ФІЗИКО-МАТЕМАТИЧНІ НАУКИ

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QUANTUM-CHEMICAL STUDIES OF QUASI-ONE-DIMENSIONAL ELECTRON SYSTEMS.
PART 2. CUMULENES AND ORIGIN OF THE FORBIDDEN ZONE

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

Keywords: *quasi-one-dimensional electron system, polyenes, cumulenes, Peierls instability, bond alternation, Mott instability, electron correlation.*

В огляді на основі результатів, отриманих київською групою квантової хімії, обговорюється основна проблема квазі-одновимірних електронних систем таких як поліени (Частина 1) і кумулени (Частина 2) – фізична природа походження забороненої зони в таких і подібних їм 1D електронних системах завдяки двом можливим ефектів – нестійкість Пайерлса (чергування довжин хімічних зв'язків) і Мотта (електронна кореляція).

Ключові слова: *квазі-одновимірні електронні системи, поліени, кумулени, нестійкість Пайерлса, чергування зв'язків, нестійкість Мотта, кореляція електронів.*

1. Introduction

This review gives detailed results and thorough discussion of basic results in quantum theory of quasi-one-dimensional electron systems like Polyenes (Part 1 [1]) and Cumulenes (Part 2), 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 began in Part 1 [1] with local electronic states in long polyene chains in the simple tight-binding approximation [2–4]. Then we gave 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 turned to theory of electronic structure of long polyene neutral alternant radicals based on the different orbital for different spins SCF method [6]. Then we ended Part 1 [1] with the local electronic states in polyene chains with an impurity atom using unrestricted Hartree-Fock approach [7].

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

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

2. Review of π-Electron Model of Cumulenes

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 [14 – 17]. 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 [18] 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 CH_2 end-groups. Rotation of one of the CH_2 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 CH_2 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 [8, 9, 19, 20]. Popov [20] 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 $2N–2$ π-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 plus 2 nonbonding levels in OCs. In the former $2N–2$ π-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 [17] 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 [21] in 1877 using the tetrahedral model of the carbon atom.

Let us choose the coordinate system in a way so that in the conformation D_{2h} π-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} π_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) [22, 23] 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 $^3A_2$, $^1B_1$, $^1A_1$, and $^1B_2$ for ECs and ^3A_u, ^1A_u, ^1A_g, and $^1A'_g$ for OCs. We shall see later that when electronic interaction is accounted for the lowest states become $^3A_2$, $^1B_1$, resp. ^3A_u, ^1A_u. The states $^1A_1$, $^1B_2$, resp. ^1A_g, $^1A'_g$ correspond to electron transfer between the perpendicular x- and y-subsystems of π-AOs. The molecule in its stable conformation, which is ^1A_g for ECs and $^1A_1$ 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 ^1A_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 [24].

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

$$\varphi_i = \sum_\nu C_{\nu i} x_\nu, \quad \varphi'_i = \sum_\nu C'_{\nu i} y_\nu .$$

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 $\hat{A}_{\bar{i}}^+$ 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^c may be written as

$$\Psi^c({}^1A_1, {}^1A_g) \equiv \Psi^c,$$

$$\Psi^c = \prod_j \hat{A}_{\bar{j}}^+ \hat{A}_j^+ \prod_{j'} \hat{A}_{\bar{j}'}^+ \hat{A}_{j'}^+ \left|0\right\rangle ,$$

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

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

$$\Psi^o({}^3A_2, {}^3A_u) = \frac{1}{\sqrt{2}} (\hat{A}_{\bar{k}'}^+ \hat{A}_k^+ + \hat{A}_{k'}^+ \hat{A}_{\bar{k}}^+) \Psi^c,$$

$$\Psi^o({}^1B_1, {}^1A_u) = \frac{1}{\sqrt{2}} (\hat{A}_{\bar{k}'}^+ \hat{A}_k^+ - \hat{A}_{k'}^+ \hat{A}_{\bar{k}}^+) \Psi^c,$$

$$\Psi^o({}^1B_2, {}^1A_g) = \frac{1}{\sqrt{2}} (\hat{A}_{\bar{k}}^+ \hat{A}_k^+ - \hat{A}_{\bar{k}'}^+ \hat{A}_{k'}^+) \Psi^c,$$

$$\Psi^o({}^1A_1, {}^1A'_g) = \frac{1}{\sqrt{2}} (\hat{A}_{\bar{k}}^+ \hat{A}_k^+ + \hat{A}_{\bar{k}'}^+ \hat{A}_{k'}^+) \Psi^c.$$

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

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

Let us introduce the standard notations:

$$H_k = \int \varphi_{\bar{k}}^* H^{core} \varphi_{\bar{k}} \, d\tau,$$

$$J_{ij} = \int \varphi_i^* \varphi_{\bar{j}}^* \frac{1}{r_{12}} \varphi_i \varphi_{\bar{j}} d\tau_1 d\tau_2,$$

$$K_{ij} = \int \varphi_{\bar{i}}^* \varphi_j^* \frac{1}{r_{12}} \varphi_i \varphi_{\bar{j}} d\tau_1 d\tau_2.$$

Then the energy of states with closed shell will be:

$$E^c({}^1A_1, {}^1A_g) = 2\sum_j H_j + 2\sum_{j'} H_{j'} + \sum_{j_1 j_2}\left(2J_{j_1 j_2} - K_{j_1 j_2}\right) +$$
$$+ \sum_{j_1 j_2'}\left(4J_{j_1 j_2'} - 2K_{j_1 j_2'}\right) + \sum_{j_1' j_2'}\left(2J_{j_1' j_2'} - K_{j_1' j_2'}\right) + E^{core},$$

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 $E^c({}^1A_1, {}^1A_g)$ above, the sums being taken over the closed shell only, the energy of the states with open shell are:

$$E^o({}^3A_2, {}^3A_u) = E_1 + J_{kk'} - K_{kk'},$$
$$E^o({}^1B_1, {}^1A_u) = E_1 + J_{kk'} + K_{kk'},$$
$$E^o({}^1B_2, {}^1A_g) = E_1 + \frac{1}{2}(J_{kk} + J_{k'k'}) - K_{kk'},$$
$$E^o({}^1A_1, {}^1A_g') = E_1 + \frac{1}{2}(J_{kk} + J_{k'k'}) + K_{kk'}.$$

Usually

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

holds. This means that among the lower singlet states the lowest are ${}^1B_1$ and ${}^1A_u$.

Reducing the MOs to AOs the integrals over the AOs

$$\langle \kappa\lambda | \mu\nu \rangle = \int x_\kappa^*(1) x_\mu^*(2) \frac{1}{r_{12}} x_\lambda(1) x_\nu(2) d\tau_1 d\tau_2$$

will have to be calculated. Zero differential overlap

$$\langle \kappa\lambda | \mu\nu \rangle = \delta_{\kappa\lambda}\delta_{\mu\nu} \langle \kappa\kappa | \mu\mu \rangle = \delta_{\kappa\lambda}\delta_{\mu\nu}\gamma_{\kappa\mu}$$

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 π_y $H_{\mu\nu'}$ are zero for symmetry reasons. Integrals $H_{\mu\mu}$ will be calculated in the Goeppert-Mayer and Sklar approximation [25], neglecting penetration integrals

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

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:

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

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

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

$$\sum_j J_{jk} = \sum_{\mu\nu} P_{\mu\mu}^c P_{\nu\nu}^o \gamma_{\mu\nu},$$
$$\sum_j K_{jk} = \sum_{\mu\nu} P_{\mu\nu}^c P_{\mu\nu}^o \gamma_{\mu\nu},$$
$$J_{kk'} = \sum_{\mu'\nu} P_{\mu'\mu'}^o P_{\nu\nu}^o \gamma_{\mu'\nu}.$$

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:

$$E^c({}^1A_1, {}^1A_g) = \sum_\nu (\gamma_{\nu\nu} - I_\nu) P_{\nu\nu}^T + \sum_{\nu'} (\gamma_{\nu'\nu'} - I_{\nu'}) P_{\nu'\nu'}^T +$$
$$+ \sum_{\mu\nu} \left\{ \left[\frac{1}{2} P_{\mu\mu}^T P_{\nu\nu}^T - P_{\nu\nu}^T - \frac{1}{4} (P_{\mu\nu}^T)^2 \right] \gamma_{\mu\nu} + P_{\mu\nu}^T \beta_{\mu\nu} \right\} +$$
$$+ \sum_{\mu'\nu''} \left\{ \left[\frac{1}{2} P_{\mu'\mu'}^T P_{\nu'\nu'}^T - P_{\nu'\nu'}^T - \frac{1}{4} (P_{\mu'\nu'}^T)^2 \right] \gamma_{\mu'\nu'} + P_{\mu'\nu'}^T \beta_{\mu'\nu'} \right\} +$$
$$+ \sum_{\mu\nu'} (P_{\mu\mu}^T P_{\nu'\nu'}^T - P_{\nu'\nu'}^T - P_{\mu\mu}^T) \gamma_{\mu\nu'}. \qquad (1)$$

Further simplifications will follow if we take into account that for alternant hydrocarbons it holds that $P_{\nu\nu}^T = P_{\nu'\nu'}^T = 1$ [26]. 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 [23, 27] 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:

$$E^c({}^1A_1, {}^1A_g) = E_x^c + E_y^c + E_{\text{int}} + E^{core},$$

where

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

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

$$E_{\text{int}} = -\sum_{\mu\nu'}\gamma_{\mu\nu'}. \qquad (2)$$

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 ${}^1B_1$ and ${}^1A_u$ lead to the following result:

$$E^o({}^1B_1, {}^1A_u) = E_x^o + E_y^o + E_{\text{int}} + E^{core},$$

where

$$E_x^o = \sum_{\nu}(\gamma_{\nu\nu} - I_\nu) +$$

$$+\sum_{\mu\nu}\left[P_{\mu\nu}^T\beta_{\mu\nu} - \frac{1}{2}\gamma_{\mu\nu} - \left(\frac{1}{2}P_{\mu\nu}^T\right)^2\gamma_{\mu\nu} - \left(\frac{1}{2}P_{\mu\nu}^o\right)^2\gamma_{\mu\nu}\right],$$

$$E_y^o = \sum_{\nu'}(\gamma_{\nu'\nu'} - I_{\nu'}) +$$

$$+\sum_{\mu'\nu'}\left[P_{\mu'\nu'}^T\beta_{\mu'\nu'} - \frac{1}{2}\gamma_{\mu'\nu'} - \left(\frac{1}{2}P_{\mu'\nu'}^T\right)^2\gamma_{\mu'\nu'} - \left(\frac{1}{2}P_{\mu'\nu'}^o\right)^2\gamma_{\mu'\nu'}\right]. \qquad (3)$$

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 ${}^1A_1$, ${}^1B_2$, ${}^1A_g$, and ${}^1A_g'$ division of the π-electron system in two subsystems is not possible despite of the fact that rule $P_{\nu\nu}^T = P_{\nu'\nu'}^T$ is satisfied.

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

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

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

Let us note one incorrectness of the Goeppert-Mayer and Sklar approximation [25] 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 [28]

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

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

$$V = E_x(D_{2d}) + E_y(D_{2d}) - E_x(D_{2h}) - E_y(D_{2h}) - \gamma_{\alpha\omega}. \quad (4)$$

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

$$V = E_x(D_{2d}) + E_y(D_{2d}) - E_x(D_{2h}) - E_y(D_{2h}) - \gamma_{\alpha\omega'}. \quad (5)$$

Barrier values by (4) and (5) are almost identical especially for large N.

As we see from (4) and (5) the barrier height is determined first of all by SCF energies of the π-electron subsystems which may be calculated from formulae (2) and (3) [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:

$$\sum_{\mu=1}^{m-1}P_{\mu,\mu+1}^T \equiv Q_m = \begin{cases}\operatorname{cosec}\dfrac{\pi}{2m+2} - 1, & m \quad \text{even}\\[2ex] \operatorname{ctg}\dfrac{\pi}{2m+2} - 1, & m \quad \text{odd}\end{cases}$$

$$\sum_{\mu=1}^{m-1}(P_{\mu,\mu+1}^T)^2 = \frac{Q_m^2}{m+1} + \begin{cases}m/(m+1), & m \quad \text{even}\\ (m-1)/m, & m \quad \text{odd}\end{cases}$$

$$\sum_{\mu=1}^{m}(P_{\mu\mu}^o)^2 = \frac{2}{m+1}, \quad m \quad \text{odd}$$

$$\sum_{\mu=1}^{m-1}(P_{\mu,\mu+1}^o)^2 = 0.$$

It is possible then to show analytically that barriers calculated by formula (4) tend asymptotically to zero with increasing N in accord with Huckel calculations in [20].

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

3. Electronic Structure of Long Cumulene Chains in the Extended Hartree-Fock Method Compared with its Unrestricted Version

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, 29–33] 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, 31, 32] and long regular cumulenes [33] 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.

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

3. 1. 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 and odd [1] number of C atoms $N \gg 1$ 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 [29, 30]

$$\hat{H} = \sum_{k\sigma} (\alpha + 2\beta \cos k) \hat{A}^{+}_{k\sigma} \hat{A}_{k\sigma} + \\ + \frac{\gamma}{2N} \sum_{k,k',k'',k''',\sigma} \hat{A}^{+}_{k\sigma} \hat{A}_{k'\sigma} \hat{A}^{+}_{k'',-\sigma} \hat{A}_{k''',-\sigma} f(k,k',k'',k'''), \quad (6)$$

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 νth 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

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

It is easy to show that functions $\varphi_k^{(0)}$ are the HF solutions for the Hamiltonian (6). In the HF approximation only averages over the ground state of the type $\left\langle \hat{A}^{+}_{k\sigma} \hat{A}_{k\sigma} \right\rangle$ do not vanish. In case of the UHF method we have also to take as non-zero the averages of the type $\left\langle \hat{A}^{+}_{k\sigma} \hat{A}_{\bar{k}\sigma} \right\rangle$, where $\bar{k} = \pi - k$. The case when the chain boundaries are neglected, *i.e.* the cyclic boundary conditions are used, see in [29, 30]. Hence it follows that

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

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

$$\hat{H}_\sigma^{(UHF)} = \sum_{k \le \pi} (2\beta \hat{A}^{+}_{k\sigma} \hat{A}_{k\sigma} \cos k + \gamma \cdot \Delta \cdot \tau_{-\sigma} \hat{A}^{+}_{k\sigma} \hat{A}_{\bar{k}\sigma}) + C , \quad (7)$$

where

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

The self-consistent value of

$$\Delta = \frac{\tau_\sigma}{N} \sum_k \left\langle \hat{A}^{+}_{k\sigma} \hat{A}_{k\sigma} \right\rangle \quad (8)$$

is defined by the equation

$$\frac{\gamma}{\pi} \int_0^{\pi/2} dk (4\beta^2 \cos^2 k + \gamma^2 \Delta^2)^{-1/2} = 1 . \quad (9)$$

Let us transform the operators $\hat{A}^{+}_{k\sigma}$ and $\hat{A}_{k\sigma}$ using Eqs (120) in [1] as

$$\hat{A}_{k\sigma} = (\hat{A}^{(1)}_{k\sigma} - \xi_k \tau_\sigma \hat{A}^{(2)}_{k\sigma}) \Im_k^{-1/2}, \\ \hat{A}_{\bar{k}\sigma} = (\hat{A}^{(2)}_{k\sigma} + \xi_k \tau_\sigma \hat{A}^{(1)}_{k\sigma}) \Im_k^{-1/2}, \quad (10)$$

where

$$0 \le k \le \pi/2, \quad \Im_k = 1 + \xi_k^2,$$

$$\xi_k = (2\beta \cos k + \sqrt{4\beta^2 \cos^2 k + (\gamma \Delta)^2}) / (\gamma \Delta) . \quad (11)$$

Substituting (10) and (11) into (07) one obtains

$$\hat{H}_\sigma^{(UHF)} = \sum_{i,k} \varepsilon_k^{(i)} \hat{A}^{(i)+}_{k\sigma} \hat{A}^{(i)}_{k\sigma} , \quad (12)$$

where

$$\varepsilon_k^{(1)} = -\varepsilon_k^{(2)} = -\sqrt{4\beta^2 \cos^2 k + \gamma^2 \Delta^2} . \quad (13)$$

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

$$\varphi^{(i)}_{k\sigma}(\vec{r}) = \sum_{\mu=1}^{N} C^{(i)}_{k\sigma}(\mu) \chi_\mu(\vec{r}) ,$$

where

$$C^{(1)}_{k\sigma}(\mu) = \sqrt{\frac{2}{N}} [1 + (-1)^{\mu+1} \xi_k \tau_\sigma] \Im_k^{-1/2} \sin \mu k, \\ C^{(2)}_{k\sigma}(\mu) = \sqrt{\frac{2}{N}} [(-1)^{\mu+1} - \xi_k \tau_\sigma] \Im_k^{-1/2} \sin \mu k. \quad (14)$$

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 (8)–(14) are valid in both cases. Consequently, in the UHF method the self-consistent functions (14) 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 $N \gg 1$. 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 (8)–(14). It should also be noted that the exact solution of the Schrodinger equation with the Hamiltonian (6) and the cyclic boundary conditions is obtained in [34]. The study of the exact solution [34, 35] 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

$$n_{\mu\sigma} = \sum_{k\le\pi/2} [C^{(1)}_{k\sigma}(\mu)]^2 . \qquad (15)$$

Substituting (14) into (15) one obtains

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

where

$$\delta_\mu = \frac{2\gamma\Delta}{\pi}\int_0^{\pi/2} dk\,(\varepsilon_k^{(2)})^{-1}\sin^2\mu k . \qquad (16)$$

The chain boundary effect is revealed in the dependence of δ_μ on μ. It follows from (16) that $\delta_1 = 0.28$, $\delta_2 = 0.18$, $\delta_3 = 0.23, ..., \delta_\mu = \Delta = 0.21$ for $\mu \gg 1\, (\beta = -2.4\, eV, \gamma = 5.4\, eV)$. Thus, the chain boundary effect extends, in fact, to only the first two – three atoms. It also follows from (15) that $n_\mu = \sum_\sigma n_{\mu\sigma} = 1$. The values $n_{\mu\sigma}$ are equal to electron populations of the μth 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 (15) can be treated as self-consistent parameters.

3. 2. Electronic Structure of Long Cumulene Chains

Now we shall turn to the treatment of long cumulenes $C_NH_4\ (N \gg 1)$ 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 CH_2. Let us denote the conformation of symmetry D_{2h} in which the end-groups lie in the same plane as $A_{\parallel}$ 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 [33] one can obtain the following expression for the Hamiltonian of a long chain $=(C=)_N$

$$\hat{H} = \sum_{k\sigma}(\alpha + 2\beta\cos k)\left(\hat{A}^+_{k\sigma}\hat{A}_{k\sigma} + \hat{B}^+_{k\sigma}\hat{B}_{k\sigma}\right) + \frac{1}{2N}\times$$
$$\times \sum_{k,k',k'',k''',\sigma}\left[\begin{array}{l}\gamma\left(\hat{A}^+_{k\sigma}\hat{A}_{k'\sigma}\hat{A}^+_{k'',-\sigma}\hat{A}_{k''',-\sigma} + \hat{B}^+_{k\sigma}\hat{B}_{k'\sigma}\hat{B}^+_{k'',-\sigma}\hat{B}_{k''',-\sigma}\right)\\ +\tilde{\gamma}\left(\hat{A}^+_{k\sigma}\hat{B}_{k'\sigma}\hat{A}^+_{k'',-\sigma}\hat{B}_{k''',-\sigma} + \hat{B}^+_{k\sigma}\hat{A}_{k'\sigma}\hat{B}^+_{k'',-\sigma}\hat{A}_{k''',-\sigma}\right)\\ +2\sum_{\sigma'}\left(\tilde{\tilde{\gamma}}\,\hat{B}^+_{k\sigma}\hat{B}_{k'\sigma}\hat{A}^+_{k''\sigma'}\hat{A}_{k'''\sigma'} - \tilde{\gamma}\,\hat{A}^+_{k\sigma}\hat{A}_{k'\sigma'}\hat{B}^+_{k''\sigma'}B_{k'''\sigma}\right)\end{array}\right], \quad (17)$$

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

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

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

$$\tilde{\gamma} = e^2\int dV_{12}\,\chi^{(a)}_\mu(\vec{r}_1)\,\chi^{(b)}_\mu(\vec{r}_1)\, r_{12}^{-1}\,\chi^{(a)}_\mu(\vec{r}_2)\,\chi^{(b)}_\mu(\vec{r}_2). \quad (18)$$

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

$$\hat{H}^{(UHF)}_{\sigma,a} = \sum_k [2\beta\hat{A}^+_{k\sigma}\hat{A}_{k\sigma}\cos k +$$
$$(\gamma\,\Delta_a\tau_{-\sigma} - \tilde{\gamma}\,\Delta_b\tau_\sigma)\hat{A}^+_{k\sigma}\hat{A}_{\bar{k}\sigma}] + C_1,$$

$$\hat{H}^{(UHF)}_{\sigma,b} = \sum_k [2\beta\hat{B}^+_{k\sigma}\hat{B}_{k\sigma}\cos k +$$
$$+(\gamma\,\Delta_b\tau_{-\sigma} - \tilde{\gamma}\,\Delta_a\tau_\sigma)\hat{B}^+_{k\sigma}\hat{B}_{\bar{k}\sigma}] + C_1, \qquad (19)$$

where

$$\Delta_a = \frac{\tau_\sigma}{N}\sum_k\left\langle\hat{A}^+_{k\sigma}\hat{A}_{\bar{k}\sigma}\right\rangle, \quad \Delta_b = \frac{\tau_\sigma}{N}\sum_k\left\langle\hat{B}^+_{k\sigma}\hat{B}_{\bar{k}\sigma}\right\rangle,$$

$$C_1 = \frac{N}{4}[2\alpha + \frac{\gamma - \tilde{\gamma}}{2} + \tilde{\tilde{\gamma}} + 2(\gamma + \tilde{\gamma})\Delta_1^2]. \quad 0 \le k \le \pi$$

According to [33], 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 [33], we shall restrict ourselves to the case $\Delta_a = \Delta_b$. Substituting this condition into Eq. (19) one obtains

$$\hat{H}_{\sigma,a}^{(UHF)} = \sum_k [2\beta \hat{A}_{k\sigma}^{+} \hat{A}_{k\sigma} \cos k +$$
$$(\gamma + \tilde{\gamma})\Delta_1 \tau_{-\sigma} \hat{A}_{k\sigma}^{+} \hat{A}_{\bar{k}\sigma}] + C_1,$$
$$\hat{H}_{\sigma,b}^{(UHF)} = \sum_k [2\beta \hat{B}_{k\sigma}^{+} \hat{B}_{k\sigma} \cos k +$$
$$+(\gamma + \tilde{\gamma})\Delta_1 \tau_{-\sigma} \hat{B}_{k\sigma}^{+} \hat{B}_{\bar{k}\sigma}] + C_1. \qquad (20)$$

The expression (20) have the same form as (3). Because of this the expressions (20) are diagonalized by canonical transformation of the type (05), namely:

$$\hat{H}_{\sigma,a}^{(UHF)} = \sum_{i,k} \varepsilon_k^{(i)} \hat{A}_{k\sigma}^{(i)+} \hat{A}_{k\sigma}^{(i)} + C_1,$$
$$\hat{H}_{\sigma,b}^{(UHF)} = \sum_{i,k} \varepsilon_k^{(i)} \hat{B}_{k\sigma}^{(i)+} \hat{B}_{k\sigma}^{(i)} + C_1,$$

where

$$\varepsilon_k^{(1)} = -\varepsilon_k^{(2)} = -\sqrt{4\beta^2 \cos^2 k + (\gamma + \tilde{\gamma})^2 \Delta_1^2},$$
$$0 \le k \le \pi / 2 \qquad (21)$$

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

$$\frac{\gamma + \tilde{\gamma}}{\pi} \int_0^{\pi/2} (\varepsilon_k^{(2)})^{-1} dk = 1. \qquad (22)$$

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

$$C_{k\sigma,a}^{(i)}(\mu) = C_{k\sigma,b}^{(i)}(\mu) = C_{k\sigma}^{(i)}(\mu), \qquad (23)$$

where $C_{k\sigma}^{(i)}$ are determined by (14) if ξ_k is substituted by

$$\xi_k = \left[2\beta \cos k + \sqrt{4\beta^2 \cos^2 k + (\gamma + \tilde{\gamma})^2 \Delta_1^2} \right] / \Delta_1 (\gamma + \tilde{\gamma}). \qquad (24)$$

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

$$\Psi_0^{(UHF)} = \prod_{k\sigma} \hat{A}_{k\sigma}^{(1)+} \hat{B}_{k\sigma}^{(1)+} \left| 0 \right\rangle. \qquad (25)$$

Using (17) and (25) one can obtain the expression for the ground state energy

$$E_0^{(UHF)} = \left\langle \Psi_0^{(UHF)} \middle| \hat{H} \middle| \Psi_0^{(UHF)} \right\rangle =$$
$$= 4 \sum_{k \le \pi/2} \left(1 - \frac{1}{2} \delta_{k,\pi/2} \right) \varepsilon_k^{(1)} +$$
$$+ N \left[2\alpha + \tilde{\tilde{\gamma}} + \frac{\gamma - \tilde{\gamma}}{2} + 2(\gamma + \tilde{\gamma}) \Delta_1^2 \right]. \qquad (26)$$

Atomic populations are defined as

$$n_{\mu\sigma}^{(a)} = n_{\mu\sigma}^{(b)} = \frac{1}{2} + (-1)^{\mu+1} \tau_\sigma \, \delta_\mu, \qquad (27)$$

where

$$\delta_\mu = \frac{2(\gamma + \tilde{\gamma}) \Delta_1}{\pi} \int_0^{\pi/2} dk [4\beta^2 \cos^2 k +$$
$$+ (\gamma + \tilde{\gamma})^2 \Delta_1^2]^{-1/2} \sin^2 \mu k. \qquad (28)$$

The analysis of (28) allows to reveal the dependence of δ_μ on μ

$$(\beta = -3.6 eV, \gamma = 5.4 eV, \tilde{\gamma} = 0.5 eV \text{ [33]})$$

$$\delta_1 = 0.16, \quad \delta_2 = 0.07,$$
$$\delta_3 = 0.13, \ldots \quad \delta_\mu = \Delta_1 = 0.11. \quad (\mu \gg 1) \qquad (29)$$

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 (23), which can be obtained by proper transformation of (21), namely:

$$\left(\varepsilon_k^{(i)} + \tilde{\tilde{\gamma}} + \frac{\gamma - \tilde{\gamma}}{2} + \alpha \right) C_{k\sigma,a}^{(i)}(\mu) = \sum_{\nu=1}^{N} \hat{H}_{\sigma,a}^{(UHF)}(\mu,\nu) C_{k\sigma,a}^{(i)}(\nu)$$
$$\equiv \beta [(1 - \delta_{\mu,1}) C_{k\sigma,a}^{(i)}(\mu - 1) + (1 - \delta_{\mu,N}) C_{k\sigma,a}^{(i)}(\mu + 1)] +$$
$$+ [\alpha + \gamma n_{\mu,-\sigma}^{(a)} - \tilde{\gamma} n_{\mu,-\sigma}^{(b)} + \tilde{\tilde{\gamma}} n_\mu^{(b)}] C_{k\sigma,a}^{(i)}(\mu). \qquad (30)$$

To obtain the equations for $C_{k\sigma,b}^{(i)}$ it is necessary to permute markings *a* and *b* in (30).

Now let us consider cumulenes taking into account the end-effects. In the conformation $A_{\parallel}$ with symmetry D_{2h} the subsystem *a* contains *N* π-electrons and the subsystem *b* contains $N - 2$ π-electrons. In the conformation $A_{\perp}$ 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 (30) 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

$$\alpha_{\nu\sigma}^{(a)} = \alpha + \gamma n_{\nu,-\sigma}^{(a)} - \tilde{\gamma} n_{\nu\sigma}^{(b)} + \tilde{\tilde{\gamma}} n_\nu^{(b)},$$
$$\alpha_{\nu\sigma}^{(b)} = \alpha + \gamma n_{\nu,-\sigma}^{(b)} - \tilde{\gamma} n_{\nu\sigma}^{(a)} + \tilde{\tilde{\gamma}} n_\nu^{(a)}. \qquad (31)$$

It follows from (31) and (29) that the effective Coulomb integrals of the end-atoms 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* [36]. 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 (31) 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 (29) and (31) one can obtain for the longer subsystem

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

and for the shorter subsystem

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

Thus, the end-effects in cumulenes are of a local nature and can be considered by means of the local perturbation theory, which was applied to long polyenes in the framework of the UHF method in [1].

The ratio $|\Delta\alpha_{\mu\sigma}^{(i)}/\beta| = |\lambda_{\mu\sigma}^{(i)}|$ is a parameter which defines the relative magnitude of a local perturbation. It follows from evaluations given above that $\mathrm{Max}|\lambda_{\mu\sigma}^{(i)}| \le 0.08$, *i. e.* the perturbation due to the end-effects in cumulenes is small enough. It was already shown in [1] that small local perturbation do not disturb the self-consistency of the UHF Hamiltonian (accurate within $\sim\lambda$). Therefore, let us consider the electronic structure of cumulenes in the conformations $A_{\|}$ 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. (21).

Let us evaluate the difference between the ground state energy of a long cumulene chain in the conformation $A_{\|}$ and that in the conformation $A_{\perp}$: $\Delta E = E_{\|} - E_{\perp}$. The value of ΔE is usually referred to as the torsion barrier of cumulene end-groups. Using the relations (17) and (25), one can obtain

$$\Delta E = \sum_{k\sigma}[\varepsilon_k^{(1)}]_N + \sum_{k\sigma}[\varepsilon_k^{(1)}]_{N-2} - 2\sum_{k\sigma}[\varepsilon_k^{(1)}]_{N-1} + \\ + N(\gamma+\tilde{\gamma})[(\Delta_1)_N^2 + (\Delta_1)_{N-2}^2 - 2(\Delta_1)_{N-1}^2], \tag{32}$$

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

$$\frac{\gamma+\tilde{\gamma}}{\pi}\sum_{i=1}^{N/2}\left[4\beta^2\cos^2\left(i\frac{\pi}{N+1}\right) + (\gamma+\tilde{\gamma})^2\Delta_1^2\right]^{-1/2} = 1. \tag{33}$$

In order to evaluate Eq. (32) it is important to note that if $f(k)$ is a continuous function of *k* then

$$f\left(\frac{a}{N+1}\right) + f\left(\frac{a}{N-1}\right) - 2f\left(\frac{a}{N}\right) = \mathrm{O}\left(\frac{1}{N^2}\right). \tag{34}$$

It follows from Eqs (34), (21), and (33) that $\Delta E = \mathrm{O}(1/N)$, *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 $\sim 1/N$ 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 § 5 in [1], 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 $\sim a\lambda^2$, 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 in [1] 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 $A_{\|}$ 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 (27) 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 $A_{\|}$ 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 $A_{\|}$ is a singlet one (*S* = *M* = 0) and its EHF wave function, as will be shown below, has the following form

$$\Psi_{A_{\|}}^{(EHF)} = \hat{O}_{S=M=0}\hat{\mathrm{A}}\phi_{A_{\|}}\ \chi_{A_{\|}}, \tag{35}$$

where $\hat{\mathrm{A}}$ is the antisymmetrization operator be specified later,

$$\phi_{A_{\|}} = \prod_{i=1}^{n_a}\varphi_{i\uparrow,a}^{(1)}(i)\prod_{i=1}^{n_b}\varphi_{i\uparrow,b}^{(1)}(i+n_a)\times \\ \times\prod_{i=1}^{m_a}\varphi_{i\downarrow,a}^{(1)}(i+n)\prod_{i=1}^{m_b}\varphi_{i\downarrow,b}^{(1)}(i+n+m_a), \tag{36}$$

$$\varphi^{(l)}_{i\sigma,j} \equiv \varphi^{(l)}_{k_i,\sigma}, \quad k_i = i\pi/(N+1),$$
$$\chi_{A_\parallel} = \alpha(1)\alpha(2)\cdots\alpha(n)\beta(n+1)\beta(n+2)\cdots\beta(n+m),$$
$$m = m_a + m_b, \quad n = n_a + n_b,$$
$$n_a = m_a = N/2, \quad n_b = m_b = \frac{N}{2} - 1. \qquad (37)$$

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 $|M_a| = |M_b| = 1/2$. To determine the total spin projection of the cumulene $M = M_a + M_b$ we shall consider the Eqs (19) 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 (19). It follows from the relation $\Delta_a = \Delta_b$ and (19) 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

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

where $\phi_{A_\perp}$ and $\chi_{A_\perp}$ are defined by Eqs (36) and (37) 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 (23) and (24) according to the UHF method one can obtain in the two conformations of cumulenes

$$\rho^{(UHF)}_z(\mu) =$$
$$= (-1)^{\mu+1}\frac{2(\gamma+\tilde{\gamma})\Delta_1}{\pi}\times$$
$$\times\int_0^{\pi/2} dk[\varepsilon_k^2]^{-1}[\sin^2 k\mu + \sin^2 k(\mu-1)] =$$
$$= (-1)^{\mu+1}2(\delta_\mu + \delta_{\mu-1}). \qquad (38)$$

To obtain spin populations in the framework of the EHF method one should multiply (38) by the factor $S/(S+1)$ in accordance to the relation (52) below. So, the AO spin populations in long cumulene chains C$_N$H$_4$ with an even number *N* vanish identically in the conformation $A_\parallel$. But, they differ from zero in the conformation $A_\perp$ and are equal to

$$\rho^{(EHF)}_z(\mu) = \frac{1}{2}\rho^{(UHF)}_z(\mu) =$$
$$= (-1)^{\mu+1}(\delta_\mu + \delta_{\mu-1}) \approx 0.22\times(-1)^{\mu+1}. \quad (\mu \gg 1)$$

3. 3. 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 in [1])

$$\Psi^{(EHF)}_0 = \hat{O}_{S,M}\Psi^{(UHF)}_0 = \hat{O}_{S,M}\hat{\mathrm{A}}\phi_0\,\chi_0, \qquad (39)$$

where

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

$$\chi_0 = \alpha(1)\alpha(2)\cdots\alpha(n)\beta(n+1)\beta(n+2)\cdots\beta(n+m). \qquad (40)$$

$\hat{O}_{S,M}$ is the operator of the projection on the state with the multiplicity 2*S* + 1,

$M = (n-m)/2$, $\hat{\mathrm{A}} = \sum_\tau \xi_\tau \hat{\tau}$ is the antisymmetrization operator. In the EHF method the ground state energy of a many electron system has the form

$$E^{(EHF)}_0 = \left\langle \Psi^{(EHF)}_0 \middle| \hat{H} \middle| \Psi^{(EHF)}_0 \right\rangle / \left\langle \Psi^{(EHF)}_0 \middle| \Psi^{(EHF)}_0 \right\rangle = T00^{-1}\times$$
$$\times\left\{\begin{aligned} &\sum_{i\sigma}\langle i\sigma|\hat{h}_1|i\sigma\rangle T01(i) + \frac{1}{2}\sum_{ij\sigma}T21(i,j)\left[\sum_{\sigma'}\langle i\sigma, j\sigma'|\,\hat{g}_{12}\,|i\sigma, j\sigma'\rangle - \sum_{\sigma'}\langle i\sigma, j\sigma|\,\hat{g}_{12}\,|j\sigma, i\sigma\rangle\right] \\ &+\sum_{i\sigma}\langle i\sigma|\hat{h}_1|i,-\sigma\rangle T11(i) + \frac{1}{2}\sum_{i\sigma}\langle i\sigma|\hat{h}_1|i,-\sigma\rangle T11(i) + \frac{1}{2}\sum_{ij}[T12(i,j)S_1(i,j) + T22(i,j)S_2(i,j)] \end{aligned}\right\}, \quad (41)$$

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

$$\left\langle \varphi_{i\sigma} \middle| \varphi_{j\sigma'} \right\rangle \equiv \langle i\sigma|\,j\sigma'\rangle = [\lambda_i + (1-\lambda_i)\delta_{\sigma\sigma'}]\delta_{ij}, \qquad (42)$$

if $S = M$, then

$$TIJ = \sum_{p=0}^{m-J} A_p \binom{n}{p+I}^{-1},$$
$$TIJ(i) = TIJ\,|_{x_i=0}, \qquad (43)$$
$$TIJ(i,j) = TIJ\,|_{x_i=x_j=0},$$

$$A_p = \sum_{\substack{(k_1,k_2,\ldots,k_p)\\(k_i\neq k_j)}} x_{k_1}x_{k_2}\cdots x_{k_p}, \quad (x_k = \lambda_k^2), \qquad (44)$$

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

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

$$\frac{TIJ}{T00} = \frac{TIJ(i)}{T00} = \frac{TIJ(i,j)}{T00} = 0 \qquad (45)$$

are valid with $I, J = 1, 2$ then the expression (41) coincides with $\left\langle \Psi^{(UHF)}_0 \middle| \hat{H} \middle| \Psi^{(UHF)}_0 \right\rangle$, i.e. $E^{(UHF)}_0 = E^{(EHF)}_0$. It is shown [37 – 39] that the relations (45) are valid for the limit case $n \approx m \to \infty$ in the one-parameter AMO method $(x_i = x,\ \ 0 < x < 1)$. In that case one may write

$$\tilde{T}0J \approx T00 \approx 1/(1-x),$$
$$\tilde{T}1J \approx \frac{1}{m}\frac{d}{dx}(T00),$$
$$\tilde{T}2J \approx \frac{1}{m(m-1)}\frac{d^2}{dx^2}(T00), \qquad (46)$$

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 (44) to the form

$$A_p = \binom{m}{p} t_p^p,$$

where

$$t_p = \left[\binom{m}{p}^{-1} \sum_{\substack{(k_1,k_2,\dots,k_p)\\(k_i \neq k_j)}} x_{k_1} x_{k_2} \cdots x_{k_p} \right]^{1/p}, \qquad (47)$$

Since, according to (42) $0 < x_i < 1$, then [40]

$$t_1 \geq t_2 \geq \cdots \geq t_m. \qquad (48)$$

Taking into account that all terms in (43) are positive and using (47) and (48) one can obtain

$$\tilde{T}IJ\,|_{x=t_m} \leq \tilde{T}IJ \leq \tilde{T}IJ\,|_{x=t_1}. \qquad (49)$$

It follows from (46), (49), and (43) that the relations (45) are also valid in the framework of the multi-parameter AMO method for the limit case $n \approx m \to \infty$. Thus, the relation

$$E_0^{(EHF)} = E_0^{(UHF)} \qquad (50)$$

is valid in general if the system under consideration consists of a large number of electrons. Besides, it follows from equation (50) 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 in [1]) obtained by Goddard.

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

$$\rho_z^{(EHF)}(\vec{R}) \equiv \left\langle \Psi_0^{(EHF)} \left| \sum_{i=1}^{N} 2\hat{S}_z(i)\,\delta(\vec{r}_i - \vec{R}) \right| \Psi_0^{(EHF)} \right\rangle / T00 =$$
$$= \frac{S}{S+1} T00^{-1} \sum_{i=1}^{m} \{ [|\varphi_{i\uparrow}(\vec{R})|^2 - |\varphi_{i\downarrow}(\vec{R})|^2]\, T01(i) +$$
$$+ [2|\varphi_{i\uparrow}(\vec{R})| - \lambda_i \varphi_{i\downarrow}^*(\vec{R})\varphi_{i\uparrow}(\vec{R}) - \lambda_i^* \varphi_{i\uparrow}^*(\vec{R})\varphi_{i\downarrow}(\vec{R})]\, T11(i) \} +$$
$$+ \frac{S}{S+1} T00^{-1} \sum_{i=m+1}^{n} |\varphi_{i\uparrow}(\vec{R})|^2\ (2T10 + T00); \qquad (51)$$

in the analogous spin density expressions [41, 42] there seems to be a mistake in the coefficients in the last term in (51).

Using (45) one can obtain from (51) for the case $N \to \infty \quad (n \approx m \to \infty)$

$$\rho_z^{(EHF)}(\vec{R}) = \frac{S}{S+1} \left[\sum_{i=1}^{n} |\varphi_{i\uparrow}(\vec{R})|^2 - \sum_{i=1}^{m} |\varphi_{i\downarrow}(\vec{R})|^2 \right] =$$
$$= \frac{S}{S+1} \rho_z^{(UHF)}(\vec{R}). \qquad (52)$$

For long polyene chain from (42) and (14) one obtains

$$x_k = \lambda_k^2 = \cos^2 k / (\cos^2 k + d^2), \qquad (53)$$

where $d = \Delta\gamma / 2|\beta|$. Using (47) and (53) let us evaluate the values of t_1 and t_m for this case, namely:

$$t_1 = \frac{1}{m}\sum_k x_k = \frac{2}{\pi}\int_0^{\pi/2} dk \cos^2 k / (\cos^2 k + d^2) \approx 0.77,$$
$$\ln t_m = \frac{1}{m}\sum_k \ln x_k = \frac{2}{\pi}\int_0^{\pi/2} dk \ln[\cos^2 k / (\cos^2 k + d^2)], \qquad (54)$$

hence

$$t_m = [1 + 2d^2 + 2\sqrt{d(1+d)}]^{-1} \approx 0.55. \qquad (55)$$

So far $t_1 \neq 0$ and $t_m \neq 0$, then the relation (50) in case of polyenes immediately follows from (55), (46), and (49). So, the orbitals $\varphi_{k\sigma}^{(i)}$ are self-consistent 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 (§ 4 in [1]) according to Eq. (52).

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

$$\omega_{S=M} = \frac{2S+1}{n+1} T00 \approx 2\frac{2S+1}{N}\frac{1}{1-\tilde{x}}, \qquad (56)$$

where $t_1 \geq \tilde{x} \geq t_m$. It is interesting to note that using the Gaussian approximation supposed by van Leuven [43, 44] one can obtain

$$\omega_{S=0} = \int_0^{\infty} \exp\left[-\theta \frac{m(1-t_1)}{4}\right] \sin\theta\, d\theta = \frac{2}{N}\frac{1}{1-t_1}. \qquad (57)$$

It follows from (57) that the Gaussian approximation gives the same value of ω_S as the approximation used for this purpose in [6]. Comparing (57) with the exact expression (56) one can see that the approximation (57) correctly reflects the asymptotic behaviour of ω_S when $N \to \infty$ (except for the constant). It should be noted that the relation (50) can be obtained also by means of the rotation group theory [43]. However, using this method we lose some important details, *e. g.* it is impossible to obtain the asymptotic form (52) for the spin density expression (51).

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 $\Psi_0^{(EHF)}$:

$$\left\langle \Psi_0^{(EHF)} \middle| \Psi_{(k\sigma)}^{(EHF)} \right\rangle = -\tau_\sigma \lambda_k T11(k)\sqrt{1-\lambda_k^2}\,. \tag{58}$$

But, when $N \to \infty$ it follows from (45) that

$$\frac{\left\langle \Psi_{(k\sigma)}^{(EHF)} \middle| \Psi_0^{(EHF)} \right\rangle}{\left\langle \Psi_0^{(EHF)} \middle| \Psi_0^{(EHF)} \right\rangle} = \frac{\left\langle \Psi_{(k\sigma)}^{(EHF)} \middle| \Psi_0^{(EHF)} \right\rangle}{\left\langle \Psi_{(k\sigma)}^{(EHF)} \middle| \Psi_{(k\sigma)}^{(EHF)} \right\rangle} \approx \frac{1}{N}\Big|_{N\to\infty} \to 0\,. \tag{59}$$

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

$$\begin{aligned} E_{(k\sigma)}^{(EHF)} &= \left\langle \Psi_{(k\sigma)}^{(EHF)} \middle| \hat{H} \middle| \Psi_{(k\sigma)}^{(EHF)} \right\rangle / T00 = \\ &= E_{(k\sigma)}^{(UHF)} = E_0^{(UHF)} + 2\varepsilon_k^{(2)}. \end{aligned} \tag{60}$$

To summarize, the ground state energy, energies of the lowest excitations and the the SCF equations for large systems ($N \gg 1$) 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 (39).

3. 4. 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 CH_2 of long cumulene chain C_NH_4 ($N \gg 1$) are placed at the large distance from one another. On the other hand, the simple MO methods give $\Delta E \to 0 (N \to \infty)$ 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 [45]. 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.

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

It has been first stated by Mott [46–54] 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 [54–56]. 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 and A are being the ionization potential and electron affinity correspondingly). The value of this important parameter should be ~10 *eV* in the case of isolated small atoms, but some factors in real systems like polarizability of the given elementary unit (CH_2 group in polyenes, TCNQ fragment in charge transfer salts) or of the neighbouring elementary units [57] reduce this gap to $\Delta \approx 3-4 eV$ 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 $\sim 4|\beta|$, where β being the resonance integral. In the case of $\Delta/|\beta| \gg 1$, 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 $\Delta/|\beta| \ll 1$, the exchange broadening is larger than the energy gap which leads to the metal type structure of the excitation spectrum of the 3d-crystal. 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 [58–60]. As a result one gets an initially continuous band of allowed states split in two bands with a forbidden zone of the width $\sim|\beta_1 - \beta_2|$, 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 [61], 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 [62–73].

The following question naturally arises: what will happen if $|\beta|$ and Δ are of the same order of magnitude? Concerning some similar problems [74, 75] 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 [76, 77]. 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

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

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 [59, 60] 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.

4. 1. Peierls and Mott Instabilities at *T*=0° *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:

$$\begin{aligned}\hat{H} = {} & \alpha\sum_{n\sigma}\hat{A}^{+}_{n\sigma}\hat{A}_{n\sigma} + \\ & +\sum_{n\sigma}[\beta-(-1)^{n}\Delta\beta](\hat{A}^{+}_{n\sigma}\hat{A}_{n-1,\sigma}+\hat{A}^{+}_{n+1,\sigma}\hat{A}_{n\sigma}) + \\ & +U\sum_{n}\hat{A}^{+}_{n\alpha}\hat{A}_{n\alpha}\hat{A}^{+}_{n\beta}\hat{A}_{n\beta} + \\ & +\frac{\gamma_{12}}{2}\sum_{n\sigma\sigma'}\hat{A}^{+}_{n\sigma}\hat{A}_{n\sigma}(\hat{A}^{+}_{n+1,\sigma'}\hat{A}_{n+1,\sigma'}+\hat{A}^{+}_{n-1,\sigma'}\hat{A}_{n-1,\sigma'}), \quad (61)\end{aligned}$$

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 (61) 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:

$$\left.\begin{aligned}\hat{A}^{+}_{n\sigma} &= \frac{1}{\sqrt{N}}\sum_{k}\hat{B}^{+}_{k\sigma}e^{-ink}\\ \hat{A}_{n\sigma} &= \frac{1}{\sqrt{N}}\sum_{k}\hat{B}_{k\sigma}e^{ink}\end{aligned}\right\}, k = \frac{n\pi}{N}, n = \pm 1, \pm 2, ..., \pm N. \quad (62)$$

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

$$\begin{aligned}&[\hat{B}^{+}_{k\sigma},\hat{B}^{+}_{k'\sigma'}]_{+} = [\hat{B}_{k\sigma},\hat{B}_{k'\sigma'}]_{+} = 0,\\ &[\hat{B}^{+}_{k\sigma},\hat{B}_{k'\sigma'}]_{+} = \delta_{kk'}\delta_{\sigma\sigma'}. \quad (63)\end{aligned}$$

The inverse relations are

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

$$\hat{B}_{k\sigma} = \frac{1}{\sqrt{N}}\sum_{n}\hat{A}_{n\sigma}e^{-ink}. \quad (64)$$

Transforming the Hamiltonian (62) to the new operators, one obtains

$$\begin{aligned}\hat{H} = {} & 2\beta\sum_{k}\hat{B}^{+}_{k\sigma}\hat{B}_{k\sigma}\cos k + 2i\,\Delta\beta\sum_{k}\hat{B}^{+}_{k\sigma}\hat{B}_{k+\pi,\sigma}\sin k\\ & +\frac{U}{N}\sum_{k\,k'q}\hat{B}^{+}_{k+q,\alpha}\hat{B}_{k\alpha}\hat{B}^{+}_{k'-q,\beta}\hat{B}_{k'\beta} + \\ & +\frac{\gamma_{12}}{N}\sum_{k_1+k_3=k_2+k_4}\hat{B}^{+}_{k_1\sigma}\hat{B}_{k_2\sigma}\hat{B}^{+}_{k_3\sigma'}\hat{B}_{k_4\sigma}\cos(k_1-k_2). \quad (65)\end{aligned}$$

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 (64) 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 (65).

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 (65) 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 (65) only two terms should be left:

(i) the q=0 term, namely:

$$\frac{U}{N}\sum_{kk'}\hat{B}^{+}_{k\alpha}\hat{B}_{k\alpha}\hat{B}^{+}_{k'\beta}\hat{B}_{k'\beta}\ . \tag{66}$$

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 (66) by the C number $UN/4$; and (ii) the q=π term, namely:

$$\frac{U}{N}\sum_{kk'}\hat{B}^{+}_{k+\pi,\alpha}\hat{B}_{k\alpha}\hat{B}^{+}_{k'+\pi,\beta}\hat{B}_{k'\beta}\equiv UN\hat{\Delta}_\alpha\hat{\Delta}_\beta\,, \tag{67}$$

where

$$\hat{\Delta}_\alpha=\frac{1}{N}\sum_{k}\hat{B}^{+}_{k+\pi,\alpha}\hat{B}_{k\alpha}\ , \tag{68}$$

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. (64). Then one obtains

$$\hat{\Delta}_\sigma=\frac{1}{N}\sum_{n}(-1)^n\hat{A}^{+}_{n\sigma}\hat{A}_{n\sigma}\,. \tag{69}$$

Equation (69) 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 (65) allows ua to consider the Peierls instability.

In the last term of (65) we preserve the following four terms:

(i) $k_1=k_2$, namely,

$$\frac{\gamma_{12}}{N}\sum_{k_1,k_3,\sigma,\sigma'}\hat{B}^{+}_{k_1\sigma}\hat{B}_{k_1\sigma}\hat{B}^{+}_{k_3\sigma'}\hat{B}_{k_3\sigma}\ , \tag{70}$$

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,

$$-\frac{\gamma_{12}}{N}\sum_{k_1,k_2',\sigma,\sigma'}\hat{B}^{+}_{k_1\sigma}\hat{B}_{k_1\sigma'}\hat{B}^{+}_{k_2\sigma'}\hat{B}_{k_2\sigma}\cos(k_1-k_2)\,, \tag{71}$$

which is the usual exchange term;

(iii) $k_1=k_2+\pi$, namely,

$$-\frac{\gamma_{12}}{N}\sum_{k_1,k_3,\sigma,\sigma'}\hat{B}^{+}_{k_1\sigma}\hat{B}_{k_1+\pi,\sigma}\hat{B}^{+}_{k_3\sigma'}\hat{B}_{k_3+\pi,\sigma'}\ , \tag{72}$$

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 (65) and (67), thus we continue to keep the terms of this kind); and finally

(iv) $k_1=k_4+\pi$, namely,

$$-\frac{\gamma_{12}}{N}\sum_{k_1,k_3,\sigma,\sigma'}\hat{B}^{+}_{k_1+\pi,\sigma}\hat{B}_{k_1,\sigma'}\hat{B}^{+}_{k_2+\pi,\sigma'}\hat{B}_{k_2,\sigma}\cos(k_1-k_2)\,, \tag{73}$$

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,

$$\langle\hat{B}^{+}_{k\sigma}\hat{B}_{k\sigma'}\rangle\approx\delta_{\sigma\sigma'},\quad \langle\hat{B}^{+}_{k\sigma}\hat{B}_{k\sigma}\sin k\rangle=0,$$
$$\langle\hat{B}^{+}_{k\sigma}\hat{B}_{k+\pi,\sigma}\cos k\rangle=0.$$

Introducing two new operators

$$\hat{\xi}_\sigma=\frac{1}{N}\sum_{k}\hat{B}^{+}_{k\sigma}\hat{B}_{k+\pi,\sigma}\sin k,$$
$$\hat{\eta}_\sigma=\frac{1}{N}\sum_{k}\hat{B}^{+}_{k\sigma}\hat{B}_{k\sigma}\cos k, \tag{74}$$

one ia able to rewrite the reduced Hamiltonian in the form

$$\hat{H}=2\beta\sum_{\sigma}\hat{\eta}_\sigma+2\Delta\beta\sum_{\sigma}\hat{\xi}_\sigma+$$
$$+\frac{U-2\gamma_{12}}{2}\sum_{\sigma}\hat{\Delta}_\sigma\hat{\Delta}_{-\sigma}-\gamma_{12}\sum_{\sigma}(\hat{\eta}^2_\sigma+\hat{\Delta}^2_\sigma+\hat{\xi}^2_\sigma)\,. \tag{75}$$

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 [78, 79], its SCF solution for a large system ($N\to\infty$) asymptotically coinsides with the exact one. Thus, what we have to do now is to solve the wave equation with Hamiltonian (75) 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

$$\hat{b}_{k\sigma}=U_{k\sigma}\hat{B}_{k\sigma}+V_{k\sigma}\hat{B}_{k+\pi,\sigma} \tag{76}$$

to define the new operators $\hat{b}^{+}_{k\sigma},\hat{b}_{k\sigma}$, satisfying the equation of motion

$$[\hat{b}_{k\sigma},\hat{H}]=\lambda_{k\sigma}\hat{b}_{k\sigma}\,. \tag{77}$$

If the coefficients $U_{k\sigma},V_{k\sigma}$ in (76) are found to satisfy Eq. (77), then the transformation (77) diaginalize Hamiltonian (75).

Requiring the new operators (76) to be of the Fermi-type

$$[\hat{b}^{+}_{k\sigma}, \hat{b}_{k'\sigma'}]_{+} = \delta_{kk'}\,\delta_{\sigma\sigma'}, \tag{78}$$

one obtains the following relation for $U_{k\sigma}, V_{k\sigma}$:

$$|U_{k\sigma}|^2 + |V_{k\sigma}|^2 = 1. \tag{79}$$

Substituting Eqs (76) and (75) into (77), and performing the calculations required using (78), 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 (79), one obtains the solution in the form

$$\lambda_{k\sigma} = \pm(4\tilde{\beta}^2\cos^2 k + 4\Delta\tilde{\beta}^2\sin^2 k + U^2\left\langle\Delta_{-\sigma}\right\rangle^2)^{1/2}, \tag{80}$$

$$|U_{k\sigma}|^2 = \frac{1}{2} \pm \frac{\tilde{\beta}\ \cos\ k}{(4\tilde{\beta}^2\cos^2 k + 4\Delta\tilde{\beta}^2\sin^2 k + U^2\left\langle\Delta_{-\sigma}\right\rangle^2)^{1/2}},$$

$$|V_{k\sigma}|^2 = \frac{1}{2} \mp \frac{\tilde{\beta}\ \cos\ k}{(4\tilde{\beta}^2\cos^2 k + 4\Delta\tilde{\beta}^2\sin^2 k + U^2\left\langle\Delta_{-\sigma}\right\rangle^2)^{1/2}}, \tag{81}$$

where

$$-\frac{\pi}{2} < k < \frac{\pi}{2}, \quad \tilde{\beta} = \beta - \gamma_{12}\left\langle\hat{\eta}_\sigma\right\rangle,$$
$$\Delta\tilde{\beta} = \Delta\beta - \gamma_{12}\left\langle\xi_\sigma\right\rangle. \tag{82}$$

To make the solution complete, we have to calculate $\left\langle\Delta_\sigma\right\rangle$, $\left\langle\hat{\eta}_\sigma\right\rangle$, and $\left\langle\xi_\sigma\right\rangle$, 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. (80), *i.e.* the ground state has the form

$$\psi_0 = \prod_{i=1}^{N} {}^{(-)}\hat{b}^{+}_{k_i}\left|0\right\rangle, \tag{83}$$

where the operators ${}^{(-)}\hat{b}^{+}_{k}$ are defined by Eqs (76) and (81) with the lower sign in (81).

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 (74) to average Δ_σ, $\hat{\eta}_\sigma$, and ξ_σ over the ground state (83). 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 $\left\langle\Delta_\sigma\right\rangle$, $\left\langle\hat{\eta}_\sigma\right\rangle$, and $\left\langle\xi_\sigma\right\rangle$:

$$\frac{U}{\pi}\int_0^{\pi/2}\frac{dk}{\sqrt{\tilde{\varepsilon}^2(k) + U^2\left\langle\Delta_\sigma\right\rangle^2}} = 1,$$

$$\tilde{\beta} = \beta\left(1 - \frac{2\gamma_{12}}{\pi}\int_0^{\pi/2}\frac{\cos^2 k\,dk}{\sqrt{\tilde{\varepsilon}^2(k) + U^2\left\langle\Delta_\sigma\right\rangle^2}}\right)^{-1},$$

$$\Delta\tilde{\beta} = \Delta\beta\left(1 + \frac{2\gamma_{12}}{\pi}\int_0^{\pi/2}\frac{\sin^2 k\,dk}{\sqrt{\tilde{\varepsilon}^2(k) + U^2\left\langle\Delta_\sigma\right\rangle^2}}\right)^{-1}, \tag{84}$$

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 $\gamma_{12} \ll \beta, U$ it breaks into

$$\Delta\tilde{\beta} \approx \Delta\beta, \quad \tilde{\beta} \approx \beta,$$

and

$$\frac{U}{\pi}\int_0^{\pi/2}\frac{dk}{\sqrt{\varepsilon^2(k) + U^2\left\langle\Delta_\sigma\right\rangle^2}} = 1, \tag{85}$$

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 [33]

$$\frac{U}{\pi}\int_0^{\pi/2}\frac{dk}{\sqrt{4\beta^2\cos^2 k + U^2\left\langle\Delta_\sigma\right\rangle^2}} = 1. \tag{86}$$

As has been stated in [87], Eq. (86) has a nonzero solution $\left\langle\Delta_\sigma\right\rangle \neq 0$ for all values of the parameters, which we will denote as Δ_0.

Let us now return to the general case of Eq. (85), assuming that

$$\beta(\delta x) = \beta_0 e^{-\alpha\delta x},$$

where δx denotes displacement from the regular, equal-bond configuration. Thus, Eq. (85) may be rewritten as

$$\frac{U}{\pi}\int_0^{\pi/2}\frac{dk}{\sqrt{(\beta_1 - \beta_2)^2 + 4\beta_0^2\cos^2 k + U^2\left\langle\Delta_\sigma\right\rangle^2}} = 1. \tag{87}$$

Comparing (87) with (86) one easily concludes that if Δ_0 is the solution of (86) then the solution of (87) is given by

$$2U^2\left\langle\Delta_\sigma\right\rangle^2 + (\beta_1 - \beta_2)^2 = U^2\left\langle\Delta_\sigma\right\rangle_0^2,$$

so that

$$\left\langle\Delta_\sigma\right\rangle^2 = \left\langle\Delta_\sigma\right\rangle_0^2 - \frac{1}{2}\left(\frac{\beta_1 - \beta_2}{U}\right)^2. \tag{88}$$

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 (75) and (80)–(83) into the usual expression for the total electronic energy in the ground state

$$\bar{E}_{el} = \left\langle\psi_0\right|\hat{H}\left|\psi_0\right\rangle,$$

one obtains

$$\bar{E}_{el} = \frac{U}{4} + \sum_k \lambda_k + U\Delta^2. \tag{89}$$

It is important to recognize that according to (80) and (88)

$$\lambda_k(\beta_1-\beta_2)^2/U$$

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 (89) in the form

$$\bar{E}_{el} = E_0 - E_1(\delta x)^2 . \qquad (90)$$

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

$$E = E_0 + \alpha(\delta x)^2 . \qquad (91)$$

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 (86) 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 (88), 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. (84) and (86), 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 [61]. 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 [58–60]. 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

$$\Delta_{alt} = 8\beta_0 e^{-\kappa/2\beta} . \qquad (92)$$

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 $U \gg |\beta|$, 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 $U < |\beta|$.

4. 2. 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 [59].

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

$$\bar{\hat{A}} = Sp\hat{A}e^{-\hat{H}/kT} / Sp\, e^{-\hat{H}/kT} . \qquad (93)$$

Bearing in mind that the Hamiltonian expressed in terms of the operators $\hat{b}_k^+, \hat{b}_k$ at (76) – (82) is diagonal, standard equation (93) is reduced to

$$\bar{\hat{A}} = \sum_{k,l} \eta_{kl,\sigma}(T) \langle kl\sigma | \hat{A} | kl\sigma \rangle , \qquad (94)$$

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. (78)), hence

$$\eta_{kl,\sigma}(T) = \{\exp[\varepsilon_{kl,\sigma}/kT]+1\}^{-1}, \quad \varepsilon_{kl,\sigma} \equiv \lambda_{k\sigma} . \qquad (95)$$

For the temperature dependent energy gap playing a central role in all the treatment using Eqs (78) and (94) one obtains

$$\langle \Delta_\sigma \rangle = \frac{1}{N}\sum_{kl} \eta_{kl} \langle \hat{B}^+_{k+\pi,\sigma} \hat{B}_{k\sigma} \rangle . \qquad (96)$$

Substituting Eqs (95) and (76)–(80) into (96) and performing the calculations required which are very similar to those leading to (85) one obtains the following equation determining $\Delta_\sigma(T)$, namely:

$$\frac{U}{2\pi}\int_0^\pi \frac{\mathrm{th}\, E(k)/2kT}{E(k)} dk = 1 , \qquad (97)$$

where

$$E(k) = [(U\Delta)^2 + \varepsilon^2(k)]^{1/2},$$

$$\varepsilon^2(k) = (\beta_1-\beta_2)^2 + 4\beta_0^2 \cos^2 k . \qquad (98)$$

Introducing the density of states, one can transform (97) into the form

$$\frac{U}{\pi}\int_{\Delta}^{\sqrt{\varepsilon^2+\Delta^2}}\frac{\text{th}\,\varepsilon/2kT}{\sqrt{\varepsilon^2+\Delta^2}\sqrt{\varepsilon_F^2+\Delta^2-\varepsilon^2}}d\varepsilon=1, \qquad (99)$$

where the same assumption $\beta(\delta x)\approx\beta_0 e^{-\delta x}$ and notation $\varepsilon_F=|\beta_0|$ have been used, but now

$$\Delta^2=|\beta_1-\beta_2|^2+\langle\Delta_\sigma\rangle^2. \qquad (100)$$

Equation (99) may be considered in the same way as it has been done concerning Eq. (87). The one-electron energy levels which are now temperature dependent are also independent on δx and all the discussion following Eq. (91) 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. (99) 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.

5. Coexistence of Mott and Peierls Instabilities in Quasi-One-Dimensional Systems

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, 1d-metal is unstable to the transition into semiconducting state. As a result the 1d-metal 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 [80], and in the Peierls semiconductors the kink-type excitations are possible [81, 82].

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 [83]. This result was obtained due to more correct treatment of pair electron correlations using varying localized geminals (VLG) approach [84–86]. It was shown that electron – electron interaction can enhance the Peierls dimerization [83]. This somewhat surprising result initiates several theoretical studies [87–92] 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 [90] and the Feynman diagram technique [91]. Numerical calculations of short polyene chains within the same geminals approach conformed this result slightly deformed by boundary conditions [83].

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 [83–86].

5. 1. 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:

$$\begin{aligned}\hat{H}=&\sum_{\sigma,m=1}^{N}\beta_m(\hat{c}^{+}_{m\sigma}\hat{c}_{m+1,\sigma}+\hat{c}^{+}_{m+1,\sigma}\hat{c}_{m\sigma})+\\&+\gamma\sum_m\hat{c}^{+}_{m\uparrow}\hat{c}_{m\uparrow}\hat{c}^{+}_{m\downarrow}\hat{c}_{m\downarrow}+\\&+\gamma_1\sum_m n_m n_{m+1}+\frac{K_\sigma}{2}\sum_m(x_m-x_{m+1})^2,\end{aligned} \qquad (101)$$

where $n_{m\sigma}=\hat{c}^{+}_{m\sigma}\hat{c}_{m\sigma}$, number of sites $N\to\infty$, x_m is the *m*th site displacement, resonance integrals

$$\begin{aligned}&\beta_m=-[\beta+(x_{m+1}-x_m)\beta']=-\beta(1+\Delta_m),\\&\beta,\beta'>0,\end{aligned} \qquad (102)$$

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 half-filled conduction band with the number of electrons $N_e=N$. The Peierls deformation in this case reduces to the chain dimerization

$$x_{m+1}-x_m=(-1)^m x_0,\quad \beta_m=-\beta[1+(-1)^m\Delta]. \qquad (103)$$

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 [80, 93], for [K$^+$–TCNQ] complexes $x_0 = 0.18A$ and a = 3.6 A [94]. For small values of x_0 the linear dependence

$$\Delta = \frac{\beta'}{\beta} x_0 \tag{104}$$

is valid. The increase of displacement $x_0 \to a$ destroys the relation (104) as well as the harmonic adiabatic approach used in (101). Thus, the method used here is valid only for small values of $\Delta \ll 1$.

In this region Hamiltonian (101) is the Frohlich-type Hamiltonian with linear relative to displacements x_m electron – phonon interaction.

Thus, when $\Delta \ll 1$ 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 (104). In other words, we need the Δ-value optimizing the expression

$$\varepsilon_t(\Delta) = \varepsilon_{el}(\Delta) + \frac{1}{2}\frac{\Delta^2}{\kappa}, \tag{105}$$

where ε_{el} is the electronic contribution into the ground state energy per an electron pair, and

$$\kappa = (\beta')^2 / (2K_\sigma \beta). \tag{106}$$

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

$$\Psi_0 = \prod_{m=1}^{M} \hat{G}_m^+ |0\rangle \equiv \prod_{m=1}^{M} (u\,\hat{f}_{m\uparrow}^+ \hat{f}_{m\downarrow}^+ + v\,\hat{\tilde{f}}_{m\uparrow}^+ \hat{\tilde{f}}_{m\downarrow}^+)|0\rangle, \tag{107}$$

where

$$\hat{f}_{m\sigma} = \sqrt{\frac{2}{N}} \sum_{|k|<K_F} \hat{A}_{k\sigma} e^{-ikR_m},$$

$$\hat{\tilde{f}}_{m\sigma} = \sqrt{\frac{2}{N}} \sum_{|k|<K_F} \hat{\tilde{A}}_{k\sigma} e^{-ikR_m}, \tag{108}$$

$$\hat{A}_{k\sigma} = a_{k\sigma} \cos\theta_k + a_{\bar{k}\sigma} i \sin\theta_k,$$

$$\hat{\tilde{A}}_{k\sigma} = a_{\bar{k}\sigma} \cos\theta_k + a_{k\sigma} i \sin\theta_k, \tag{109}$$

$$a_{k\sigma} = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} c_{n\sigma} e^{-ikna}, \tag{110}$$

$$u = \cos\varphi, \quad v = \sin\varphi, \tag{111}$$

$$2\theta_k = \arctan(\lambda \mathrm{tg} ka), \quad k = 2\pi l / Na,$$
$$(l = 0, \pm1, \pm2, \ldots) \tag{112}$$

φ and λ are the variational parameters, the Fermi operators $\hat{f}_{m\sigma}$ and $\hat{\tilde{f}}_{m\sigma}$ correspond to the orbitals $f_{m\sigma}$ and $\tilde{f}_{m\sigma}$ which are partially localized near points

$$R_m = (2m + \delta)a. \tag{113}$$

The ground state energy in units of β per electron pair has the form

$$\varepsilon_{el} = 2t\cos 2\varphi - k_0 \sin 2\varphi - v_1\left(\frac{2}{N}\sum_l |P_l|^2\right)\cos^2 2\varphi, \tag{114}$$

where the kinetic energy average

$$t = \sum_m [1 + (-1)^m \Delta]\, f_m(n) f_m(n+1) =$$
$$= \langle 0|\, \hat{f}_{m\sigma} \hat{T}\, f_{m\sigma}^+ |0\rangle, \tag{115}$$

$$\hat{T} = \sum_m (\hat{c}_{m\sigma}^+ \hat{c}_{m+1,\sigma} + \hat{c}_{m+1,\sigma}^+ \hat{c}_{m\sigma}), \tag{116}$$

the exchange integral

$$K = \langle 0|\, \hat{f}_{m\uparrow} \hat{f}_{m\downarrow} \hat{V}_{ee}\, f_{m\uparrow}^+ f_{m\downarrow}^+ |0\rangle =$$
$$= U\sum_n |f_0(n)|^4 - U_1 \sum_n |f_0(n)|^2 \cdot |f_0(n+1)|^2, \tag{117}$$

$$U = \gamma / \beta, \quad U_1 = \gamma_1 / \beta,$$

average of non-diagonal density or bond order

$$P_l = \langle \Psi_0 | \hat{c}_{l\sigma}^+ \hat{c}_{l+1,\sigma} + \hat{c}_{l+1,\sigma}^+ \hat{c}_{l\sigma} | \Psi_0 \rangle =$$
$$= \sum_m f_m^*(l) f_m(l+1) =$$
$$= \left[\frac{1}{\pi} + (-1)^l \frac{\lambda}{4\pi} \ln\lambda\right] \cos 2\varphi. \tag{118}$$

Now we consider the Hubbard approach $\gamma_1 = 0$ in (101). Then, variation of the energy (314) with respect to φ gives

$$\varepsilon_{el} = -\varepsilon_g + U/2, \tag{119}$$

where

$$\varepsilon_g = \sqrt{4t^2 + K^2}. \tag{120}$$

The values of t, K, P depend on the value of λ [83, 90], so

$$t(\lambda) = -\frac{4}{\pi}\left[E(1-x^2) + (4-\lambda)\frac{\partial E(1-\lambda^2)}{\partial\lambda}\right], \tag{121}$$

where the $E(x)$ is the elliptic integral.

The explicit form of λ-dependence of K

$$K(\lambda) = \frac{U}{3} - \mathrm{Const} \cdot \lambda \cdot \ln\lambda. \tag{122}$$

can be obtained in the limit of small λ. We can see from (122) that when λ and, as a result, U are small the energy dependence (120) 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 $U \to 0$ and $U \to \infty$ will be given.

When $U \to 0$ the non-interacting-electron model is valid and the energy is defined by the value of (121) and its optimization with respect to λ gives $\lambda = \Delta$. The energy minimum corresponds to

$$\Delta_0 = 4\exp(-\pi / 8\kappa)|_{U\to 0} \qquad (123)$$

due to the fact that [83]

$$\varepsilon_t = 2\left(-\frac{4}{\pi} - \frac{2\Delta^2}{\pi}\ln\frac{4}{\Delta}\right) + \frac{\Delta^2}{2\kappa}. \qquad (124)$$

When $U \geq 4$ one can use the simpler approach instead of (112), namely:

$$\theta_k = \tilde{\lambda} k. \qquad (125)$$

Using (325) one obtains [84, 85]

$$\tilde{t}(\lambda) = -\frac{4}{\pi}\frac{\cos\pi\tilde{\lambda}}{1-4\tilde{\lambda}^2},$$

$$\tilde{K}(\lambda) = \frac{U}{3}\left(1+\frac{1}{2}\sin\pi\lambda\right).$$

Substituting $\tilde{t}(\lambda)$ and $\tilde{K}(\lambda)$ in (119) and (105) and optimizing Δ one obtains

$$\Delta_0 = \frac{8\kappa}{U}\left(1-\frac{4}{U^2}\right). \qquad (126)$$

We note that Eqs (121), (122), and (119) describe well the dependence of the total energy on *U* for any value of *U*>0 [84, 85]. 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 (112) to (125) [83].

Now we consider the effect of electron – electron interaction at neighboring sites resulting from the terms with γ_1 in (101). One can conclude from (114) and (118) that γ_1-term increases the amplitude of dimerization. In the limiting case of weak interactions $U_1 < U \to 0$ one obtains

$$\Delta_0(U_1) = \Delta_0|_{U_1=0} \times \exp(\frac{\pi U_1}{24\kappa^2}) =$$
$$= 4\exp(-\frac{\pi}{8\kappa})\cdot\exp(\frac{\pi U_1}{24\kappa^2}). \qquad (127)$$

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 (105) taking into account (119) in the space of Δ_0 and λ variables, namely:

$$E(\lambda,\Delta,U) = -[4t^2(\lambda,\Delta) + K^2(\lambda,U)]^{1/2} + \frac{\Delta^2}{2\kappa}, \quad (128)$$

where *t* and *K* are defined by (115) and (117), respectively. This task is not too complicated, but when $U \gg 1$ some difficulties arise with the increase of the chain length due to the logarithmic Δ-dependence of the electronic energies in (119) and (124). 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,

$$\Delta_0 = \frac{\beta'}{N}\frac{P_l}{K_\sigma}. \qquad (129)$$

Some calculations of PA chains based on formula (129) 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: $\beta = 2.4eV, \beta' = 4eV/A, K_\sigma = 47\,eV/A^2$ [95]. These values are consistent with the parameters available for small conjugated molecules [55, 95] and with frequencies of vibrations active in IR and Raman spectra of PA [95]. Using these values of parameters one obtains from (106) 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 [86] one can write

$$\Delta E = 2[\varepsilon_g - t_0(1+U^2) + T_k U^2], \qquad (130)$$

where

$$T_k = \sum_m e^{ikm}\left\langle f_n\right|\tilde{T}\left| f_{n+m}\right\rangle.$$

The gap value (130) consists of two contributions: correlation contribution ΔE_{corr} and dimerization contribution ΔE_{dim}. When *U* is small one can assume

$$\Delta E_{corr} = 2\varepsilon_g - 2t_0, \quad \Delta E_{\mathrm{dim}} = 4\beta\Delta_0,$$

where ε_g is determined by (120) and t_0 – by (121′).

The dependence of correlation ΔE_{corr} and dimerization contributions ΔE_{dim} on the value of *U* is shown on Fig. 1.

It follows from fig. 1 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 (126) of Δ_0 on *U*. Using data of Fig. 1 one can now reevaluate the parameters of real organic conductors.

We can conclude from experimental data for trans-PA that $\Delta E = 1.9\,eV$ [95]. Using the estimation of the electron – phonon interaction constant $\kappa = 0.07$ above one obtains $U = 2.5$, thus $\gamma = 6.2\,eV$. It is interesting to note that in this region, according to Fig. 1, $\Delta E_{corr} < \Delta E_{\dim}$. Nearly the same situation occurs in PDA where $\Delta E = 2.5\,eV$.

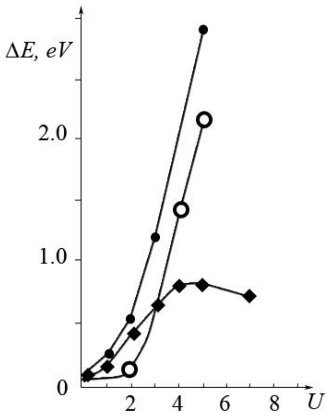

Fig. 1. The *U*-dependence of the energy gap in electronic spectra of the Mott – Peierls semiconductors like PA or PDA: ■ – $\Delta E_{\dim}$, ○ – ΔE_{corr}, • – ΔE

Now using data of Fig. 1 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 $\Delta E_{\dim}$ 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 (126) 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 (104) 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.

6. 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 [55] and conducting donor – acceptor molecular crystals TTF-TCNQ [96]. One of the promising families of quasi-2d systems are new high temperature superconductors (HTSC) based on cooper oxides La_2CuO_4, $YBa_2Cu_3O_{6+y}$ [97] and organic superconductors based on BEDT-TTF molecules [98].

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. The standard perturbation theory is inapplicable for treating both 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 many-electron 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 $N \to \infty$ 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 § 3 in [1], the spinless fermion approximation in case of strong interactions 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 two-electron 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, three-dimensional. 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

$$\hat{H} = \sum_n \hat{H}_n + \frac{1}{2}\sum_{n,m} \hat{V}_{nm} , \qquad (131)$$

where $\hat{H}_n$ is the Hamiltonian of a *n*-th quasi-1d subsystem (filaments, needles, chains, stacks, *etc*), and the operators $\hat{V}_{nm}$ 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 (131). 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

$$\hat{H} = \sum_m \alpha \hat{C}^+_{m\sigma}\hat{C}_{m\sigma} + \sum_{mm'\sigma} \beta_{mm'}\hat{C}^+_{m\sigma}\hat{C}_{m'\sigma} + \\ + \frac{1}{2}\sum_{mm'\sigma} \gamma_{mm'}\hat{C}^+_{m\sigma}\hat{C}_{m\sigma}\hat{C}^+_{m'\sigma}\hat{C}_{m'\sigma} \qquad (132)$$

is very popular and useful to study many properties of molecules with conjugated bonds.

As a rule, it is sufficient in (132) to account for resonance interaction (so called electron hopping) for the adjacent atoms only, namely:

$$\beta_{mm'} = \beta(R_{mm'})\delta_{m',m+1} . \qquad (133)$$

As far as the electron interaction in (132) is consernied only the first several terms are usually accounted for. As an example, in the Hubbard – Anderson (HA) Hamiltonian

$$\gamma_{mn} = \gamma_0 \delta_{mn} . \qquad (134)$$

Interaction between two neighbouring atoms is only often used:

$$\gamma_{mn} = \begin{cases} \gamma_0 \delta_{mn}, \\ \gamma_1 \delta_{m\pm 1,n}. \end{cases} \qquad (135)$$

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 $R_0 = 1.397 A$ which corresponds to the C=C bond length in benzene

$$\beta(R) = \beta_0 - (R - R_0)\beta' . \qquad (136)$$

To account for vibrational degrees of freedom the phonon Hamiltonian

$$\hat{H}_{ph} = \sum_{ki} \hbar\omega_{ki}(\hat{B}^+_{ki}\hat{B}_{ki} + \frac{1}{2}) \qquad (137)$$

is added to (132), where $\hat{B}^+_{ki}$ is a phonon creation operator for the *i*th mode with a quasimomentum *k*. Starting from (136), the operator of electron – phonon subsystem interactions may be chosen as suggested by Frohlich

$$\hat{H}_{e/ph} = \sum_{kq} \lambda_{qi}(\hat{B}^+_{q,i} - \hat{B}_{-q,i})\hat{A}^+_{k,\sigma}\hat{A}_{k+q,\sigma} \qquad (138)$$

where a constant λ is proportional to the β derivative with respect to R, that is β' in (136). 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

$$\hat{H}_{ph} = \frac{1}{2}\sum_{mi} M_i \dot{\vec{R}}^2_{mi} + \frac{1}{2}\sum_{mi} K_i(\vec{R}_{mi} - \vec{R}_{m+1,i})^2, \qquad (139)$$

and

$$\hat{H}_{e/ph} = \sum_{m\sigma}(R_0 - R)\beta'(\hat{C}^+_{m+1,\sigma}\hat{C}_{m\sigma} + h.c.) . \qquad (140)$$

The Hamiltonian (132) together with the expressions for the matrix elements (133)–(136) 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 [55, 96–98].

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 3d-crystal. The Hamiltonian of each needle is supposed to be the first term in the general expression (131)

$$\hat{H} = -\beta_0 \sum_{m\sigma} (\hat{C}^{+}_{m\sigma}\hat{C}_{m+1,\sigma} + h.c.)\,, \qquad (141)$$

where the same notifications as in (132) are used and let the number of particles $N \to \infty$. The 1d-system with Hamiltonian (141) is a metal independently on the number of electrons in the conduction band N_e with density

$$\rho = \frac{N_e}{N} = \frac{1}{N}\sum_{m\sigma}\left\langle \hat{C}^{+}_{m\sigma}\hat{C}_{m\sigma}\right\rangle, \qquad (142)$$

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° K even within a weak coupling constant $U = \gamma / \beta_0$ in the Hamiltonian (132).

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 [55]. However, further analysis have shown that, in fact, a coexistence of different instabilities is possible. Thus, in [83] 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 sysnthesis 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, ½, ⅓ 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 (141) at $\rho = 1$ is a metal. Adding an Interaction operator like (131) to (141) we obtain the system with the Hubbard Hamiltonian

$$\hat{H} = \sum_{m\sigma}\{(-\beta)[\hat{C}^{+}_{m\sigma}\hat{C}_{m+1,\sigma} + h.c.] + \\ + \frac{1}{2}\beta_0 U \hat{C}^{+}_{m\sigma}\hat{C}_{m\sigma}\hat{C}^{+}_{m,-\sigma}\hat{C}_{m,-\sigma}\}. \qquad (143)$$

The spectrum of a cyclic chain with Hamiltonian (143) 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 [55].

The Peierls metal – insulator transition. Let us consider a system with the Hamiltonian which can be represented as the sum of (139), (140), and (141)

$$\hat{H} = \sum_{m\sigma}\{-[\beta_0 + \beta'(\vec{R}_m - \vec{R}_{m+1})]\hat{C}^{+}_{m\sigma}\hat{C}_{m+1,\sigma} + h.c.\} + \\ + \frac{1}{2}k\sum_{m}(\vec{R}_m - \vec{R}_{m+1})^2. \qquad (144)$$

The energy minimum of an infinite chain is reached with the Hamiltonian (144) when

$$R_m = R_0 \cos(Qam + \varphi_0), \qquad (145)$$

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

$$R_0 = 2\frac{\beta_0}{\beta'}\exp\left[-\frac{\pi\beta k}{(\beta')^2}\right]. \qquad (146)$$

The energy spectrum of conduction electrons for a half-filled band is given by

$$\varepsilon_{1,2} = \pm 2\beta_0\sqrt{\cos^2 k + 4\left(\frac{\beta'}{\beta_0}\right)R_0^2\sin^2 k}\,, \qquad (147)$$

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

$$\Delta E_g = 8\beta' R_0. \tag{148}$$

The ground state energy correction is

$$\Delta E_c = 4\beta R_0^2 \ln R_0 + \frac{1}{2} K R_0^2. \tag{149}$$

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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