

## NON-CLASSICAL POLYMERS WITH SUPERCONDUCTING GROUND STATE

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Dedicated to Professor Milcho Natov on the occasion of his 80<sup>th</sup> birth day.

### ABSTRACT

The structure of non-classical (non-Kekulé) polymers (NCP) possessing condensed-superconducting ground state have been investigated theoretically.

Different theoretical models of one-dimensional NCP are proposed. Their energy spectra and structure correspond to the condition for arising of superconducting ground state.

**Keywords:** non-classical polymers, superconducting state.

### INTRODUCTION

Investigations of the physical properties of non-classical (non-Kekulé) organic polymers (NCP), are focused mainly of their magnetic properties-organic ferromagnets [1, 2 and references given therein].

The idea of the studies presented in this communication, is stems from the papers of Yang [3] (see also the paper of Rensink [4] and refs. 5, 6) and Mestechkin [7].

According to Yang, the presence of great characteristic numbers  $\Lambda^{(s)} \sim N$  in the spectral expansion of the reduced density matrix for a system of  $N$  electrons:

$$P_s^{(N)}(x|x') = \sum_r \Lambda_r^{(s)} \varphi_{(s)r}(x) \varphi_{(s)r}^*(x') \quad (1)$$

corresponds to a condensed- superconducting state. The general result obtained by Yang is not connected with a concrete chemical structure.

In the paper of Mestechkin [7] it is shown, that the condition for great numbers  $\Lambda^{(s)}$  in eq. (1), can be realized in molecular systems with great MO number with equal-degenerate or close energies.

The NCPs are characterized with band(s) with degenerate non-bonding molecular orbitals (NBMO), which correspond exactly to the condition of Mestechkin.

The NCPs with intra- and inter-  $\pi$ -systems of conjugation, are a great group organic compounds [1, 2]. The impressing types of the the NCPs with bands with degenerate NBMOs determine the expediency of this investigation.

### STRUCTURAL PRINCIPLES OF THE NON-CLASSICAL $\pi$ -SYSTEMS

Non-classical (non-Kekulé)  $\pi$  - molecular systems are those for which no classical (valence) formula can be attributed [8]. The term non-classical systems and polymers (NCP) was first proposed in [9]. Theoretical and experimental investigations are focused mainly on di-, polyradicals, and 1-D polymers. The first NCPs are described in the papers of Itoh [10], Wasserman [11], and Iwamura [12].

There are two classes of non-classical  $\pi$ -systems with NBMO's, determined by the molecular topology- homonuclear alternant systems and quasi-alternant systems.

#### Homonuclear alternant systems

According to the theorem of Coulson-Rushbrooke-Longuet-Higgins (CRLH) [13, 14], a homonuclear alternant  $\pi$ -system (hydrocarbon) has at least:

$$N = S^* - U^0 \quad (2)$$

NBMOs, where  $\{S^*\}$  and  $\{U^0\}$  are the number of the starred and unstarred  $\pi$ -centers, respectively. Examples for which the CRLH theorem is valid are the benzyl radical (**Bz**) and *m*-xylylidene (**Xy**) ( here and below only one resonance formula is depicted), Fig.1

### Quasialternant systems

The application of the CRLH theorem is limited *only* to homonuclear alternant systems, i. e., alternant radicals. The theorem has been extended (ECRLH) [15, 16]. Radicals for which the ECRLH theorem is valid are designated as quasi-alternant non-classical (Non-Kekulé) (QANC) radicals.

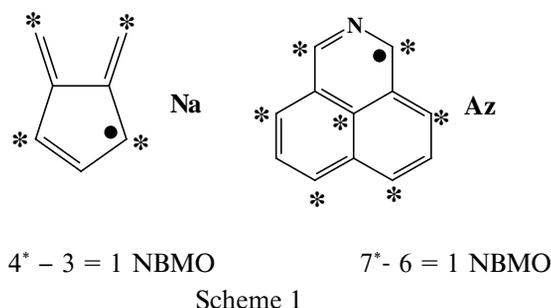
Within the CRLH theorem one always considers two subsets of homonuclear non-bonded  $\pi$ -centers: the subset of starred  $\{S^*\}$  and the subset of unstarred  $\{U^0\}$  ones. According to the ECRLH theorem, *only* one subset of non-bonded (disjoint)  $\pi$ -centers is responsible for the appearance of NBMOs. A system with  $M$   $\pi$ -centers and a maximum set of starred homo-nuclear nonbonded (disjoint)  $\pi$ -centers  $\{S^*\}$  must have at least

$$N = 2S^* - M \quad \text{NBMOs.} \quad (3)$$

The NBMOs are present even if the  $\pi$ -system is non-alternant and if the  $\pi$ -centers belonging to the non-starred subset  $\{U^0\}$  are heteroatomic. A typical example is the radical **Na**, and the stable 2-aza-phenalenyl (**Az**) radical (see Scheme 1) which has been synthesized and characterized by Rubin et al. [17].

### 1-D Polymers with NBMO-bands

The synthesized NCP are high-spin systems [10-12, 18]. The electrons within the NBMO band are ferromagnetically coupled, however bulk magnetism seems to be negligible.



Bulk magnetism and superconductivity are cooperative phenomena since they result from the interaction of a large number of electrons ( $N \gg 1$ ) [19,20] - probably the number of the elementary units in the synthesized NCP is small.

In Fig. 1 are shown examples of 1-D NCP with NBMOs. It follows from the theorem of Yang, that in these polymers superconductive states, with physical nature similar similar to that in the model described by Smith and Boring [21] arise.

A theoretical model of a 2-D polymer with an NBMO band is proposed by Mataga [22].

The conductivity properties of these types of polymers have not been established, because the effective mass of the electrons within the NBMO band  $m_{\text{eff}} = m_0 / \Delta E \gg 1$  - the band width  $\Delta E(\text{NBMO}) \rightarrow 0$ .

A new theoretical approach to the design of NCP with two bands with degenerate NBMOs is proposed in [23].

### TWO BAND 1-D POLYMERS WITH NBMOs

In Fig. 2 is shown an example of 1-D NCP with two bands with NBMOs.

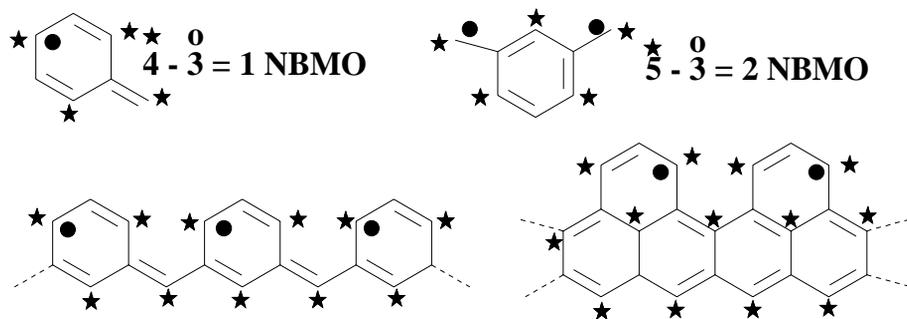


Fig. 1. Alternant systems with a NBMOs. A polymer consisting of  $N$  elementary units has  $N (S^* - U^0)$  degenerate NBMOs.

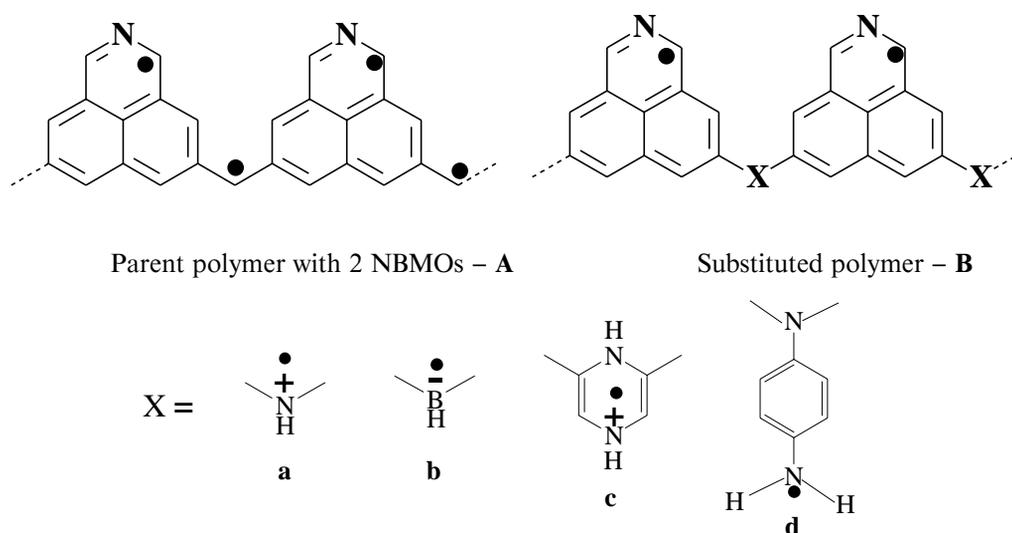


Fig. 2. Example of 1-D NCP with two bands with NBMOs.

In accordance with the ECRLH theorem, the parent polymer **A** has two NBMO bands. The substitution of the C\*H group with an other atom or atomic group, **X**, is connected with splitting of the degenerated NBMO bands. The character and degree of perturbation depends on the structure of **X**. If **X** is a closed-shell system, only indirect magnetic interaction arises between the strictly localized NBMOs within the **Az** radicals. If **X** is methylene:  $>CH_2$ , the indirect exchange parameter,  $J_{ind} = -2.2$  meV. If **X** is an *open-shell* system with even  $\pi$ -electrons (shown in Fig.2), the energy spectra of the polymers are connected with splitting of the degenerated NBMO bands.

**Corollaries**

The following corollary rooted in the ECRLH theorem [16] determines the structural principle, and the properties of the investigated polymers.

Let us consider a  $\pi$ -system consisting of a radical subunit **R'**, for which the CRLH or the ECRLH theo-

rem is valid, linked with one arbitrary radical  $L' : R' - L'$ .

i-  $L'$  is a homonuclear alternant radical.

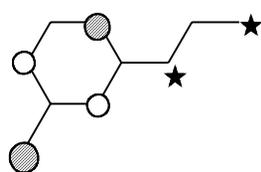
If the  $\pi$ -center **r** of **R'**, which is connected with a  $\pi$ -center **s** of  $L'$ , belongs to the set of the starred atoms  $\{S^*\}$ , then the system has two NBMOs. One NBMO is localized in the subunit **R'**, and one NBMO is localized within the subunit  $L'$ . An example, allyl substituted benzyl radical, is shown in Fig. 3.

Examples with substituted benzyl radical (**I**) are shown in Fig. 3.

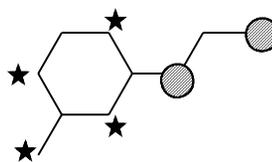
ii-  $L'$  is a heteronuclear radical, for instance the radicals shown in Fig. 2.

The energy spectra of the polymers are characterized with two frontier bands with different symmetry. One band of NBMO is localized in the **Az** fragment, and another band is of delocalized MOs (see Fig. 4).

If we consider only the frontier bands (see Fig. 4), the condition for the existence of a high-spin state in the polymers is given by



NBMO localized in benzyl fragment



NBMO localized in allyl fragment

Fig. 3. Localization of the NBMOs within the benzyl and allyl radical, respectively, in the case of allyl-substituted benzyl radicals.

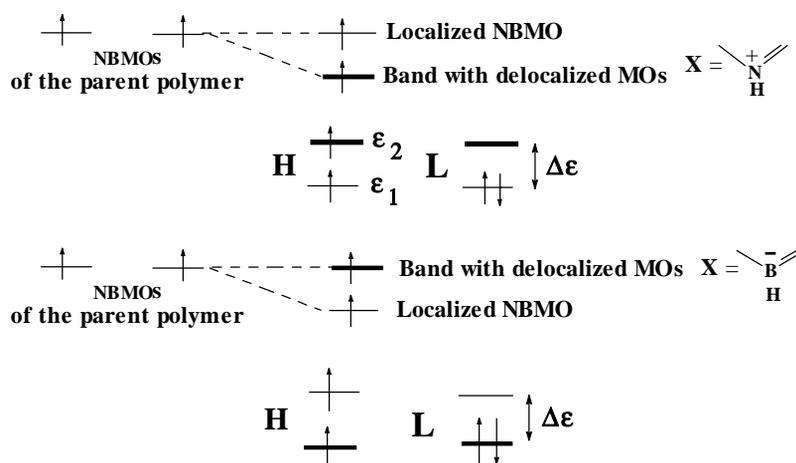


Fig. 4. Energy spectra of the polymers of the types **I-a(b)** ( see Fig. 2). With **H** and **L** are denoted the high- and low spin states.

$$\mathbf{E}(\mathbf{L}) - \mathbf{E}(\mathbf{H}) = \Delta\mathbf{E}_{\text{LH}} > 0 \quad (5)$$

and

$$\Delta\mathbf{E}_{\text{LH}} = 2\varepsilon_1 + \mathbf{I}_{11} - [\varepsilon_1 + \varepsilon_2 + \mathbf{J}_{\text{ind}}(1) + \mathbf{J}_{\text{eff}}(2) + \mathbf{I}_{12}] = \Delta\varepsilon + \mathbf{I}_{11} - \mathbf{I}_{12} - \mathbf{J}_{\text{eff}}(1,1) - \mathbf{J}_{\text{eff}}(1,1) - \mathbf{J}_{\text{eff}}(1,2)$$

Because the two-electron Coulomb integrals are  $\mathbf{I}_{11} - \mathbf{I}_{12} > 0$ , for the condition  $\Delta\mathbf{E}_{\text{LH}} > 0$  one obtains

$$\Delta\mathbf{E}_{\text{LH}} = \Delta\varepsilon - \mathbf{J}_{\text{ind}}(1) - \mathbf{J}_{\text{eff}}(2) - \mathbf{J}_{\text{eff}}(1,2) \quad (5a)$$

In eq. (5)  $\mathbf{J}_{\text{ind}}(1)$  is the indirect exchange integral between the electrons within the localized NBMOs, and  $\mathbf{J}_{\text{eff}}(2)$  is the effective exchange integral between the electrons in the delocalized HFB. The condition (5) is satisfied for the polymers **I-a**, **I-b**, and **I-c**.

### Energy Spectra

If the MOs of the 1-D system have the form of Bloch running waves

$\Psi(k) = N^{-1/2} \sum_{\mu} \sum_r C_r(k) \exp(-ik\mu) |r, \mu\rangle$  ( $k \in [-\pi, \pi]$ ) is the wave vector,  $\mu$  denotes the number of the elementary units (EU) and  $|r, \mu\rangle$  is the  $r$ -th AO within the  $\mu$ -th EU), in the Hückel-Hubbard version of the Bloch method the MO energies  $\varepsilon(k)$  are eigenvalues of the energy matrix [24]:

$$E(k) = E_0 + V \exp(ik) + V^+ \exp(-ik) \quad (6)$$

where  $E_0$  is the energy matrix for the EU,  $V$  is the interaction matrix between neighbouring EUs ( $\mu$ -th and  $\mu+1$ -th),  $V^+$  is the transposed matrix.

In Table 1 are collected the results for the calculated values of the splitting parameter  $\Delta\varepsilon$  of polymers **I-a** - **I-c**.

Table 1. Splitting parameter  $\Delta\varepsilon$  (in meV) of the bands with delocalized MOs (see Figs. 2 and 4).

Polymer	$\Delta\varepsilon$
<b>a</b>	27
<b>b</b>	30
<b>b</b>	67

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