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Electronic Structure of Long Polyene Chains with an Impurity Atom

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The influence of an impurity atom on the π-electronic structure of long polyenes is considered using the unrestricted Hartree-Fock (UHF) method. It is shown that the substitution of a carbon atom in a long polyene chain is a local perturbation in spite of the nonlinearity of the UHF Hamiltonian. The conditions under which the local states appear in the forbidden zone of long polyenes are stated. Some experiments are proposed to elucidate the nature of the forbidden zone in the π-electron spectra of long polyene chains.

Der Einfluß eines Fremdatoms auf die π-Elektronenstruktur langer Polyene wird mit Hilfe der uneingeschränkten Hartree-Fock-Methode (UHF) untersucht. Es wird gezeigt, daß die Substitution eines C-Atoms in einer langen Polyenkette eine lokale Störung darstellt, obwohl der UHF-Hamiltonoperator nicht linear ist. Die Bedingungen, unter denen die lokalen Zustände in der verbotenen Zone für die langen Polyene erscheinen, werden dargestellt. Einige Experimente zur Aufklärung der Natur der verbotenen Zonen in den π-Elektronen-Spektren langer Polyenketten werden vorgeschlagen.

La méthode Hartree-Fock sans restrictions (UHF) est utilisée pour étudier l'influence d'une impureté atomique sur la structure électronique π des grands polyènes. On montre que la substitution d'un atome de carbone dans une longue chaîne polyénique est une perturbation locale en dépit de la non linéarité de l'hamiltonien UHF. On énonce les conditions d'apparition des états locaux dans la zone interdite des longs polyènes. Certaines expériences sont proposées pour élucider la nature de la zone interdite dans le spectre d'électrons π des longues chaînes polyéniques.

Introduction

The optical experiments have shown [1] that the frequency of the first electronic transition in polyenes tends to a non-zero value when the polyene chain is lengthened. Until recently this energy gap was supposed to arise from the instability of the equal-bond polyene configuration with respect to the bond alternation [2, 3]. Nevertheless, it has recently been shown that the unrestricted Hartree-Fock (UHF) method taking into account electron correlation can be used to describe[1] the π-electronic spectra of large conjugated systems (polyenes, cumulenes, polyacenes, graphite) [4–11]. The papers [4, 9–11] have dealt with the electronic structure of ideal polyene chains consisting of an even [4, 9] or odd [10, 11] number of carbon atoms.

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[1] Effect of projecting of the UHF wave function on the pure spin state is considered in Ref. [22] for the case of large systems.

Comparing with experiment only the values of energy gaps, obtained in the two different models, do not make it clear which of these models (or their combination [12]) is more realistic. One of the possible methods of investigating the electronic structure of periodic systems is to study the influence of the appropriately introduced defects on the energy spectra of these systems. That is why, to study the effect of disturbed periodicity on the electronic structure of polyene chains by means of the UHF method is of interest. The same problem has been discussed in [13–15] under the assumption that the energy gap is due to the bond alternation.

The UHF Solution for Long Polyene Chains with an Impurity Atom

The UHF equations for an ideal polyene chain have the following form in the orthogonal AO representation [4, 9–11]

$$\begin{aligned}\left(\alpha_0+\frac{\gamma}{2}+\varepsilon_k^{(j)}\right)C_{k\sigma}^{(j)}(\mu)&=\sum_{\nu=1}^{N}\boldsymbol{H}_\sigma(\mu,\nu)\,C_{k\sigma}^{(j)}(\nu)\\ &\equiv[\alpha_0+\gamma n^{(0)}_{\mu,\bar\sigma}]\,C_{k\sigma}^{(j)}(\mu)+\beta[(1-\delta_{\mu,1})\,C_{k\sigma}^{(j)}(\mu-1)+(1-\delta_{\mu,N})\,C_{k\sigma}^{(j)}(\mu+1)]\,,\end{aligned}\tag{1}$$

where α_0 and β are the Coulomb and resonance integrals, γ is the electron repulsion integral, $n^{(0)}_{\mu\sigma}=\sum_{k<\frac{\pi}{2}}[C_{k\sigma}^{(1)}(\mu)]^2$ are the electron populations of the μ-th AO with σ-spin, $\sigma=\uparrow,\downarrow$.

The solution of (1) is defined by the relations

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

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

$$\varepsilon_k^{(1)}=-\varepsilon_k^{(2)}=-\sqrt{4\beta^2\cos^2k+a^2}\,,\tag{3}$$

where $N\gg1$ is the number of carbon atoms in the chain. The self-consistent value of a is found from the equation

$$\begin{gathered}\frac{\gamma}{\pi}\int_0^{\pi/2}dk(4\beta^2\cos^2k+a^2)^{-1/2}=1\,;\\ \tau_\sigma=\begin{cases}1, & (\sigma=\uparrow)\\ -1, & (\sigma=\downarrow)\end{cases}\end{gathered}\tag{4}$$

$$\xi_k=[2\beta\cos k+\sqrt{4\beta^2\cos^2k+a^2}]/a\,.\tag{5}$$

The width of the forbidden zone between the energy levels $\varepsilon_k^{(1)}$ occupied in the ground state and empty levels $\varepsilon_k^{(2)}$ is equal to $2a$. It follows from (2)–(5) that

$$n^{(0)}_{\mu\sigma}=\frac{1}{2}+(-1)^{\mu+1}\frac{2\tau_\sigma\gamma}{\pi}\int_0^{\pi/2}dk\,\frac{\sin^2\mu k}{\varepsilon_k^{(2)}}=\frac{1}{2}+(-1)^{\mu+1}\delta_\mu\,.\tag{6}$$

As is seen from (6) the values of δ_μ depend on an atom number μ. The analysis of (6) shows that this dependence occurs near the chain boundary:

$$\delta_\mu \approx \delta + (\tfrac{1}{2})^{\mu-1} \Delta\delta , \tag{7}$$

where $\delta = a/\gamma = 0.21$, $\Delta\delta = 0.06$ ($\beta = -2.4$ eV, $\gamma = 5{,}4$ eV [4]).

Using the UHF method we now consider the electronic structure of a long polyene chain with the ν-th atom substituted. We make an assumption that such a substitution can be approximated by changing an appropriate Coulomb integral as: $\alpha_\nu = \alpha_0 + t$. As seen from (1), the change of γ corresponding to perturbed atom can be taken into account by an appropriate change of the effective value of α. We shall consider here such substitutions which can be described by the change of the parameters α and γ only, i.e. the values of β are considered to be close to those for ideal polyenes. There are a number of substitutions which satisfy the above conditons, e.g. $H \rightarrow CH_3$, $C \rightarrow N$.

The UHF Hamiltonian for polyenes (1) is a non-linear operator since it contains $n_{\mu\sigma}^{(0)}$ (6). Therefore, a direct application of the local-perturbation theory [16] developed for linear Hamiltonians [17, 18] (e.g., for the tight binding method) requires an justification. The correct solution involves an iteration procedure usual for the calculations by the SCF methods. Consequently, one can use the local-perturbation theory for each iteration. The equation for eigenfunctions and eigenvalues in the case of long polyenes with the substitution has the following form for the first iteration (e.g., see [17])

$$(\hat{H}_\sigma + t\hat{\Lambda} - z_\sigma)\varphi_\sigma = 0 , \tag{8}$$

where $\hat{H}_\sigma$ is given by (1), the operator $\hat{\Lambda}$ is defined by

$$(g, \hat{\Lambda}\varphi) \equiv \sum_{\mu,\,\mu'} g^*(\mu)\Lambda(\mu,\mu')\varphi(\mu') = g^*(\nu)\varphi(\nu) . \tag{9}$$

Let us present some general results which follow from [17]. Eigenvalues $z_{q\sigma}^{(i)}$ of the Eq. (8) are determined by

$$1 + t\sum_{k,\,j} \frac{[C_{k\sigma}^{(j)}(\nu)]^2}{\varepsilon_k^{(j)} - z_{q\sigma}^{(i)}} = 0 . \tag{10}$$

It follows from (10) that a perturbation of type (9) gives rise to the infinitesimal shifts of zone levels:

$$z_{k\sigma}^{(i)} = \varepsilon_k^{(i)} + \frac{\pi}{N}\,\frac{d\varepsilon_k^{(i)}}{dk}\,\Theta_{k\sigma}^{(i)} . \tag{11}$$

The perturbation of the type (9) can also give rise to a local state splitting off zones. This question will be discussed in the next section. Now, we consider the effect of the substitution of an atom placed near the end of polyene chain ($\nu \ll N$). Then the shifts in a quasi-continuous spectrum are determined by the equation (see Appendix)

$$\operatorname{ctg}\pi\Theta_{k\sigma}^{(i)} = -\frac{\sin 2k}{2\lambda L_{k\sigma}^{(i)}(\nu)\sin^2\nu k}\left[1 - \lambda L_{k\sigma}^{(i)}(\nu)\frac{\sin 2\nu k}{\sin 2k}\right] , \tag{12}$$

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

$$L_{k\sigma}^{(i)}(\nu) = \frac{1}{2|\beta|}\left[\varepsilon_k^{(i)} + (-1)^{\nu} a\tau_\sigma\right]. \tag{13}$$

The eigenfunctions corresponding to the eigenvalues (11) can be written as (for the derivation, see Appendix)

$$\varphi_{k\sigma}^{(i)}(\mu) = \sqrt{\frac{2}{N}}\,\tilde{C}_{k\sigma}^{(i)}(\mu)\sin(k^*\mu - \pi\Theta_{k\sigma}^{(i)}), \qquad (\mu > \nu), \tag{14}$$

$$\varphi_{k\sigma}^{(i)}(\mu) = \sqrt{\frac{2}{N}}\,\tilde{C}_{k\sigma}^{(i)}(\mu)\sin(\nu k - \pi\Theta_{k\sigma}^{(i)})\sin\mu k/\sin\nu k, \qquad (\mu < \nu), \tag{15}$$

$$\varphi_{k\sigma}^{(i)}(\nu) = \sqrt{\frac{1}{2N}\,\frac{d\varepsilon_k^{(i)}}{dk}}\,\sin\pi\Theta_{k\sigma}^{(i)}/(t\tilde{C}_{k\sigma}^{(i)}(\nu)\sin k\nu), \tag{16}$$

where $C_{k\sigma}^{(i)}(\mu) = \sqrt{\frac{2}{N}}\,\tilde{C}_{k\sigma}^{(i)}(\mu)\sin\mu k$, $k^* = k + \frac{\pi}{N}\,\Theta_{k\sigma}^{(i)}$. It follows from (14) that the perturbation results in the phase shift of the eigenfunctions for $\mu > \nu$. In order to define under what conditions the relations (10)–(16) correspond to the self-consistent solution of Eq. (8) we evaluate $n_{\mu\sigma}$. Transforming (14) yields for the zone-state density at the μ-th atom

$$\begin{aligned}[n_{\mu\sigma}^{(1)}]_{\text{zone}} &= \sum_k [\varphi_{k\sigma}^{(1)}(\mu)]^2 = \frac{1}{2} + (-1)^{\mu+1}\delta_\mu\tau_\sigma \\ &\quad + \frac{a}{\pi}\int_0^{\pi/2} dk\,[\cos(2\mu k - 2\pi\Theta_{k\sigma}^{(i)})]/\varepsilon_k^{(2)} \qquad (\mu > \nu).\end{aligned} \tag{17}$$

Comparing (17) with (6) one can see that the perturbation effect on the zone-state density is transferred along the chain in the same way as the influence of its boundary, i.e. it sharply attenuates ($2^{|\mu-\nu|}$ times at the distance $|\mu-\nu|$). Thus, if $\mu - \nu \gg 1$ then (17) leads to $n_{\mu\sigma}^{(1)} = n_{\mu\sigma}^{(0)}$. It means that regardless of the non-linearity of the UHF equations, the impurity effect is local as in the case of linear Hamiltonians. Following [17] one can obtain for the electron density at the impurity atom (see Appendix)

$$n_{\nu\sigma}^{(1)} = \frac{d}{dt}\sum_k (z_{k\sigma}^{(1)} - \varepsilon_k^{(1)}). \tag{18}$$

Taking into consideration Coulson's and Lonquet-Higgins' relation [19], we reduce the expression (18) to the form

$$n_{\nu\sigma}^{(1)} = \frac{d}{dt}\,\frac{1}{2\pi i}\oint_C z\,d\ln[M_\sigma(z)/M_\sigma^{(0)}(z)], \tag{19}$$

where the integration is in the positive direction along the infinite half-circle ($\mathrm{Re}\,z < 0$) and imaginary axis in the complex plane z; $M_\sigma(z)$ and $M_\sigma^{(0)}(z)$ are determinants which vanish at the points $z = z_{k\sigma}^{(i)}$ and $z = \varepsilon_k^{(1)}$, respectively. The expression (19) can be written as [20]

$$\begin{aligned} n^{(1)}_{\nu\sigma} &= \frac{d}{dt}\frac{1}{2\pi i}\oint_C z\, d \ln[1 - t\,G_{0\sigma}(\nu, \nu; z)] \\ &= -\frac{1}{2\pi i}\oint_C dz \frac{d}{dt}\ln[1 - t\,G_{0\sigma}(\nu, \nu; z)]\,, \end{aligned} \tag{20}$$

where the function

$$G_{0\sigma}(\nu, \mu; z) = \sum_{kj} \frac{C^{(j)}_{k\sigma}(\nu)\, C^{(j)}_{k\sigma}(\mu)}{z - \varepsilon^{(j)}_k} \tag{21}$$

is the Green function:

$$\sum_{\mu'=1}^{N} [H_\sigma(\mu, \mu') - z\delta_{\mu\mu'}]\, G_{0\sigma}(\mu', \nu; z) = -\delta_{\mu\nu}\,.$$

The equivalence of expressions (19) and (20) results from the fact that in accordance with (10) the functions in bracets in (19) and (20) have simple poles and zeroes at the same points. Having failed to obtain general analytical expressions for (17) or (19) we now discuss some limiting cases. Let $|\lambda| \ll 1$. Then the integrand in (20) can be expanded in the series of λ

$$n^{(1)}_{\nu\sigma} = \frac{1}{2\pi i}\oint_C dz\, G_{0\sigma}(\nu, \nu; z) \sum_{n=0}^{\infty} [\lambda|\beta|\, G_{0\sigma}(\nu, \nu; z)]^n\,. \tag{22}$$

According to (21) $|\beta G_{0\sigma}(\nu, \nu; z)| < 1$ if $z \in C$. Therefore, the series in (22) converges regularity if $|\lambda| < 1$ and $z \in C$. As a consequence, integrating (22) term by term yields

$$n^{(1)}_{\nu\sigma} = \sum_k [C^{(1)}_{k\sigma}(\nu)]^2 \sum_{n=0}^{\infty} [\lambda L^{(1)}_{k\sigma}(\nu) \sin 2\nu k / \sin 2k]^n\,. \tag{23}$$

It follows from (23) that

$$n^{(1)}_{\nu\sigma} = n^{(0)}_{\nu\sigma} + 0(\lambda),\ |\lambda| \ll 1\,. \tag{24}$$

Thus, if $|\lambda|$ is small, the solution of (8) given by (10)–(18) and corresponding to the first iteration of the self-consistency procedure for a long polyene chain with impurity is a self-consistent one. The equation of second iteration has the following form

$$\sum_{\mu'=1}^{N} \{H_\sigma(\mu, \mu') + t A(\mu, \mu') + \gamma[n^{(1)}_{\mu\sigma} - n^{(0)}_{\mu\sigma}]\,\delta_{\mu\mu'} - z\,\delta_{\mu\mu'}\}\, \varphi_\sigma(\mu') = 0\,. \tag{25}$$

Let us consider this equation for the case $\nu = 1$, i.e. when the perturbation is localised at the first atom of the chain. It follows from (23) that

$$n^{(1)}_{1\sigma} - n^{(0)}_{1\sigma} = \sum_{n=1}^{\infty} \lambda^n (-1)^n f_{n\sigma} = -\lambda \Delta^{(1)}/\gamma\,, \tag{26}$$

where $\Delta^{(1)} > 0$,

$$f_{n\sigma} = \frac{1}{\pi} \int_0^{\pi/2} dk \sin^2 k \frac{(\sqrt{\cos^2 k + d^2} + d\tau_\sigma)^{n+1}}{\sqrt{\cos^2 k + d^2}}.$$

As seen from (26), the correction $-\lambda\Delta^{(1)}$ to the perturbation has the opposite sign to the initial perturbation $\lambda|\beta|$. Consequently, if λ is finite, the impurity is screened with zone electrones, as one should expect. It means that the effective value of the perturbation parameter $|\lambda'|$ is less than $|\lambda|$. It is easy to verify using (23) that this result is also valid if $\nu \neq 1$.

In order to evaluate differences $n_{\mu\sigma}^{(1)} - n_{\mu\sigma}^{(0)}$ for $\mu > \nu$ we now concider another limiting case: $|\lambda| \to \infty$. Then it follows from (12) that $\pi\Theta_{k\sigma}^{(i)} \to \nu k$. Hence, the relations (14)–(16) take the form

$$\lim_{|\lambda|\to\infty} \varphi_{k\sigma}^{(i)}(\mu) = \begin{cases} C_{k\sigma}^{(i)}(\mu - \nu), & (\mu > \nu) \\ 0 & (\mu \leqq \nu). \end{cases} \tag{27}$$

It follows from (27) that a strong perturbation tears the link consisting of ν atoms off the chain. It is obvious that the functions (27) are self-consistent for the chain consisting of $N - \nu \approx N$ atomes because they coincide with the self-consistent zone functions of an ideal polyene chain. Substituting (27) into (17) and using (6) and (7) we obtain

$$|n_{\mu\sigma}^{(1)} - n_{\mu\sigma}^{(0)}| = |\delta_{\mu-\nu} - \delta_\mu| \leqq |\delta_1 - \delta_2| = 0.09. \tag{28}$$

It means that the changes of values $n_{\mu\sigma}(\mu > \nu)$ are small even though the parameter $|\lambda|$ changes from zero to infinity. Thus, in order to obtain the zone functions $\varphi_{k\sigma}^{(i)}(\mu)$ of a long polyene chain with the ν-th atom substituted ($\nu \ll N$) as $\mu > \nu$, it is quite sufficient to restrict oneself to the first iteration of the self-consistency procedure for any value of the perturbation parameter λ. In particular, if $\nu = 1$ one can suppose that $n_{\mu\sigma}^{(1)} - n_{\mu\sigma}^{(0)} = \delta_{\mu 1}\left(\frac{-\lambda\Delta^{(1)}}{\gamma}\right)$. It means that the non-linearity of Eq. (8) can be neglected except for the fact that an initial perturbation parameter λ is to be replaced by its effective value λ', $|\lambda'| < |\lambda|$. On the other hand, if $\nu \neq 1$ and $|\lambda| \gg 1$ then functions $\varphi_\sigma(\mu)$ $(\mu < \nu)$ are to be close to the corresponding functions of a short polyene chain consisting of $\nu - 1$ atoms. It should be also noted that calculating $n_{\mu\sigma}^{(1)}$-values, we neglect the contribution of local-state functions, which have the amplitude (see Appendix):

$$|\varphi_{p\sigma}(\mu)| = C(e^{-\frac{1}{2}|\mu-\nu|q_0} + e^{-\frac{1}{2}(\mu+\nu)q_0}), \tag{29}$$

where $q_0 > 0$. Hence it is clear that the functions are localized near the substituted atom. If $|\lambda| \gg 1$ then $q_0 \gg 1$, i.e. $\varphi_{p\sigma}(\mu) \sim \delta_{\mu\nu}$, if $|\lambda| \ll 1$ then $\varphi_{p\sigma}(\mu) \sim \lambda$ (see Appendix, the relation (A 17)). Thus, taking into account the local-state functions does not affect the relations (24) and (28).

Local States

General results obtained in the preceeding section can be used to consider the local electronic states in polyene chains with impurity.

As stated by Lifshits [17] and Koster and Slater [18], the wave functions of local states are determined by the equations

$$\varphi_\sigma(\nu) = -\sum_{\mu,\mu'} G_{0\sigma}(\nu,\mu';z)\, t_{\mu'\mu}\varphi_\sigma(\mu)\,. \tag{30}$$

Here $t_{\mu\nu}$ is the matrix of perturbation produced by substitution. If, for example, only one of the Coulomb integrals $\alpha_\nu \to \alpha_{\nu_0} + t\Delta\alpha_{\nu_0}$ changes, then $t_{\mu\mu'} = t\delta_{\mu\mu'}\delta_{\mu\nu_0}$. To solve (30) the following relation should be satisfied

$$\mathrm{Det}\,[\delta_{\mu\mu'} + t_{\mu\mu'}G_{0\sigma}(\mu,\mu';z)] = 0\,. \tag{31}$$

The relation (31) gives the equation for evaluating the energies of local states. Substituting $\varepsilon_k^{(j)}$ and $C_{k\sigma}^{(j)}(\mu)$ from (2)–(3) into (21) one can obtain expressions for $G_{0\sigma}(\mu,\nu;z)$ for the most interesting case of local states in the forbidden zone:

$$\begin{aligned}
&G_{0\sigma}(2\mu,2\nu;z_\sigma) = (z_\sigma - a\tau_\sigma)\,(2\beta^2\,\mathrm{sh}\,\Theta)^{-1}(-1)^{\mu-\nu}[e^{-|\mu-\nu|\Theta} - e^{-|\mu+\nu|\Theta}]\\
&G_{0\sigma}(2\mu-1,2\nu-1;z_\sigma) = (z_\sigma + a\tau_\sigma)\,(2\beta^2\,\mathrm{sh}\,\Theta)^{-1}(-1)^{\mu-\nu}[e^{-|\mu-\nu|\Theta} + e^{-|\mu+\nu|\Theta}]\\
&G_{0\sigma}(2\mu-1,2\nu;z_\sigma) = (-1)^{\mu-\nu}(\beta\,\mathrm{sh}\,\Theta)^{-1}[\mathrm{sh}\,\mu\Theta - \mathrm{sh}(\mu-1)\Theta] \qquad (\nu \geqq \mu)\\
&G_{0\sigma}(2\mu-1,2\nu;z_\sigma) = (-1)^{\mu-\nu}(\beta\,\mathrm{sh}\,\Theta)^{-1}[1-e^{\Theta}]\,e^{-\mu\Theta}\,\mathrm{sh}\,\mu\Theta \qquad (\nu < \mu)
\end{aligned} \tag{32}$$

where Θ is given by the relation $\mathrm{ch}\,\Theta = \dfrac{-(z_\sigma^2 - a^2 - 2\beta^2)}{2\beta^2}$.

The Green functions determined by (32) are identical with those for a diatomic (... A – B – A – B ...) chain with equal bonds in tight binding approximation (see the expressions (9a)–(9g) in [15] for $\beta_1 = \beta_2$ and $z = a\tau_\sigma$). If the values of $n_{\nu\sigma}$ were independent of ν this fact would be concidered as trivial because the Hamiltonian (1) and that of [15] are identical. However, as follows from (6), $n_{\nu\sigma}$ depends on ν and the self-consistent field near the end of a chain differs from the one in the middle of a chain. Thus, the Hamiltonian (1) differs from the Hamiltonian of [15] and coincides with the tight binding Hamiltonian for the diatomic chain in the case of the specific change of the Coulumb integrals $\alpha_{\mu\mathrm{A}}$ and $\alpha_{\mu\mathrm{B}}$ when μ increases. As the Green functions of [15] and (32) are identical, one can use the results of [15] to consider the conditions under which the local states arise. These conditions corresponding to the simplest perturbation, which is described by the change of the Coulomb integral of an atom or resonance integral of a bond, can be formulated as follows.

The infinitesimal change $\Delta\alpha$ of the Coulomb integral of an odd atom is sufficient to give rise to a local state in the forbidden zone.

On the other hand, the perturbation of an even atom with number $2l$ generates the local state in the forbidden zone only if

$$|\Delta\alpha| > 2\beta^2\,[\sqrt{a^2 + 4\beta^2} \pm a]^{-1}\,\frac{1}{l}\,. \tag{33}$$

The wave function and the energy of the local state caused by the perturbation of the first atom will be considered in more detail. Substituting $\nu = 1$ and $t_{\mu\nu} = t\delta_{\mu\nu}\delta_{\mu 1}$ into (31) one can obtain

$$0 = 1 + \lambda[\tilde{z}_{p\sigma} - d\tau_\sigma]\,(1 + e^{-q_0})/\mathrm{sh}\,q_0\,, \tag{34}$$

with

$$\mathrm{ch}\, q_0 = 1 + 2(d^2 - \tilde{z}^2_{p\sigma}); \quad z_{p\sigma} = \frac{z_{p\sigma}}{|2\beta|} < d\,, \tag{35}$$

and

$$0 = 1 - \lambda [\tilde{z}_{p\sigma} - d\tau_\sigma]\, (1 - e^{-Q_0})/\mathrm{sh}\, Q_0\,, \tag{36}$$

with

$$\mathrm{ch}\, Q_0 = 2[\tilde{z}^2_{p\sigma} - d^2] - 1; \quad |\tilde{z}_{p\sigma}| > \sqrt{1 + d^2}\,. \tag{37}$$

As seen from (34), the infinitesimal change of the Coulumb integral of the first atom actually leads to the local state appearing in the forbidden zone. Its energy distance from the edge of the gap is equal to

$$|\tilde{z}_{p\sigma} - a| \approx a\lambda^2 = 1{,}1\,\lambda^2\,(\mathrm{eV})\,.$$

In the case of large perturbations $\lambda \to \pm\infty$ the Eq. (36) gives for the energy of local state: $\tilde{z}_{p\sigma} \to \pm\infty$.

Using the general Eq. (30) one can obtain the wave function of a local state, the first atom being perturbed

$$\varphi_{p\sigma}(\mu) = \tau_{p\sigma}(-1)^{\frac{\mu-1}{2}} e^{-\frac{\mu-1}{2} q_0}\,, \qquad (\mu \text{ is odd}) \tag{38}$$

$$\varphi_{p\sigma}(\mu) = \tau_{p\sigma}\lambda(-1)^{\frac{\mu}{2}} e^{-\frac{\mu}{2} q_0}\,. \qquad (\mu \text{ is even})\,. \tag{39}$$

Here $\tau_{p\sigma} = (1 - e^{-2q_0})/(1 + \lambda^2 e^{-2q_0})$ and q_0 are determined by (35). In accordance with (36) the greater the perturbation parameter the higher the degree of the localisation of the wave function of the impurity level in the region of impurity. It can be shown that the situation is exactly the same when $\nu \neq 1$.

If the perturbation of a chain can be simulated by a small change of the resonance integral of a bond, then it does not cause the local states to splitt off the allowed bands.

Discussion

Derived in the preceding section properties of local states differ essentially from those obtained under the assumption that the energy gap in the spectra of long polyene chains is due to the bond alternation [13]. In the latter case the perturbation giving rise to the local state in the forbidden zone is $\sim 1/l$ (l is the number of a perturbed atom) both for even and odd l. Thus, in contrast to the above model, the generation of a "surface" state ($l = 1$) is most difficult. In addition, the appropriate change of the resonance integral of a bond (weakening of a stronger bond or strengthening of a weaker bond) leads to two local states appearing in the forbidden zone.

The recent theoretical results [6, 12, 21, 22] provide an evidence in favour of the electron-correlation nature of the polyene-spectrum gap. But it appears likely that the question still remains doubtful [see, e.g., 23–25]. The above mentioned differences in the properties of local states can be used to investigate experimentally whether the energy gap is due to electron correlations or its appearence is a consequence of the bond alternation.

The results obtained seem to be useful in the study of the following question. In contrast to polyenes, the first optical transition frequency in the symmetric cyanide dyes tends to zero when the conjugated chain of the dye is lengthened [26]. Nevertheless, the long conjugated chains cyanine dyes and polyenes differ by their end groups only. Then, it is natural to correlate the above difference in the optical spectra of these molecules with the effect of nitrogenium atoms of the end groups of cyanine dyes. Indeed, the insertion of nitrogenium atoms into the chain can give rise to a local state near the bottom of an empty zone. As a consequence, the first optical transition corresponds to the transition of an electron from this local level[2] to an empty zone. The energy of this transition is small for long chains. Then, the extrapolation of experimental data can give zero value (or nearly zero value) of the first transition frequency.

Appendix

In this section we deal with the derivation of main relations used in the previous section. At first, we shall consider the sum in (10).

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

$$+0\left(\frac{1}{N}\right) \equiv [\varepsilon_q^{(i)} + (-1)^v a\tau_\sigma] S^{(i)}(q, \sigma),$$

where we have used (11). To calculate $S^{(i)}(q, \sigma)$ we shall use the method developed by Lifshits [17]. Let us denote

$$S^{(i)}(q, \sigma) = S_1^{(i)}(q, \sigma) + S_1^{(i)}(q, \sigma) \tag{A 2}$$

and evaluate apart each of the two sums.

$$S_1^{(i)}(q\sigma) = \frac{4}{N^2} \sum_{k \neq q} \frac{2\pi \Theta_{q\sigma}^{(i)} d\varepsilon_q^{(i)}/dq\, \varepsilon_q^{(i)} \sin^2 kv}{(\varepsilon_k^2 - \varepsilon_q^2)\left(\varepsilon_k^2 - \varepsilon_q^2 - 2\frac{\pi}{N} \Theta_{q\sigma}^{(i)} \frac{d\varepsilon_q^{(i)}}{dq}\right)}$$

$$-\frac{2}{\pi} \frac{\sin^2 qv}{\Theta_{q\sigma}^{(i)} \varepsilon_q^{(i)} \frac{d\varepsilon_q^{(i)}}{dq}} = \frac{2\sin^2 qv}{\frac{d\varepsilon_q^{(i)}}{dq} \varepsilon_q^{(i)}} \left\{\frac{2}{N^2} \sum_{k \neq q} \frac{\pi \Theta_{q\sigma}^{(i)}}{(k-q)\left(k - q - \frac{\pi}{N} \Theta_{q\sigma}^{(i)}\right)} - \frac{1}{\pi \Theta_{q\sigma}^{(i)}}\right\}$$

$$+0\left(\frac{1}{N}\right) \approx \frac{2\sin^2 qv}{\varepsilon_q^{(i)} \frac{d\varepsilon_q^{(i)}}{dq}} \left\{\sum_{n \neq 0} \frac{\pi \Theta_{q\sigma}^{(i)}}{\pi n(\pi n - \pi \Theta_{q\sigma}^{(i)})} - \frac{1}{\pi \Theta_{q\sigma}^{(i)}}\right\} \tag{A 3}$$

$$= -2\sin^2 qv \operatorname{ctg} \pi \Theta_{q\sigma}^{(i)}/(\varepsilon_q^{(i)} d\varepsilon_q^{(i)}/dq);$$

$$S_2^{(i)}(q, \sigma) = \frac{4}{N} \sum_{k \neq q} \frac{\sin^2 kv}{\varepsilon_k^2 - \varepsilon_q^2} = \frac{1}{2\pi\beta^2} \fint_0^\pi \frac{1 - \cos vk}{\cos k - \cos 2q} dk + 0\left(\frac{1}{N}\right), \tag{A 4}$$

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[2] The conjugated chains of cyanine dyes consist of an odd number of atoms (N). But, the number of π-electrons N_e is even: $N_e = N \mp 1$. If $N_e = N + 1$ then the local state considered above is occupied in the ground state. If $N_e = N - 1$ then there is a hole in a valency zone of cyanine dye and the explanation of optical experiments is trivial.

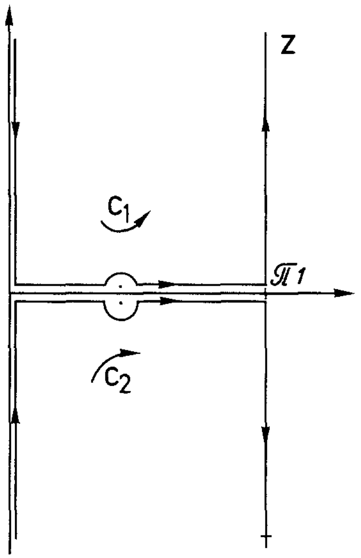

Fig. 1. The contours for the evaluation of integrals in (A 6)

where $\fint$ denotes the value principale (V.p.) of a corresponding integral. In order to evaluate (A 4) it needs to calculate

$$\fint_0^\pi \frac{\cos\nu k}{\cos k - \cos 2q}\, dk = I_1 + I_2 \equiv I\,, \tag{A 5}$$

where

$$\begin{aligned} I_1 &= \frac{1}{2} \fint_0^\pi dx \frac{e^{i\nu x}}{\cos x - \cos q}\,, \\ I_2 &= \frac{1}{2} \fint_0^\pi dx \frac{e^{-i\nu x}}{\cos x - \cos q}\,. \end{aligned} \tag{A 6}$$

The integrals (A 6) can be evaluated by means of the residuum theory. The integral I_1 is taken along the contour C_1, I_2-along C_2. The contours C_1 and C_2 are given on Fig. 1. After the calculations required performed one can obtain

$$I = \frac{\pi i}{2} \operatorname{res} \left(\frac{e^{i\nu z} - e^{-i\nu z}}{\cos z - \cos q} \right) \Bigg/_{z=q} = \pi \frac{\sin \nu q}{\sin q}\,. \tag{A 7}$$

The substitution (17) into (A 5) and (A 4) results in the relation

$$S_2^{(i)}(q, \sigma) = -\frac{1}{2\beta^2} \frac{\sin 2\nu q}{\sin 2q}\,. \tag{A 8}$$

The Eq. (12) can be obtained from (A 3), (A 8), (A 1) and (10). The eigenfunctions of (8) are defined as [17]

$$\varphi_{q\sigma}^{(i)}(\mu) = -t\tau_{q\sigma}^{(i)} \sum_{k,j} \frac{C_{k\sigma}^{(j)}(\mu)\, C_{k\sigma}^{(j)}(\nu)}{\varepsilon_k^{(j)} - z_{q\sigma}^{(i)}}\,. \tag{A 9}$$

The sum which stands in (A 9) is calculated just like as $S^{(i)}(q,\sigma)$. Let us evaluate a normalisation constant $\tau_{q\sigma}^{(i)}$.

$$\sum_{\mu=1}^{N}[\varphi_{q\sigma}^{(i)}(\mu)]^2=\left[\frac{\tilde{C}_{q\sigma}^{(i)}(v)\sin qv}{d\varepsilon_q^{(i)}/dq}t\tau_{q\sigma}^{(i)}\right]^2\frac{2}{N}\sum_k\frac{1}{\left(k-q-\frac{\pi}{N}\Theta_{q\sigma}^{(i)}\right)^2}$$
$$+0\left(\frac{1}{N}\right)=2N(t\tau_{q\sigma}^{(i)})^2\left[\frac{\tilde{C}_{q\sigma}^{(i)}(v)\sin qv}{(d\varepsilon_q^{(i)}/dq)\sin\pi\Theta_{q\sigma}^{(i)}}\right]^2=1\,. \tag{A 10}$$

Substituting $\tau_{q\sigma}^{(i)}$ from (A 10) into (A 9) one obtains (14)–(16). It follows from (A 10) that

$$[t\tau_{q\sigma}^{(i)}]^2=\sum_{k,j}\left[\frac{C_{k\sigma}^{(j)}(v)}{\varepsilon_k^{(j)}-z_{q\sigma}^{(i)}}\right]^2$$
$$=\left[\frac{dz_{q\sigma}^{(i)}}{dt}\right]^{-1}\frac{d}{dt}\sum_{k,j}\frac{C_{k\sigma}^{(j)}(v)\,C_{k\sigma}^{(j)}(v)}{\varepsilon_k^{(j)}-z_{q\sigma}^{(i)}}=-\frac{1}{t^2}\left[\frac{dz_{q\sigma}^{(i)}}{dq}\right]^{-1}. \tag{A 11}$$

Taking also into account that in accordance with (A 9) and (10) $\varphi_{q\sigma}^{(i)}(v)=\tau_{q\sigma}^{(i)}$, one obtains (18).

Now let us consider functions $G_{0\sigma}(v,\mu;z)$, where $\frac{|z|}{2|\beta|}\notin[d,\sqrt{1+d^2}]$, i.e. for states splitting off zones. Using (2), (3) one obtains

$$G_{0\sigma}(v,v;z)=-\sum_{k,j}\frac{[C_{k\sigma}^{(j)}(v)]^2}{\varepsilon_k^{(j)}-z}$$
$$=\frac{\tilde{z}+(-1)^v d\tau_\sigma}{\pi|\beta|}\int_0^\pi dk(1-\cos vk)/(\cos k+\alpha)\,, \tag{A 12}$$

where

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

The integral in (A 12) is calculated like as the integral (A 5) except the poles of the integrand are in the complex plane k on the lines $\mathrm{Re}\,k=0$ ($\tilde{z}^2>1+d^2$) and $\mathrm{Re}\,k=\pi$ ($|\tilde{z}|<d$). Having carried out the calculations required one obtains

$$\int_0^\pi dk\frac{\cos vk}{\cos k+\alpha}=\begin{cases}(-1)^v\pi e^{-vq_0}/\mathrm{sh}\,q_0, & (\alpha>0)\\ \pi e^{-vQ_0}/\mathrm{sh}\,Q_0, & (\alpha<0)\end{cases} \tag{A 13}$$

where

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

Using (A 13) one can calculate all functions $G_{0\sigma}(v,\mu,z)$ with $\tilde{z}^2>1+d^2$ or $\tilde{z}^2<d^2$. In particular, one can obtain equations for local energies

$$1-tG_{0\sigma}(v,v;z_{p\sigma})=0 \tag{A 14}$$

and for corresponding functions

$$\varphi_{p\sigma}(\mu)=t\tau_{p\sigma}G_{0\sigma}(\mu,v;z_{p\sigma})\,. \tag{A 15}$$

The relations (29), (32), (34)–(39) results from (A 14) and (A 15). If $|\lambda| \gg 1$, then it follows from (A 13) and (A 14) that $q_0(Q_0) \gg 1$. Using (29) and (16) one can see that if $|\lambda| \ll 1$ then

$$\tau_{p\sigma}^2 \sim t^{-2}(1-e^{-2q})\,\mathrm{sh}^2 q\,, \quad (q = q_0, Q_0)$$

hence

$$|\varphi_{p\sigma}(v)|^2 \sim \lambda^2\,. \tag{A 16}$$

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