

Electronic Structure of High π -Electron Systems (Graphite, Polyacene, Cumulene)

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The electronic structure of graphite, polyacene and cumulene are calculated by a generalised Hartree-Fock method, where electrons with different spins occupy different molecular orbitals.

Die Elektronenstruktur von Graphit, Polyacen und Cumulen wurden mittels einer verallgemeinerten Hartree-Fock-Methode berechnet, wobei Elektronen mit verschiedenem Spin verschiedene Orbitale besetzen können.

Les structures électroniques du graphite, du polyacène et du cumulène sont calculées par la méthode de Hartree-Fock généralisée, ou des électrons de spin différent occupent des orbitales moléculaires différentes.

In paper [1], we examined the electronic structure of a polyene chain in the approximation of the generalized Hartree-Fock method (GMHF). In an isolated polyene chain, enclosed in a weak electric field, the electrons will not be collected at one end of the chain because of the repulsion of the electrons by each atom. Therefore, the system calculated by us should possess semiconductor properties with a gap ΔE . That means the metal becomes a dielectric when the repulsion of the electrons is sufficiently high. This was noticed by Mott [2]. However, Mott's considerations are very general. In particular, it is not possible to explain with this theory using one and the same electron interaction parameters, why graphite is a metal and polyenes are dielectrics. Our consideration makes Mott's model of the metal-dielectric transition more concrete. For example, in [1] it is shown, that within the limits of strong interaction, the ground state of a polyene chain is antiferromagnetic and is separated from the excited state by a gap $\Delta E = \gamma$ in conformity with Mott's considerations [2] ($\gamma =$ Coulomb integral, corresponding to the electron interaction with one atom). Below the electronic structures of graphite, polyacenes and cumulenes will be considered in the GMHF approximation.

1. Layers of carbon atoms in graphite form a planar network, consisting of regular hexagons with sides 1.42 Å. The planes of these networks are separated by ~ 3.35 Å. At such distances the interaction between layers can be neglected (in the zeroth approximation) and graphite can be considered as a two-dimensional crystal (Fig. 1). Each carbon atom contributes one $2p_z$ electron to the general system of π electrons, which are responsible for the electronic properties of graphite. It is easy to see that two carbon atoms, that is two $2p_z$ electrons, enter the elementary cell. Therefore two π zones can be constructed from $2p_z$ orbitals, the lower of which will be completely filled. In this approximation, graphite should be a semiconductor. However, the computations of the zonal structure of two-

dimensional graphites indicates [3] that the filled and empty zones touch at two points, so that in this approximation we have a semiconductor with a forbidden zone equal to zero. If a three dimensional structure is considered where the small interaction between planes cannot be neglected, a weak intersection of two zones is obtained [4]. Therefore part of the electrons pass into the upper zone, thus creating a hole in the lower zone. Then graphite becomes a weak metal in agreement with experimental data [5].

We shall examine the electronic structure of graphite in the GMHF approximation. The main aim of such a calculation is to examine the possibility of a metal-dielectric transition and the appearance of a state with an antiferromagnetic structure. Elementary cells are numbered with two indices (m, n) as shown in

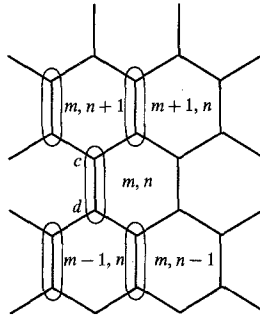


Fig. 1. Structure of the graphite network

Fig. 1. If $c_{mn}^+(c_{mn})$ is an electron creation (annihilation) operator for the "upper" atom of the cell (m, n) , and $d_{mn}^+(d_{mn})$ an electron creation (annihilation) operator for the "lower" atom of this cell (Fig. 1) then the Hamiltonian system for the π electrons can be written as follows:

$$\begin{aligned}
 H = & \sum_{mns\sigma} \beta (c_{mns\sigma}^+ d_{mns\sigma} + c_{mns\sigma}^+ d_{m+1n\sigma} + c_{mns\sigma}^+ d_{m-1n\sigma} \\
 & + d_{mns\sigma}^+ c_{mns\sigma} + d_{mns\sigma}^+ c_{m-1n\sigma} + d_{mns\sigma}^+ c_{m+1n\sigma}) \\
 & + \frac{\gamma}{2} \sum_{mns\sigma} (c_{mns\sigma}^+ c_{m-1n\sigma}^+ c_{m-1n\sigma} c_{mns\sigma} + d_{mns\sigma}^+ d_{m-1n\sigma}^+ d_{m-1n\sigma} d_{mns\sigma}),
 \end{aligned}$$

where β is the resonance integral. The GMHF approximation consists in linearizing the equation of motion for $c_{mns\sigma}$ [1] by introducing the average $\langle \dots \rangle$ of the state we are searching for:

$$\langle c_{mns\sigma}^+ c_{mns\sigma} \rangle = \langle d_{mns\sigma}^+ d_{mns\sigma} \rangle = \frac{1}{2} + \delta,$$

$$\langle c_{mns\sigma}^+ c_{m-1n\sigma} \rangle = \langle d_{mns\sigma}^+ d_{m-1n\sigma} \rangle = \frac{1}{2} - \delta,$$

$$\langle d_{mns\sigma}^+ d_{m-1n\sigma} \rangle = 0 = \langle c_{mns\sigma}^+ c_{m-1n\sigma} \rangle.$$

The secular equation and their solutions are found as in paper [1]. We obtain the following one-electron energy levels

$$E_{jk} = \frac{\gamma}{2} \pm \sqrt{(\gamma\delta)^2 + |\varepsilon(jk)|^2},$$

where $\varepsilon(jk) = \beta \left(1 + e^{i\frac{2\pi}{N}k} + e^{i\frac{2\pi}{N}j} \right)$ and where the levels of the lower zone (with the minus sign before the root) are filled $\left(-\frac{N}{2} \leq j, k \leq \frac{N}{2} \right)$. When $\delta = 0$ we have the well known equation

$$E_{jk} = \frac{\gamma}{2} \pm \beta \sqrt{3 + 2 \cos \frac{2\pi}{N}k + 2 \cos \frac{2\pi}{N}j + 2 \cos \frac{2\pi}{N}(k-j)}.$$

Here the expression under the root is equal to zero at two points $\left(j = \frac{N}{3}, k = -\frac{N}{3} \right)$ and $\left(j = -\frac{N}{3}, k = +\frac{N}{3} \right)$ within the range of the first zone $\left(-\frac{N}{2} \leq k, j \leq \frac{N}{2} \right)$. These are the points where the two zones touch, in the neighbourhood where filled and empty zones intersect in a real model of graphite. If $\delta \neq 0$, then in the zeroth approximation, the two zones do not touch and are separated from one another by a gap $\Delta E = 2\gamma\delta$, so that with certain values of ΔE , we do not get the intersection of these zones even if we consider the three dimensional graphite model. Thus, we have the possibility of a metal-dielectric transition in graphite in our approximation. To reveal the possibility of such a transition, let us consider the self-consistency condition (equation for δ)

$$\frac{1}{2N^2} \sum_{j,k \in \left[-\frac{N}{2}, \frac{N}{2}\right]} \frac{\gamma\delta}{\sqrt{(\gamma\delta)^2 + |\varepsilon(jk)|^2}} = \delta. \quad (1)$$

As has been mentioned earlier, the function $|\varepsilon(jk)|$ is equal to zero only at two points (points of contact of the two zones) and the twofold integral in Eq. (1) has no singularity in these points. For a non-trivial solution $\delta \neq 0$ the following condition is necessary:

$$\frac{\gamma}{2N^2} \sum_{j,k} |\varepsilon(jk)|^{-1} \geq 1. \quad (2)$$

Thus, in a two-dimensional case (graphite), the transition to a nontrivial state is possible only if we have

$$\frac{\gamma}{2|\beta|} > \left(\frac{\gamma}{2|\beta|} \right)_{\text{critical}}$$

In a one-dimensional case (polyene) such a transition is always possible (when $\gamma > 0$). The critical value of the interaction parameter is determined from Eq. (2);

it is equal (to an accuracy of 1–2%) to:

$$\left(\frac{\gamma}{2|\beta|}\right)_{\text{crit.}} \approx \frac{79}{70} = 1.13.$$

In a polyene chain, where electron interaction parameters should not noticeably differ from the corresponding parameters of graphite, we get $\frac{\gamma}{2|\beta|} \approx 1.13$ [1]. This

unexpected approximate equality $\frac{\gamma}{2|\beta|} \approx \left(\frac{\gamma}{2|\beta|}\right)_{\text{crit.}}$ for graphite leads us to the following conclusions:

1) The real electron interaction in graphite is such, that the condition for the appearance of a nontrivial state with a semiconductor gap (and an antiferromagnetic structure), is perhaps not fulfilled. Therefore the state with $\delta=0$ is a ground state, which, if three dimensions are taken into consideration, is responsible for the observed electronic structure of graphite. Here it is necessary to mention, that our consideration does not lead to a nontrivial state, which would have contradicted to the experiment and would have meant an unsatisfactory selection of parameters.

2) The closeness of the electron interaction parameter to the critical value indicates that if all graphite bonds are stretched (if $|\beta|$ is decreased), we would have observed Mott's metal-dielectric transition.

2. Naphthalene, anthracene, tetracene, pentacene, hexacene are the first few members of the series of polyacenes having $N = 2, 3, 4, 5, 6$ rings respectively. Experimental material on the first electronic transition in a number of polyacenes [6] seems to indicate that a finite limit to the first electron transition exists. As polyacenes with $N \geq 7$ are unstable, experimental investigation of such molecules are difficult. Nevertheless, the question of polyacenes with large N is not devoid of interest; in particular, Salem and Longuet-Higgins [7] have investigated theoretically the possibilities of a state with alternation of the lengths of the external bonds in polyacenes. They concluded that such a state is not advantageous with respect to the energy for any value of N . This is because, in polyacenes there are four zones, two of which are completely filled, and the third is free and lies in close contact with the second filled zone. The magnitude of gap in the spectrum therefore is equal to zero. Two adjacent zones, one filled and the other empty, have different symmetries. Therefore the electron-phonon-interaction does not mix the states of these zones and thus a stabilization with respect to a transition to a state with alternation of bond length results. In the case of the polyenes, we have only one zone, and therefore the filled and empty levels are mixed by electron-phonon interaction, and that could lead, in principle, to the formation of a state with alternation of bond lengths and with an electron-phonon gap. It appears that we have a general theorem according to which an electron-phonon interaction does not shift the adjoining filled and empty zones, i.e., does not lead to the formation of an electron-phonon gap in this case. In this connection, it is interesting to consider another mechanism of gap formation in electron interaction.

Let us examine the possibilities of a transition of a polyacene into a state with a gap in the spectrum (and with an antiferromagnetic structure) in the GMHF approximation. The Hamiltonian of the π electrons of a polyacene with N rings

has the following form in the second quantization representation.

$$\begin{aligned}
 H = \sum_{m\sigma} \{ & \beta_1 (a_{m\sigma}^+ b_{m+1\sigma} + a_{m\sigma}^+ b_{m\sigma} + b_{m\sigma}^+ a_{m-1\sigma} + b_{m\sigma}^+ a_{m\sigma}) \\
 & + \beta_1 (d_{m\sigma}^+ c_{m+1\sigma} + d_{m\sigma}^+ c_{m\sigma} + c_{m\sigma}^+ d_{m-1\sigma} + c_{m\sigma}^+ d_{m\sigma}) \\
 & + \beta_2 (b_{m\sigma}^+ c_{m\sigma} + c_{m\sigma}^+ b_{m\sigma}) \} \\
 & + \frac{\gamma}{2} \sum_{m\sigma} (a_{m\sigma}^+ a_{m-\sigma}^+ a_{m-\sigma} a_{m\sigma} + b_{m\sigma}^+ b_{m-\sigma}^+ b_{m-\sigma} b_{m\sigma} \\
 & + c_{m\sigma}^+ c_{m-\sigma}^+ c_{m-\sigma} c_{m\sigma} + d_{m\sigma}^+ d_{m-\sigma}^+ d_{m-\sigma} d_{m\sigma}),
 \end{aligned}$$

where the $a_{m\sigma}$, $b_{m\sigma}$, $c_{m\sigma}$, $d_{m\sigma}$ operators belong to respective atoms of the m th elementary cell; β_1 and β_2 are the resonance integrals of external and internal bonds of the polyacene (Fig. 2). Here, as in the case of the polyene chain [1] and

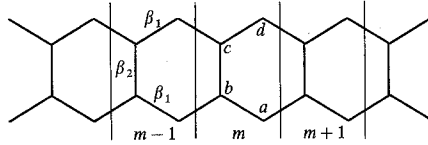


Fig. 2. Structure of polyacenes

graphite, in the interaction term only one coulomb integral γ corresponding to the electron interaction on one atom is retained.

The GMHF approximation consists in linearizing the equations of motion for the $a_{m\sigma}$, $b_{m\sigma}$, $c_{m\sigma}$ and $d_{m\sigma}$ operators [1] by introducing the average $\langle \dots \rangle$ over the ground state for which we are searching:

$$\begin{aligned}
 \langle a_{m\alpha}^+ a_{m\alpha} \rangle = \langle b_{m\beta}^+ b_{m\beta} \rangle = \langle c_{m\alpha}^+ c_{m\alpha} \rangle = \langle d_{m\beta}^+ d_{m\beta} \rangle &= \frac{1}{2} + \delta, \\
 \langle a_{m\beta}^+ a_{m\beta} \rangle = \langle b_{m\alpha}^+ b_{m\alpha} \rangle = \langle c_{m\beta}^+ c_{m\beta} \rangle = \langle d_{m\alpha}^+ d_{m\alpha} \rangle &= \frac{1}{2} - \delta, \\
 \langle a_{m\sigma}^+ a_{m-\sigma} \rangle = \langle b_{m\sigma}^+ b_{m-\sigma} \rangle = \langle c_{m\sigma}^+ c_{m-\sigma} \rangle = \langle d_{m\sigma}^+ d_{m-\sigma} \rangle &= 0,
 \end{aligned} \tag{3}$$

where the parameter δ is determined from the self-consistency conditions.

Secular equations and their solutions are found as given in paper [1]. Finally, we obtain the following one-electron energy levels

$$E_i^{1,2,3,4} = \frac{\gamma}{2} \pm \sqrt{(\gamma\delta)^2 + \frac{1}{4} (\beta_2 \pm \sqrt{4F \cdot F^* + \beta_2^2})^2}, \quad F \equiv \beta_1 \left(1 + e^{i\frac{2\pi}{N}l} \right).$$

In the ground state, the levels of two zones are filled

$$E_i^{1,2} = \frac{\gamma}{2} - \sqrt{(\gamma\delta)^2 + \frac{1}{4} (\beta_2 \pm \sqrt{4F \cdot F^* + \beta_2^2})^2}.$$

The third empty zone is isolated from the second filled zone by the gap

$$\Delta E = 2\gamma\delta,$$

where $\delta > 0$ is determined from the self-consistency condition, which, when $N \rightarrow \infty$, takes the form

$$1 = \frac{\gamma}{2\pi} \int_0^{\frac{\pi}{2}} \frac{d\varphi}{R} \left\{ \frac{R - \frac{\beta_2}{2}}{\sqrt{(\gamma\delta)^2 + \left(R + \frac{\beta_2}{2}\right)^2}} + \frac{R + \frac{\beta_2}{2}}{\sqrt{(\gamma\delta)^2 + \left(R - \frac{\beta_2}{2}\right)^2}} \right\}, \quad (4)$$

$$R \equiv \sqrt{4\beta_1^2 \cos^2 \varphi + \frac{\beta_2^2}{4}}.$$

This equation has a nontrivial solution $\delta \neq 0$ for all values of $\gamma > 0$, as in the case of polyene chains. The secular equations have, of course, a trivial solution with $\delta = 0$, corresponding to the usual MO method [7]. In the state with $\delta \neq 0$, electrons with different spins are found in different orbitals and the energy of this state is less than that of the state with $\delta = 0$.

A nontrivial state is characterised by a definite distribution of spin density (see Eq. (3) and Fig. 3a) on the carbon atoms. The magnetic moment perpendicular to the molecular plane can be replaced by a ring current flowing in the molecular plane. Different directions of the ring current correspond to different directions of the magnetic moment. Therefore it is clear that the structure "b" is less symmetrical than the symmetrical magnetic structure "a" which is calculated here in detail (Fig. 3). Direct calculations show, that the energy of the structure "b" is higher than the energy of the structure "a" according to symmetry considerations.

From Eq. (4) with parameters taken from calculations of the polyene chain [1], we obtain almost the same value for δ as for the polyene. This means that in a polyacene the magnitude of the gap is $\Delta E \sim 2$ eV. If we take into account the fact that for *a* and *d* atoms (Fig. 2) δ may be equal to δ_1 , and for *b* and *c* atoms $\delta = \delta_2 \neq \delta_1$, then this estimation can be altered. Thus we can say, that the above mechanism leads to a gap $\Delta E \sim 1 \div 2$ eV in polyacenes with a large number of rings, and this does not contradict the experimental data [6]. A better comparison is not possible because of the lack of experimental data for polyacenes with $N \geq 7$.

3. The electronic structure of the cumulene has been considered until now from the standpoint of states with alternating bond lengths [8]. Popov and Shustorovich, in considering the electronic structure of cumulenes, have obtained results

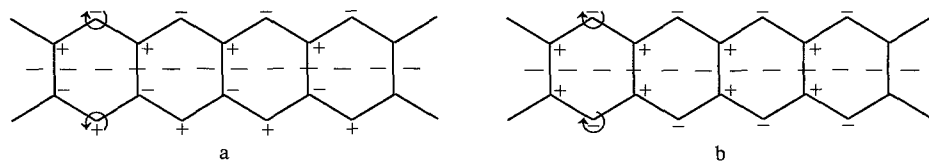


Fig. 3a and b. Two types of the magnetic structure of polyacenes with magnetic moments, perpendicular to the molecular plane: a) Magnetic structure calculated in this paper; this structure is symmetrical with respect to reflection in the molecular plane and with respect to reflection in a plane perpendicular to the molecular plane and passing through the middle of the internal molecular bonds. b) Magnetic structure of polyacenes, symmetric with respect to reflection in the molecular plane and antisymmetric with respect to reflection in a plane perpendicular to the molecular plane and passing through the middle the of internal bonds

[8] which agree with the alternation theory. However, their parameters, which were taken from spectroscopic data, are not comparable with experiments on vibrations of conjugate systems. Although the electronic interaction was taken into consideration in [8], the electronic correlation was not taken into account. However, as we have shown in [1] that, in examining the electronic structure of polyenes, the consideration of the electronic correlation within the GMHF framework enables us to explain the observed peculiarities of the electronic structure of the polyenes without taking into account the electron-phonon interaction, which in this case should lead to insignificant changes only. In this connection, it is interesting to consider the effect of the electronic correlation in cumulenes neglecting in the first approximation the electron-phonon interaction. Perhaps, the effect of this interaction on the electronic structure is less significant than the effect of the electronic interaction.

In a cumulene $(=C=)_{2N}$, two subsystems of π electrons analogous to the π electron systems in a polyene exist. If the electronic interaction in each of these subsystems "a" and "b" is taken into account and the interaction between the subsystems is neglected, then by analogy to the polyenes [1], we obtain the result that each subsystem passes into a state with a gap in the spectrum and with an antiferromagnetic spin structure. Here, with regard to the antiferromagnetic structure of the cumulene, it is necessary to consider several possibilities:

1. If the magnetic moments of the subsystems "a" and "b" are perpendicular to the molecular axis, then for the cumulene as a whole we have an antiferromagnetic spin structure independent of the interaction of the subsystems;

2. If the magnetic moments in the subsystems are directed along the molecular axis, then two states are possible: either a state with an antiferromagnetic structure when the moments on each carbon atom of the two subsystems are parallel and are summed, or a state without an antiferromagnetic structure when the moments on each atom of the two subsystems are antiparallel (i.e., are compensated). Now we shall consider the electronic structure of the cumulene when both electronic interactions (i.e., the internal interaction in each subsystem and the interaction between the subsystems) are taken into account.

The Hamiltonian of the cumulene in the second quantization representation has the form:

$$\begin{aligned}
 H = & \sum_{ik\sigma} T_{ik}(a_{i\sigma}^+ a_{k\sigma} + b_{i\sigma}^+ b_{k\sigma}) \\
 & + \frac{\gamma}{2} \sum_{n\sigma} (a_{n\sigma}^+ a_{n\sigma} a_{n-\sigma}^+ a_{n-\sigma} + b_{n+\sigma}^+ b_{n\sigma} b_{n-\sigma}^+ b_{n-\sigma}) \\
 & + \frac{\tilde{\gamma}_{ab}}{2} \sum_{n\sigma} (a_{n\sigma}^+ b_{n\sigma} a_{n-\sigma}^+ b_{n-\sigma} + b_{n\sigma}^+ a_{n\sigma} b_{n-\sigma}^+ a_{n-\sigma}) \\
 & + \frac{\tilde{\gamma}_{ab}}{2} \sum_{n\sigma\sigma'} (a_{n\sigma}^+ b_{n\sigma} b_{n\sigma'}^+ a_{n\sigma'} + b_{n\sigma}^+ a_{n\sigma} a_{n\sigma'}^+ b_{n\sigma'}) \\
 & + \tilde{\gamma}_{ab} \sum_{n\sigma\sigma'} b_{n\sigma}^+ b_{n\sigma} a_{n\sigma'}^+ a_{n\sigma'}
 \end{aligned}$$

Here $a_{i\sigma}^+(a_{i\sigma})$ and $b_{i\sigma}^+(b_{i\sigma})$ are electron creation (annihilation) operators with a spin σ on the i th atom in a state with the atomic function $2p_x$ (subsystem "a") and with

the atomic function $2p_y$ (subsystem "b") respectively. If these functions are denoted by $\varphi_a^i(\bar{r})$ and $\varphi_b^i(\bar{r})$ (from the i th atom), for the electronic interaction integrals then we have the following expressions in the Hamiltonian:

$$\begin{aligned}\gamma &= \iint \frac{|\varphi_a^i(\bar{1})|^2 |\varphi_a^i(\bar{2})|^2}{|\bar{1}-\bar{2}|} d\bar{1} d\bar{2} = \iint \frac{|\varphi_b^i(\bar{1})|^2 |\varphi_b^i(\bar{2})|^2}{(\bar{1}-\bar{2})} d\bar{1} d\bar{2}, \\ \tilde{\gamma}_{ab} &= \iint \frac{|\varphi_a^i(\bar{1})|^2 |\varphi_b^i(\bar{2})|^2}{|\bar{1}-\bar{2}|} d\bar{1} d\bar{2}, \\ \tilde{\gamma}_{ab} &= \iint \frac{\varphi_a^i(\bar{1}) \varphi_b^i(\bar{1}) \varphi_a^i(\bar{2}) \varphi_b^i(\bar{2})}{|\bar{1}-\bar{2}|} d\bar{1} d\bar{2} = \frac{\gamma - \tilde{\gamma}_{ab}}{2}.\end{aligned}$$

Further $T_{ik} = \beta(\delta_{k,i+1} + \delta_{k,i-1})$, where β is the resonance integral for adjacent carbon atoms. All bond lengths are assumed to be equal. We shall see that the electronic interaction integrals in the Hamiltonian are fully sufficient for a consideration of the electronic interaction in the cumulene, because electronic interaction of electrons on one carbon atom is the only significant factor in our approximation, in complete analogy with the corresponding calculation for polyenes [1].

The equation of motion has the form ($\hbar = 1$)

$$\begin{aligned}i \frac{\partial a_{m\alpha}}{\partial t} &= a_{m\alpha} H - H a_{m\alpha} = \sum_k T_{mk} a_{k\alpha} + \gamma \alpha_{m\beta}^+ a_{m\beta} a_{m\alpha} \\ &+ \tilde{\gamma}_{ab} (\alpha_{m\beta}^+ b_{m\beta} b_{m\alpha} + b_{m\alpha}^+ a_{m\alpha} b_{m\alpha} + b_{m\beta}^+ a_{m\beta} b_{m\alpha}) \\ &+ \tilde{\gamma}_{ab} (b_{m\alpha}^+ b_{m\alpha} + b_{m\beta}^+ b_{m\beta}) a_{m\alpha},\end{aligned}$$

where the spin indices correspond to the two spin projections. A similar equation holds for $b_{m\alpha}$.

The GMHF approximation consists in linearizing these equations by introducing the average $\langle \dots \rangle$ over that ground state we are searching. Let us consider the two possible states:

$$\begin{aligned}\text{I.} \quad \langle a_{n\alpha}^+ a_{n\alpha} \rangle &= \langle b_{n\alpha}^+ b_{n\alpha} \rangle = \frac{1}{2} + \delta \cdot (-)^n, \\ \langle a_{n\beta}^+ a_{n\beta} \rangle &= \langle b_{n\beta}^+ b_{n\beta} \rangle = \frac{1}{2} - \delta \cdot (-)^n, \\ \text{II.} \quad \langle a_{n\alpha}^+ a_{n\alpha} \rangle &= \langle b_{n\beta}^+ b_{n\beta} \rangle = \frac{1}{2} + \delta \cdot (-)^n, \\ \langle a_{n\beta}^+ a_{n\beta} \rangle &= \langle b_{n\alpha}^+ b_{n\alpha} \rangle = \frac{1}{2} - \delta \cdot (-)^n.\end{aligned}$$

In both these cases the averages of the type $\langle a^+ b \rangle$ are equal to zero. If the magnetic moments are directed along the molecular axis, then in the state I, there is an antiferromagnetic structure, while in state II the spin density on each atom is equal to zero. The computations are analogous to those for the polyene chains [1]. As a result of these calculations, we find that in Case I the one-electron

spectrum (of the energy level of the molecular orbitals) has the following form:

$$E_1^l = \tilde{\gamma}_{ab} + \frac{\gamma - \tilde{\gamma}_{ab}}{2} \pm \sqrt{(\gamma + \tilde{\gamma}_{ab})^2 \delta_1^2 + 4\beta^2 \cos^2 \frac{\pi l}{N}}, \quad l \in \left(-\frac{N}{2}, \frac{N}{2}\right)$$

where the minus sign before the root corresponds to filled orbitals. The magnitude of the gap in the spectrum is

$$\Delta E_1 = 2(\gamma + \tilde{\gamma}_{ab}) \delta_1,$$

where δ_1 is determined from Eq. [1]

$$\frac{\pi}{p} = \int_0^{\frac{\pi}{2}} \frac{d\varphi}{\sqrt{(p \delta_1)^2 + \cos^2 \varphi}}, \quad p = p_1 = \frac{\gamma + \tilde{\gamma}_{ab}}{2|\beta|}. \quad (5)$$

In Case II, one-electron spectrum has the form

$$E_{II}^l = \tilde{\gamma}_{ab} + \frac{\gamma - \tilde{\gamma}_{ab}}{2} \pm \sqrt{(\gamma - \tilde{\gamma}_{ab})^2 \delta_2^2 + 4\beta^2 \cos^2 \frac{\pi l}{N}}$$

and the gap magnitude in the spectrum is

$$\Delta E_{II} = 2(\gamma - \tilde{\gamma}_{ab}) \delta_2$$

where δ_2 is determined from Eq. (5) with

$$p = p_2 = \frac{\gamma - \tilde{\gamma}_{ab}}{2|\beta|}.$$

It is clear that the gap is smaller in Case II than in Case I. Let us compare the states I and II with respect to the total energy. Total energies in the calculations for one π electron will have the form (in units of $2|\beta|$)

$$\varepsilon_I = -\frac{2}{\pi} \int_0^{\frac{\pi}{2}} \sqrt{(p_1 \delta_1)^2 + \cos^2 \varphi} d\varphi + \delta_1^2 \cdot p_1,$$

$$\varepsilon_{II} = -\frac{2}{\pi} \int_0^{\frac{\pi}{2}} \sqrt{(p_2 \delta_2)^2 + \cos^2 \varphi} d\varphi + \delta_2^2 p_2$$

where we have omitted several constants for ε_I and ε_{II} . It is easy to verify that $\varepsilon_I < \varepsilon_{II}$, i.e., the state I is more favoured than state II with respect to energy. Here the exchange of the interaction of two electrons belonging to one atom but in two different subsystems is very significant. In estimating the electronic structure parameters of the cumulenes, we shall take $\gamma \approx 5.4$ eV (as in the polyenes [1]), $\tilde{\gamma}_{ab} \approx 0.5$ eV and $\beta = k\beta_0$, where $k \approx 1.5$ according to [9] corresponds to C-C bond lengths in cumulenes ≈ 1.28 Å [8] and $\beta_0 = -2.4$ eV (as in polyenes [1]). For such electron interaction parameters the gap magnitude in the cumulene spectrum (when $N \rightarrow \infty$) is $\Delta E \approx 1.2$ eV (the experiment gives $\Delta E \approx (0.8 - 1.0)$ eV [8]). Here $\delta \approx 0.11$ gives a magnitude of $\sim 0.44 \mu_B$ (Bohr magnetons) for the magnetic moment on the carbon atom, parallel to the molecular axis. The non-

trivial state ($\delta \neq 0$) becomes more favoured (with respect to energy) than the trivial states starting from $N \geq 11$, i.e., for cumulene molecules having 22 or more atoms. The above antiferromagnetic structure should appear in neutron diffraction studies of polycrystalline samples in the form of small magnetic scattering peaks ($\sim 3\%$ of neutron diffuse background) on the curves of the differential cross-section of elastic scattering $\frac{d\sigma}{d\Omega}(q)$ when the scattering vector is $q \approx \frac{2\pi}{2a}$ (the position of the first Bragg peak in the scattering on the magnetic structure with a period of $2a$, where $a = \text{C-C}$ bond length in cumulene. The magnitude of the magnetic scattering was estimated by formulas given in paper [10] with the help of Slater $2p_z$ functions with $Z_{\text{eff}} \approx 3.2$.

High values of the first magnetic peak correspond to high Z_{eff} . The corresponding experiments on neutron diffraction are still under way.

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