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Commentationes

Local Electronic States in Long Polyene Chains

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The local electronic states in long polyene chains are considered analytically in the Hückel approximation with and without taking account of bond alternation. The following types of chain defects which might be responsible for an appearance of local states are discussed: change of the Coulomb integral of one atom, identical change of the Coulomb integrals of two atoms, strengthening or weakening of one bond, simultaneous change of the resonance and Coulomb integrals of the end bond or of the end atom. The conditions for removing the local states from the allowed bands depending on the positions of the defects in the chain are given.

Die lokalisierten Elektronenzustände in langen Polyenketten werden im Rahmen der Hückelschen Theorie ohne und mit Berücksichtigung der Bindungsalternierung auf analytischem Wege behandelt. Folgende Möglichkeiten von Defekten in der Kette, die zu lokalisierten Zuständen führen können, werden in Betracht gezogen. Änderungen des Coulombintegrals eines Atoms, gleiche Änderung der Coulombintegrale zweier Atome, Vorhandensein einer schwächeren oder stärkeren Bindung, gleichzeitige Änderung von Resonanz- und Coulombintegral von Bindung bzw. Atom am Kettenende. Schließlich werden die Bedingungen, unter denen sich die lokalisierten Zustände von den möglichen Bändern entfernen, in Abhängigkeit von der Lage der Defekte angegeben.

Les états électroniques locaux des longues chaînes polyéniques sont étudiés analytiquement dans l'approximation de Hückel, avec et sans alternance des doubles liaisons. On discute des types de défauts dans la chaîne susceptibles d'être responsables de l'apparition d'états locaux: modification de l'integrale coulombienne sur un atome, variation identique des intégrales de Coulomb sur deux atomes, renforcement ou affaiblissement d'une liaison, changement simultané des intégrales de résonance et coulombiennes sur la liaison et l'atome terminaux. On donne les conditions pour écarter les états locaux des bandes permises selon les positions des défauts dans la chaîne.

Introduction

It is well known that the energy spectrum of π-electrons in the long polyene chains has two bands for allowed states – valence and conduction bands separated by the forbidden zone of width $\triangle E$ (see e.g. [1]). According to Peierls' theorem on nonstability of a one-dimensional metal with respect to nuclear displacement [2], the value $\triangle E$ must be different from zero. It was recently shown [3–7] that the electronic interaction plays an important role in this effect.

It is reasonable to ask the following question: how would the energy picture change with the introduction of defects into the polyene chain? The defects may appear to be due to the heterogeneous atoms in the carbon chain, to the substituents

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of the hydrogen atoms, to the space distortion, etc. In all quantum-mechanical models based on the π-electron approximation which take account of the interaction of a limited number of the nearest neighbours[1] the appearance of the defects is described by the change of some parameters in the effective π-electron Hamiltonian. For a long chain this change might be considered as a local perturbation. In particular, the following problem is of interest. How much should the parameters be changed in order to obtain the local states? These are the electronic states located outside the allowed bands in the forbidden zone, above and below the allowed bands.

A general method for solving problems of this type has been worked out by Lifshits [10] in application to vibrations in defective crystals and then, independently, by Koster and Slater [11] in a study of the impurity levels in crystals. The method gives a possibility of getting expressions in closed form for the energy and wave functions of the local states through the property of unperturbed systems and has at least three important aspects. 1) It permits a study of the local states without determination of the band state properties. 2) One must solve the system of equations which has an order not higher than the number of perturbed atoms. 3) In some cases the method opens up the possibility of finding exact solutions. In quantum-chemical applications the method was succesfully used by Koutecký in his work on the theory of chemisorbtion [12].

In the present communication this method is applied to the study of the local states in long polyene chains. Wishing to obtain mainly qualitative results in terms of simple analytical formulae we restrict ourselves to the Hückel approximation taking into account bond alternation. We shall also consider chains with all bond lengths equal, which is not applicable to polyenes, but may be useful in some other situations, i.e., removing the local states from an allowed band in the case were the forbidden zone is broad, surface defects in simple cubic crystals, etc. Detailed derivations of some results presented here are given in [13–15].

General Relations

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

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

where $H_{nn'}$ and $V_{nn'}$ are matrix elements of the Hamiltonian of the unperturbed problem and of the perturbation in the AO's representation, respectively. Following the procedure developed in [16] for the study of the local vibrations in crystals let us introduce the Green function of the Eq. (1)

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

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

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[1] For the justification of the latter approximation see e.g. [8, 9].

U_n are the solutions of the following system of equations:

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

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

As it is well known, the wave functions ψ_k and energies E_k of the states of the unperturbed chains without bond alternation are (see e.g. [17]):

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

where N is the number of atoms in the chain, β is the resonance bond integral, and $k = \pi s/(N+1)$ $(s = 1, 2, \ldots, N)$. For the corresponding Green function (2) one has

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

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

$$g^0_{mn}(E) = \frac{\operatorname{sh} n\varkappa\, e^{-m\varkappa}}{\beta \operatorname{sh} \varkappa} \left[(-1)^{m-n} Q(E) - Q(-E)\right], \tag{5}$$

where a step-function

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

Here we introduced a change in notation

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

and without a loss in generality assumed that $m \geqq n$.

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

$$\begin{aligned} \psi_k^{(1)} &= \frac{1}{\sqrt{N}} \sum_{n=1}^{N} \left[\chi_{2n} \sin kn - \chi_{2n-1} \frac{\beta_1 \sin kn + \beta_2 \sin k(n-1)}{\sqrt{\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos k}}\right], \\ E_1(k) &= E_0 - \sqrt{\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos k}\,, \end{aligned} \tag{6'}$$

$$\begin{aligned} \psi_k^{(2)} &= \frac{1}{\sqrt{N}} \sum_{n=1}^{N} \left[\chi_{2n} \sin kn + \chi_{2n-1} \frac{\beta_1 \sin kn + \beta_2 \sin k(n-1)}{\sqrt{\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos k}}\right], \\ E_2(k) &= E_0 + \sqrt{\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos k}\quad . \end{aligned} \tag{6''}$$

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

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

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

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

Inserting the corresponding coefficients $\varphi_k(m)$ from (6′) and (6″) into (2), changing the summation over k to integration, and summing up over both allowed bands, one obtains the following expressions for those Green functions which will be used later:

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

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

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

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

where

$$E' = E - E_0 \, ,$$

$$E' = \pm \sqrt{\beta_1^2 + \beta_2^2 - 2\beta_1 \beta_2 \operatorname{ch} \varkappa} \, .$$

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

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

Single Substitution

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

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

Then Eq. (3) becomes

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

the condition of solvability of which

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

determines the energies of the local states.

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

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

Eq. (10) can be solved analytically for two limiting cases: 1) when $n\to\infty$ that is the substitution is made far away from the edge of the chain, and 2) when $n=1$ (surface state). When $n\to\infty$, neglecting in Eq. (10) the term $\sim e^{-nx}$ and solving the corresponding equation, one obtains the known expression for the energy of the state localized in the middle of the chain [11]

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

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

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

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

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

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

For $n\neq 1$ and $n\neq\infty$ Eq. (10) can be solved only numerically. Nevertheless, the asymptotic result can be found for the exact value of the minimal perturbation needed for removing the local state as a function of the value n. It follows from (5) that the minimal distance of the local level from the band corresponds to $\varkappa\to 0$ (or $|E-E_0|\to|2\beta|$). Substituting $\varkappa\to 0$ into (10) one concludes that perturbation of the n-th atom leads to the appearance of the local level only when

$$|\Delta\alpha/\beta|>\frac{1}{n}\,. \tag{13}$$

Now we shall consider the chain with alternating bonds. It follows from (8a) and (8d) that the results should be different for even and odd perturbed atoms. However, for $n\to\infty$ these differences are exponentially small and equations of the type (9) should be the same for the states localized in the middle of the chain. Substituting $n\to\infty$ into (8a) and (8d) and putting a corresponding expression into (9), one obtains an equation for the energy of the local states in the forbidden zone. An analogous equation could be obtained for the levels located above and below both allowed bands. We have not written down the Green functions which correspond to $|E|>|\beta_1+\beta_2|$. A solution of these equations gives the energy of the local states E_∞ for a single substitution in the middle of the chain, namely:

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

The positive sign here corresponds to the level located above or below both allowed bands, and the negative sign to the level in the forbidden zone. It follows from (14) that even an infinitely small perturbation of the distant atom leads to two local levels. One of them is located outside of the bands, and the other in the forbidden zone. When $\Delta\alpha > 0$, the level in the forbidden zone is filled, and the other is empty. When $\Delta\alpha < 0$, the situation is reserved. If $\Delta\alpha$ is small, the energy of both levels depends quadratically upon the perturbation. When $|\Delta\alpha| > |\beta_1|$ and $|\Delta\alpha| > |\beta_2|$, the energy of the out-of-band level depends linearly on $\Delta\alpha$; whereas, the energy of the other level is approximately proportional to $1/\Delta\alpha$. The latter means that one must apply an infinitely large perturbation in order for the local level to reach the middle of the forbidden zone. Thus, the level removed from the edge of the valence band cannot be transfered to the district $E > 0$ by any single substitution, and vice versa.

Now we shall consider the dependence of the minimal value of the perturbation needed for an appearance of the local level, on the number of the perturbed atom. Substituting (8a) for the even atoms into (9), one obtains

$$1 + \Delta\alpha \frac{E' \operatorname{sh} m\varkappa e^{-m\varkappa}}{\beta_1 \beta_2 \operatorname{sh} \varkappa} = 0, \tag{15}$$

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

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

and for the out-of-band levels

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

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

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

only one out-of-band level appears. If

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

the local states do not appear at all.

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

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

and for the out-of-bond level

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

Comparing (18) and (19) with (16) and (17) one sees that for large values of l the criteria for the appearance of the local states on even and on odd atoms coincide. It is also seen from (18) and (19) that the appearance conditions for the surface level ($l=1$) outside the bands and in the forbidden zone are the same, namely:

$$|\Delta\alpha^{(1)}_{\min}(1)| = |\Delta\alpha^{(2)}_{\min}(1)| = |\beta_2|\,, \tag{20}$$

that is the surface states always appear in pairs.

Let us now suppose that the polyene chain begins with the weak bond with $|\beta_1| < |\beta_2|$. This may happen, e.g., if an unpaired electron is located at the edge of the chain [18, 19]. We shall see how the results will change. In this case besides volume solutions (6′) and (6″) of an unperturbed problem (the number of solutions in the even chain is equal to $2N-2$) there are two more surface solutions localized at the edges of the chain. For a long chain when interaction of both surface states could be neglected, their energy is equal to zero, and the wave function of the state localized, say at the left edge of the chain, is

$$\psi^{(3)} = \sum_l \varphi_3(l)\chi_l\,, \qquad \varphi_3(l) = \begin{cases} \dfrac{\sqrt{\beta_2^2-\beta_1^2}}{\beta_2}\,(\beta_1/\beta_2)^{l-1}, & \text{if } l = 2m+1\,, \\ 0 & \text{if } l = 2m\,. \end{cases}$$

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

$$\frac{2\cdot\Delta\alpha\cdot E}{\pi}\int\limits_0^\pi \frac{|\varphi_1(k,l)|^2}{E^2-E_1^2(k)}\,dk + \frac{\Delta\alpha}{E}\,|\varphi_3(l)|^2 = 1\,, \tag{21}$$

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

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

instead of (18).

Eq. (22) gives an appearance condition of the local state only for

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

In the opposite case it gives a disappearance condition of the local state genetically linked to the surface state of the unperturbed chain. To illustrate the situation let us consider an exact solution of (21) for $l=1$ (perturbed surface level). The energy of the level in the forbidden zone

$$E = \operatorname{sign}(\Delta\alpha)\sqrt{\beta_1^2+\beta_2^2-2\beta_1\beta_2\operatorname{ch}\varkappa}\,, \tag{23′}$$

where

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

It is seen from (23) than when $\Delta\alpha = 0$, then $E = 0$ (level in the center of the forbidden zone). With an increase of $|\Delta\alpha|$ the level is moving to the edge of one of the allowed bands, and if $|\Delta\alpha| \to |\beta_2|$, then $|E| \to |\beta_2 - \beta_1|$ which is in agreement with the criteria (22). Further increase of $|\Delta\alpha| > |\beta_2|$ leads to the infusion of the local level into the allowed band. It follows from (19), when $|\Delta\alpha| \geqq |\beta_2|$, the surface level appears with an energy $|E| \geqq |\beta_1 + \beta_2|$, which means that it is located above or below both allowed bands. In other words for any value of $|\Delta\alpha|$ in the chain with a broken strong edge-bond there may be one and only one surface state. As it is seen from (22), for

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

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

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

is in agreement with the known fact [12] of the difficulty of producing two local states which are situated in the immediate neighborhood of one another. The extent of the chain region in which this effect can be observed is greater if the width of the forbidden zone is smaller.

Double Substitution

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

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

and (3) is reduced to

$$U_l + \Delta\alpha[g_{lm}(E)\,U_m + g_{ln}(E)\,U_n] = 0\,. \tag{24}$$

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

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

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

Let us first consider the chain without bond alternation. Substituting the necessary Green functions from (5) into (25), one obtains

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

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

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

If $m, n \gg 1$, but $|m-n| \sim 1$, then neglecting terms like $\sim \exp(-m\varkappa)$, $\exp(-n\varkappa)$, one obtains from (26)

$$\left|\frac{\Delta\alpha}{\beta}\right| \frac{1 \pm e^{-|m-n|\varkappa}}{\operatorname{sh}\varkappa} = 1\,. \tag{27}$$

The solution of (27) with the positive sign exists for any value of $|\Delta\alpha/\beta|$ and $\varkappa \to 0$, that is an appearance of the local level corresponds to $|\Delta\alpha/\beta| \to 0$. If one considers the negative sign in (27), then a solution does not always exist. An appearance of a solution ($\varkappa \to 0$) which corresponds to the second local level is possible only when $|\Delta\alpha/\beta| > 1/(m-n)$. Thus, if in the case of infinitely distant impurities located in the middle of a chain, there are always two (degenerate) local states, but when defects approaching one other, degeneracy is removed, and if the perturbation is not large enough, i.e.,

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

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

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

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

$$\operatorname{ch}\varkappa_0 = \sqrt{1 + \left(\frac{\Delta\alpha}{2\beta}\right)^2}\,.$$

The corresponding value of $\varkappa_0$ is substituted into (27), then $\varkappa_1$ is found, etc. After the first iteration the solution is as follows:

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

To analyse the appearance conditions of the local states when both perturbed atoms are located not far from the chain edge, we should return to (26). Letting $\varkappa \to 0$, one obtains the following appearance conditions for one

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

and for two local levels

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

It is easy to see that the right-hand side of (30′) is smaller than $1/m$ but that of (30″) is larger than $1/n$. Thus, the perturbation needed for an appearance of one local level in the case of two interacting impurities is smaller, but for the appearance of two levels is larger than the perturbation needed for an appearance of one local level on any of the two (n and m) single impurities.

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

Let us first consider the interaction of two even atoms. Substituting (8a) into (25) one obtains an equation for the determination of local state energies, namely:

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

Analysis of the appearance conditions having one or two solutions of (31) is analogous to the analysis of Eqs. (26) and (27). In fact, this analysis was based on the consideration of these equations in the limiting case where $\varkappa\to 0$ which in the present case corresponds to an approach up to the edges of the allowed bands, that is $|E|\to|\beta_1-\beta_2|$. Comparing asymptotic expressions for (26) and (27) we see that they become the same if $1/\beta$ is changed to $(\beta_1-\beta_2)/(\beta_1\beta_2)$. Thus, by analogy with (28)–(30) we have the following conclusions. The value of the perturbation $|\Delta\alpha|$ needed for an appearance of one local state in the forbidden zone is

$$|\Delta\alpha_1| \geqq \left|\frac{\beta_1\beta_2}{\beta_1-\beta_2}\right| \frac{m+n-\sqrt{(m+n)^2-4n(m-n)}}{2n(m-n)}, \tag{32}$$

and for a perturbation which leads to the two local states

$$|\Delta\alpha_2| \geqq \left|\frac{\beta_1\beta_2}{\beta_1-\beta_2}\right| \frac{m+n+\sqrt{(m+n)^2-4n(m-n)}}{2n(m-n)}. \tag{33}$$

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

$$|\Delta\alpha_1| \geqq 0\,, \qquad |\Delta\alpha_2| \geqq \left|\frac{\beta_1\beta_2}{\beta_1-\beta_2}\right| \frac{1}{m-n}. \tag{34}$$

In the latter case (31) is simplified to

$$\frac{\Delta\alpha\cdot E'}{2\beta_1\beta_2\,\mathrm{sh}\,\varkappa}\left(1\pm e^{-|m-n|\varkappa}\right)=-1 \tag{35}$$

and can be solved by the iteration method if the second term of the left-hand side of (35) is small enough. As a zero approximation, we may take the values of E'

and $\varkappa_0$ for infinitely distant impurities given by (14). The solution after the first iteration is

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

where
$$(\Delta\alpha')^2 = (\Delta\alpha)^2[1 \mp 2e^{-(m-n)\varkappa_0}].$$

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

Finally considering the interaction of two even defects we note, as is seen from (31), that the local level cannot be shifted to the center of the forbidden zone ($E'=0$) by any finite perturbation $\Delta\alpha$.

Now we shall consider the behaviour of the local states in the case of the interaction of even and odd defects. Substituting (8c)–(8d) into (25), one obtains the following equation for the energies of the local states:

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

It is seen from (37) that unlike to the interaction of even impurities, an increase of $|\Delta\alpha|$ may shift the local level to the center of the forbidden zone and one may even pass through the whole forbidden zone from the bottom to the top. However, it may be shown that the perturbation needed for this increases exponentially with the increase of the distance between the impurities. Therefore, an analysis of (37) when $\varkappa \to 0$ should be carried out with care for here we meet cases of not only the appearance of the local states (removing from the bands) but also disappearance of the local states when for large $|\Delta\alpha|$ they are removed from one of the allowed bands, going through the whole of the forbidden zone, and flow into another band.

It is obvious for physical reasons (see also results for single substitution), that when approaching the lower edge of the upper band $[E' \to -(\beta_1-\beta_2)]$ the perturbation $\Delta\alpha < 0$ corresponds to an appearance of the local level and a $\Delta\alpha > 0$ to an infusion of the previously existing level into the band. The situation is reversed when approaching the upper edge of the lower band. Substituting $\varkappa \to 0$ and $E \to (\beta_1-\beta_2)$ into (37), one obtains a quadratic equation with respect to $\Delta\alpha$, namely:

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

As it is seen from (38), for $|n-m| > \beta_2/(\beta_1-\beta_2)$ both roots are positive. This means that for sufficiently large $\Delta\alpha$ two local levels may be removed from the lower band. The values of $\Delta\alpha$ needed for removing one or two levels should satisfy the inequalities $\Delta\alpha \geqq \alpha_1$ and $\Delta\alpha \geqq \alpha_2$, where α_1 and α_2 are the larger and smaller roots of (38) in the absolute sense.

If $|m-n| < \beta_2/(\beta_1-\beta_2)$, then one solution of (38) is positive, and the other which is larger in the absolute sense is negative. The value $\Delta\alpha \geqq \alpha_1$ leads to an appearance of one local level, and any further increase in $\Delta\alpha$ cannot lead to removing the second level. The value $\alpha_2 < \Delta\alpha < -\alpha_1$ corresponds to the local level which is removed from the lower edge of the upper band when $\Delta\alpha = -\alpha_1$ and shifted to the upper edge of the lower band when $\Delta\alpha \to \alpha_2$. Thus, if the perturbed even and odd atoms are located sufficiently close to one another so that their numbers $2n$ and $2m-1$ satisfy the inequality

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

then any identical perturbation of both atoms cannot lead to an appearance of more than one local level in the forbidden zone. In particular, as it follows from (39), two neighbouring perturbed atoms ($n=m$) linked by a stronger bond for any values β_1 and β_2 can give only one local level in the forbidden zone. It may also be shown that there is another situation for the levels located above and below the edges of both bands, namely: it is always possible to find such a value $|\Delta\alpha|$ that two levels will be removed.

Perturbed Bond

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

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

Then Eq. (3) is transformed to

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

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

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

It follows from (5), (8a)–(8d) that Eq. (41) has the same pattern for both signs of the energy. It means that the present local states always appear in pairs and that their energies differ only in the sign.

We shall first consider the chain without bond alternation. Substituting the necessary Green functions from (5) into (41), one obtains

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

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

$$E = E_0 \pm \left(\beta' + \frac{\beta^2}{\beta'}\right) \qquad \beta' = \beta e^{\varkappa}. \tag{43}$$

It follows from (43) that an appearance of a pair of local states is possible only when the bond is strengthened.

An analytical solution can also be found if the perturbed bond is located at the end of the chain. Substituting $n=1$ into (42) and solving the corresponding equation, one obtains

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

It follows from (44) that the local states exist only when the end-bond is sufficiently strengthened, namely, when $|\beta'/\beta| > \sqrt{2}$.

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

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

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

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

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

It follows from (46) that an appearance of the local state with an energy E_- located above the valence band is possible when

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

and for the level E_+ located below the same band

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

It means that there are two local levels if

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

and only one if

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

The Eq. (42) permits the derivation of a relationship between the minimum perturbation needed for the appearance of paired local states and the number n of the perturbed bond. Letting $\varkappa \to 0$ in (42) we see that the local states appear only if

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

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

Substituting corresponding Green functions from (8a)–(8d) into (41), the following equation is obtained for the local levels appearing under the perturbation of the weaker bond

$$\begin{aligned}\left[1+\frac{\Delta\beta}{\beta_1\beta_2}(\beta_2-\beta_1 e^{-\varkappa})\frac{\operatorname{sh} n\varkappa\, e^{-n\varkappa}}{\operatorname{sh}\varkappa}\right]^2 &= \frac{(\Delta\beta)^2 E'^2 \operatorname{sh} n\varkappa}{2\beta_1^2\beta_2^2 \operatorname{sh}^2\varkappa}\, e^{-n\varkappa} \\ &\quad\cdot\left[1-\frac{e^{-(2n+1)\varkappa}}{E'^2}(\beta_2 e^{\varkappa/2}-\beta_1 e^{-\varkappa/2})^2\right],\end{aligned} \tag{48}$$

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

$$E' = \pm\sqrt{\beta_1^2+\beta_2^2-2\beta_1\beta_2 \operatorname{ch}\varkappa}, \tag{49}$$

where

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

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

$$\Delta\beta = \beta_2' - \beta_2 .$$

An analysis of (49) shows that this solution exists only when $|\beta_2'| > |\beta_2|$. This means that any small strengthening of the weaker bond in the middle of the chain always leads to the appearance of two local states in the forbidden zone.

Eq. (48) also permits the derivation of the dependence of the perturbation needed for an appearance of paired local states on the number of the perturbed bond. Letting $\varkappa \to 0$ in (48), the following condition for their appearance is obtained

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

where l is the number of the perturbed bond.

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

$$\begin{aligned}&\left\{1+\frac{\Delta\beta\, e^{-m\varkappa}}{\beta_1\beta_2 \operatorname{sh}\varkappa}[\beta_1 \operatorname{sh} m\varkappa - \beta_2 \operatorname{sh}(m-1)\varkappa]\right\}^2 \\ &\quad= \frac{1}{2}\left(\frac{\Delta\beta}{\beta_1\beta_2 \operatorname{sh}\varkappa}\right)^2 e^{-m\varkappa} \operatorname{sh} m\varkappa\,[E^2 - e^{-2m\varkappa}(\beta_2 e^{\varkappa}-\beta_1)^2],\end{aligned} \tag{51}$$

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

$$E_\pm = \pm\sqrt{\beta_1^2+\beta_2^2-2\beta_1\beta_2 \operatorname{ch}\varkappa}, \tag{52}$$

where

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

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

$$\Delta\beta = \beta_1' - \beta_1\,.$$

An analysis of (52) shows that any small weakening of the stronger bond located far away from the chain edge is sufficient for an appearance of the local levels.

Substituting $m=1$ into (51) one obtains for the surface state

$$E_{\text{surf.}} = \pm\sqrt{\beta_1^2 + \beta_2^2 - 2\beta_1\beta_2 \operatorname{ch}\varkappa}\,, \tag{53}$$

where

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

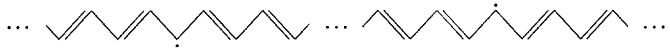
It is easy to see that the solution of (53) as well as the surface state exists only when the first bond is sufficiently relaxed, namely, when

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

From Eq. (51) the relationsip of a perturbation needed for the appearance of the local states on the number m of the perturbed bond can be obtained. It follows from (51) that the local states appear only if

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

The characteristic nontrivial property of polymers with conjugated bonds is the presence of paramagnetic centers. This was repeatedly proved experimentally by the ESR method [20–24]. A satisfactory explanation of the general regularities of this phenomena is possible in terms of the local defect centers and the charge transfer between macromolecules [18, 19, 25–29]. In particular it was suggested [18] that an experimentally observed ESR signal in long conjugated systems may be connected with an appearance of a pair of defects of the type



These defects have been interpreted [18] as radicals. The energy of the unpaired electrons localized on the defects situated at large distance from one another is equal to zero (Fig. 1).

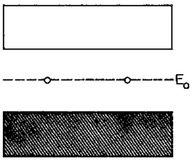


Fig. 1. Energy pattern of electrons when defects are infinitely distant from one another

Pople and Walmsley [18] noted that when defects approach each other, for vibrations of the nuclei core, the zero degenerate level is split and both electrons should drop to the lower level. The following valence sheme is obtained when the defects approach one another as closely as possible

This state is not a triplet state. In fact this defect may originate simply by the weakening of one of the double bonds so that its resonance integral becomes equal to β_2 instead of β_1. This could be obtained, e.g., by a distortion of the chain co-planarity. The energies of these local states thus obtained, are given by formulae (52) with $\beta' = \beta_2$. The picture of the energy levels is given in Fig. 2a. Transition to the lowest excited state (Fig. 2b) requires an energy $E_+ - E_-$. If one assumes that spontaneous (thermal) appearance of such states is possible only for the scheme 2b, then it is obvious that within the framework of the method used here and by the authors of [18] the energies of the states pictured in Fig. 1 and Fig. 2b are the same and are equal to the energy of the transition of one electron from the valence band to the conduction band. This simply means that a consideration of such defects without accounting for the deformation of the σ-core and the electronic interaction is not correct.

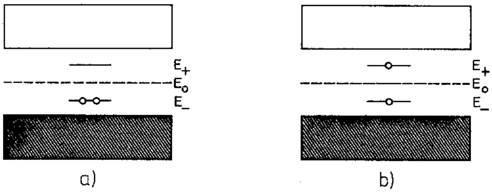


Fig. 2. Energy pattern of electrons when defects are close to each other: *a* ground state, *b* excited state

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