – insulator transitions is to shift electron density

 ρ from the values approaching 1, $\frac{1}{2}$, $\frac{1}{3}$ and other fractions with small denominators. This can be achieved by crystal doping with electron donors ot acceptors or by violation of a simple stoichiometric ratio. To understand why this simple and clear method is so efficient we shall discuss the instabilities and their descriptions for a system with a half-filled band with $\rho = 1$ in more details.

The Mott metal – insulator transition. A system with Hamiltonian (341) at $\rho = 1$ is a metal. Adding an Interaction operator like (331) to (341) we obtain the system with the Hubbard Hamiltonian

$$\hat{H} = \sum_{m\sigma} \{ (-\beta) [\hat{C}^{+}_{m\sigma} \hat{C}_{m+1,\sigma} + h.c.] + \frac{1}{2} \beta_0 U \hat{C}^{+}_{m\sigma} \hat{C}_{m\sigma} \hat{C}^{+}_{m,-\sigma} \hat{C}_{m,-\sigma} \} .$$
(343)

The spectrum of a cyclic chain with Hamiltonian (343) is the spectrum of an insulator at any U > 0, that is, the excitation of states with charge transfer requires an energy ΔE . For the first time a conclusion on the energy gap formation in such a system appeared in calculations by EHF method [106].

The Peierls metal – insulator transition. Let us consider a system with the Hamiltonian which can be represented as the sum of (339), (340), and (341)

$$\hat{H} = \sum_{m\sigma} \{-[\beta_0 + \beta'(\vec{R}_m - \vec{R}_{m+1})]\hat{C}^+_{m\sigma}\hat{C}_{m+1,\sigma} + h.c.\} + \frac{1}{2}k\sum_m(\vec{R}_m - \vec{R}_{m+1})^2.$$
(344)

The energy minimum of an infinite chain is reached with the Hamiltonian (344) when

$$R_m = R_0 \cos(Qam + \varphi_0), \tag{345}$$

where *a* is a non-deformed lattice parameter, φ_0 is the phase of bond deformation, $Q = 2k_F$, and

 $\hbar k_F$ is the Fermi momentum.

For a half-filled band $k_F = \pi / 2a$ and

$$R_0 = 2\frac{\beta_0}{\beta'} \exp\left[-\frac{\pi\beta k}{\left(\beta'\right)^2}\right].$$
(346)

The energy spectrum of conduction electrons for a half-filled band is given by

$$\varepsilon_{1,2} = \pm 2\beta_0 \sqrt{\cos^2 k + 4\left(\frac{\beta'}{\beta_0}\right)R_0^2 \sin^2 k}, \qquad (347)$$

where "–" sign corresponds to a completely filled conduction subband, and "+" sign corresponds to the vacant subband.

Thus, the gap in the one-particle spectrum is

$$\Delta E_g = 8\beta' R_0. \tag{348}$$

The ground state energy correction is

$$\Delta E_c = 4\beta R_0^2 \ln R_0 + \frac{1}{2}KR_0^2.$$
 (349)

Some specific features of physics in one dimension remain valid also in two dimensions. Theoretical treatment of 2d-models is more complicated. For example, The Mott and Anderson metal – insulator transitions can occur also in quasi-2d systems. However, the Peierls transition in 2d case can appear only for special forms of the Fermi surface in the case of so called "nesting". Generally speaking, the conditions for the metal – insulator transitions in 2d-systems are stronger than those in 1d case. Passing to 2d-systems one can stabilize conducting and superconducting states.

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