Local state spectrum of end substituted polyenes

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Local state spectrum of end substituted polyenes

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Starting from the electronic part of the Su–Schrieffer–Heeger [Phys. Rev. B **22**, 1099 (1980)] Hamiltonian with a strict account to the end effects, it is shown that the π-electron spectrum of substituted polyenes is determined by solutions of the Lennard-Jones type equation, where each end group is represented by a single energy dependent parameter associated with the diagonal component of the end-group Green function referred to the binding site. The conditions of the appearance/disappearance of in-gap and out-of-band local π-electron states are found in the form of analytical relations between the conjugated bridge length, the C–C bond alternation parameter, and parameters of end-groups included in the above mentioned Green functions. These relations determine a set of critical parameters (defined explicitly), at which the local state spectrum undergoes qualitative transformations. On the basis of the obtained results we propose a certain procedure that allows us to predict the number of in-gap and out-of-band states in any substituted polyene provided the π-electronic structure of end groups and the bridge parameters are known. Throughout the discussion, several conclusions are made concerning the dependence of the electron localization on the finite-length and bond-alternation effects. © *1996 American Institute of Physics.* [S0021-9606(96)50148-0]

I. INTRODUCTION

The inhomogeneous distribution of the electric charge due to the localization of π-electrons in certain parts of molecules plays the crucial role in determining physical and chemical properties of organic compounds in the ground state and changing these properties under excitation. The problem of localization is especially sound for complex molecules which can be decomposed on smaller ones. In this case the challenge is presented to express characteristics of the electron localization in terms of parameters of molecule structural components. In this context it should be addressed to, in particular, substituted polyenes for developing an in-depth understanding of their electronic structure and potential use in photonics materials and molecular electronic devices.

The presence of local states in the π-electron spectrum supplies one with convincing proof of the preferable location of electrons in the system and thus, of the macroscopically inhomogeneous charge distribution. Therefore, various aspects of the electron localization problem in linear conjugated molecules have been in focus of a substantial effort.[1–7] Still, this problem seems not yet exhausted since only the simplest case of substituted polyenes, where the end groups can be modeled by heteroatoms, are studied in most detail.[2,3,7] In particular, the conditions of the existence of local states in heteropolyenes of the type $X-(CH)_{2N_d}-X$, $X^+-(CH)_{2N_d}-X^-$, and $X-(CH)_{2N_d}=CH_2$ have been found in Ref. 7. These conditions are represented by a set of critical values of the perturbation parameter ε—the difference in Coulomb integrals between carbon atom and heteroatom, which determines the number of local states with energies lying in the gap between the valence and conduction

π-electron bands in polyenes, (in-gap states) and below/above the valence/conduction bands (out-of-band states). The analytical dependence of the critical values $\varepsilon_{cr}^{(i)}$ obtained in Ref. 7 on the number of double bonds in the polyene chain N_d and alternation parameter η (see the definition below) allows one to make certain qualitative as well as quantitative conclusions with regard to the character of the electron localization in heteropolyenes, its dependence on the parameters of the molecule, and changes in preferable location of electrons caused by the molecule excitation. In the main body of this paper, Secs. II–IV, we develop further the approach proposed in Ref. 7, making it applicable to substituted polyenes with arbitrary end groups. Examples of its application to dialkyl- and diphenylpolyenes with the use of established end-group parameters are given in Sec. V, and the concluding section outlines implications and limitations of the theoretical results obtained.

II. MODEL

The structural components of the chromophore in focus include conjugated bridge—a sequence of an even number of CH (methine) groups connected by alternating single and double C–C bonds, and two end groups Γ_X and Γ_Y connected with end carbon atoms of the polyene chain. This structure can be considered as a result of substitution of end groups in an ideal polyene by molecules Γ_X and Γ_Y: $H_2C=(CH)_{2N_d}=CH_2 \rightarrow \Gamma_X-(CH)_{2N_d}-\Gamma_Y$.

As is commonly accepted with disregard of electron correlation effects which are responsible, e.g., for weak dipole forbidden transitions,[8,9] the π-electronic structure of polyenes is adequately described by the appropriately parametrized Hückel Hamiltonian with three parameters: α_C—the Coulomb integral of carbon atom (determines only the point of reference in the energy scale), β—the electron transfer resonance integral of adjacent carbon atoms in the undimerized carbon chain (determines the energy units), and

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η—the alternation parameter (determines the energy of electron transfer between carbon atoms connected by double and single bonds in units β, exp η and exp$(-\eta)$, respectively). In brief, here the bridge is supposed to be described by the electronic part of the Su–Schrieffer–Heeger Hamiltonian.[10] However, the essential feature is that we take strict account of the end effects.

Strictly speaking, C–C bonds in real polyenes are not exactly alternated, especially near the chain ends but, as shown experimentally,[11] deviations are small and play minor role. By contrast, in substituted polyenes the end C–$\Gamma_{X(Y)}$ bonds can be substantially different from both double and single bonds of the conjugated bridge. To account for this effect one has to introduce at least two additional dimensionless parameters (denoted below by β_X, β_Y) which refer to the above indicated bonds.

There can be a vast variety of particular chemical realizations of end groups in substituted polyenes, see, e.g., Refs. 12, 13. In relevant treatments, the problem of the electron localization has been often examined for certain end groups by using numerical methods. The results obtained are then discussed within analytical models too simplified to be realistic (e.g., models of equalized C–C bonds,[4] or of the infinite bridge[5,6]). In the framework of the present approach based on the Green function technique, we obtain conditions of the existence of local states in substituted polyenes taking into account the finite length of the conjugated bridge and C–C bond alternation. As shown below, the conditions mentioned can be found in the general form and expressed in terms of only one effective parameter for each end group (i.e., the π-electronic structure of end groups need not be specified and the results are applicable to any end substituted polyene). On this basis, we propose the strategy of systematic study of electron localization effects in end substituted polyenes which starts from answering fundamental questions: are there local states, of what kind, and how deep they are?

III. π-ELECTRONIC STRUCTURE OF SUBSTITUTED POLYENES

The electronic structure of substituted polyenes can be uniquely described by using the definition of the π-electron spectrum in the form $E = \pm\sqrt{2(\cosh 2\eta + \cos \xi)}$ suggested by Lennard and Jones for unsubstituted polyenes, in which case values of ξ are determined by $N_D + 1$ roots of a well known equation

$$\frac{\sin((N_d+1)\xi)}{\sin((N_d+2)\xi)} = -\exp(2\eta).$$

(We use here the notations accepted in Ref. 7.) It can be shown that in the general case of arbitrary end groups, values of ξ must obey the following transcendent equation

$$\left(1 - \exp(2\eta)\beta_X^2 G_{diag} G_{diag}^{\Gamma_X}\right)\left(1 - \exp(2\eta)\beta_Y^2 G_{diag} G_{diag}^{\Gamma_Y}\right)$$
$$- \exp(4\eta)\beta_X^2\beta_Y^2 G_{nondiag}^2 G_{diag}^{\Gamma_X} G_{diag}^{\Gamma_Y} = 0, \qquad (1)$$

where quantities $G_{diag} = E\exp(-\eta)\sin(N_d\xi)Z^{-1}$, $Z = \exp(-\eta)\sin((N_d+1)\xi) + \exp\eta\sin(N_d\xi)$, and $G_{nondiag}$

$= \exp(-2\eta)\sin\xi Z^{-1}$, represent the diagonal and nondiagonal matrix elements of the Green function operator which are calculated with the use of the end-site atomic orbitals for an ideal polyene chain with N_d double bonds and terminated by single bonds (see Ref. 7 for details). The diagonal matrix element of the Green function operator for $\Gamma_{X(Y)}$ end group, $G_{diag}^{\Gamma_{X(Y)}}$, refers to the binding site (atom) of $\Gamma_{X(Y)}$ end group, which is, at the same time, the first (last) ''site'' in the chain Γ_X–$(CH)_{2N_d}$–Γ_Y.

Equation (1) can be derived straightforwardly by using the same technique as in the case of heterosubstitution, in which case $G_{diag}^{\Gamma_{X(Y)}} = (E - \varepsilon_{X(Y)})^{-1}$ and Eq. (1) coincides with that obtained in Ref. 7. For unsubstituted ideal polyenes, $G_{diag}^{\Gamma_{X(Y)}} = E^{-1}$, $\beta_{X(Y)} = 1$, Eq. (1) reduces to the Lennard-Jones equation cited above. Thus, the advantages of Eq. (1) in comparison with the initial Schrödinger equation are the same as of the Lennard-Jones equation but applications of the former are much wider, than those of the latter.

To determine the position of any desired π-electron level in the presence of end groups of the given structure, one needs to use in Eq. (1) one diagonal component of the end-group Green functions and to specify parameters of the polyene bridge including parameters $\beta_{X(Y)}$. Provided these data known, the determination of the full π-electron spectrum is a matter of simple and fast computational routine as was demonstrated previously by calculations for heteropolyenes. Here, we concentrate our attention only on the local levels of the π-electron spectrum placing accents on analytical results.

Equation (1) may have both real and imaginary roots. The former correspond to extended or band-like π-electron states with energies lying within intervals $2\sinh|\eta| < |E| < 2\cosh\eta$, which correspond to the valence and conduction bands of the infinite polyene chain. Furthermore, if Eq. (1) has solutions for $\delta = i\xi$ or/and $\delta' = i(\pi - \xi)$, there exist in-gap ($|E| < 2\sinh|\eta|$) or/and out-of-band ($|E| > 2\cosh\eta$) local states. Being in such a state, the electron tends to reside near one of the chain ends. The smaller the localization radius is, the more pronounced the tendency of the charge separation along the molecule. As mentioned in Sec. I, the inhomogeneity of the charge density distribution has numerous physical and chemical consequences. Therefore, it is of prime importance to determine the condition of the existence of local states, the number of these states and their character.

IV. CONDITIONS OF THE EXISTENCE OF LOCAL STATES

A. General case

A remarkable feature of Eq. (1) is that it allows one to describe the perturbation, which is produced by an end group of arbitrary complexity, by only one effective energy-dependent parameter of perturbation referred to the end site, the 1st or $(2N_d+2)$th in these notations. Indeed, we can introduce

$$\varepsilon_{\Gamma_{X(Y)}}(E) = E - (\beta_{X(Y)}^2 G_{diag}^{\Gamma_{X(Y)}})^{-1}, \qquad (2)$$

where the effective site energy $\varepsilon_{\Gamma_{X(Y)}}(E)$ acquires its literal meaning of the site energy in the case of heteropolyenes if, additionally, $\beta_{X(Y)} = 1$. With account to (2) Eq. (1), which is valid in the general case of substitution, formally coincides with the description of the π-electron spectrum in the framework of the simplest heteropolyene model. To ''visualize'' this statement, we rewrite Eq. (1) making use of the notation introduced above

$$\left(1 - \frac{\exp(2\eta)G_{diag}}{E - \varepsilon_{\Gamma_X}(E)}\right)\left(1 - \frac{\exp(2\eta)G_{diag}}{E - \varepsilon_{\Gamma_Y}(E)}\right)$$
$$- \frac{\exp(4\eta)G_{nondiag}^2}{(E - \varepsilon_{\Gamma_X}(E))(E - \varepsilon_{\Gamma_Y}(E))} = 0. \qquad (3)$$

The solutions of Eq. (3) have already been examined in detail for particular types of heteropolyenes $\varepsilon_{\Gamma_{X(Y)}} = \varepsilon_{X(Y)}$, $\varepsilon_X \equiv \varepsilon$, and $\varepsilon_Y = -\varepsilon + \Delta$, where $\Delta = 0$ for $X^+ -(CH)_{2N_d} - X^-$, ε for $X -(CH)_{2N_d} - CH_2$, and 2ε for $X -(CH)_{2N_d} - X$.[7] Therefore, for further use of Eq. (3) it is convenient to redefine the effective parameters $\varepsilon_{\Gamma_{X(Y)}}$ in the following way

$$\varepsilon_{\Gamma_X}(E) \equiv \widetilde{\varepsilon}(E), \quad \varepsilon_{\Gamma_Y}(E) = -\widetilde{\varepsilon}(E) + \widetilde{\Delta}(E), \qquad (4)$$

where $\widetilde{\Delta}(E) = 2E - (\beta_X^2 G_{diag}^{\Gamma_X})^{-1} - (\beta_Y^2 G_{diag}^{\Gamma_Y})^{-1}$. Also substituting in Eq. (3) the explicit expressions for the polyene Green functions we get

$$\widetilde{\varepsilon}^2(E) - \widetilde{\Delta}(E)[\widetilde{\varepsilon}(E) - EZ^{-1}\exp(-\eta)\sin((N_d + 1)\xi)]$$
$$= \exp(-2\eta)Z^{-1}[\exp\eta\,\sin((N_d + 2)\xi)$$
$$+ \exp(-\eta)\sin((N_d + 1)\xi)]. \qquad (5)$$

Now, setting in Eq. (5) $\xi = i\delta$, $\delta \to 0$, and $E = \pm 2\cosh\eta$, we arrive at the conditions of the appearance/disappearance of out-of-band local states above the conduction ($-$) and below valence ($+$) bands ($\beta < 0$)

$$\widetilde{\varepsilon}(E)[\widetilde{\varepsilon}(E) - \widetilde{\Delta}(E)]$$
$$= \exp(-2\eta)\left(1 + 2\exp\eta\,\frac{1 \mp (N_d + 1)\cosh\,\eta\widetilde{\Delta}(E)}{2N_d\cosh\,\eta + \exp(-\eta)}\right), \qquad (6)$$

where $E = \pm 2\cosh\eta$. Similarly, finding the limit $\xi = \pi + i\delta$, $\delta \to 0$ of Eq. (5), where $E = \pm 2\sinh|\eta|$, we obtain the conditions of the appearance/disappearance of in-gap local states below the conduction ($-$) and above valence ($+$) bands

$$\widetilde{\varepsilon}(E)[\widetilde{\varepsilon}(E) - \widetilde{\Delta}(E)]$$
$$= \exp(-2\eta)\left(1 + 2\exp\eta\,\frac{1 \pm (N_d + 1)Z\,\sinh|\,\eta|\widetilde{\Delta}(E)}{2N_d\sinh\,\eta - \exp(-\eta)}\right), \qquad (7)$$

where $E = \pm 2\sinh|\eta|$.

The above relations between parameters of the polyene chain (N_d and η) and parameters of end groups (included in

$\beta_{X(Y)}^2 G_{diag}^{\Gamma_{X(Y)}}$) determine the number of in-gap and out-of-band states induced by end groups of the given structure. Thus, to predict the local state spectrum of substituted polyene, one must calculate first the corresponding Green functions taken at the energies of four edge band states of the infinite polyene chain. If the indicated values of the Green functions, as well as parameters $\beta_{X(Y)}$, η, and N_d, are known, the number of in-gap and out-of-band local states can be easily found from Eqs. (6) and (7). Moreover, changes in the local state spectrum under variation of the chain length can be also overseen. At the least, this provides a useful tool for the verification of quantitative models for the end group π-electron spectra and their effect on the electron localization in substituted polyenes.

Since, as shown above, the localization effect produced by any end groups is described by two uniquely defined effective parameters $\widetilde{\varepsilon}$ and $\widetilde{\Delta}$, one can find the dependence of the local state spectrum on ε and Δ for heteropolyenes and then, predict the local state spectrum in the presence of any other end groups. Therefore, we proceed with a discussion of conditions (6) and (7) in the case of heteropolyenes.

B. Heteropolyenes

It is instructive to consider briefly three representative types of heteropolyenes, namely, $X^+ -(CH)_{2N_d} - X^-$ ($\Delta = 0$), $X -(CH)_{2N_d} - CH_2$ ($\Delta = \varepsilon$), and $X -(CH)_{2N_d} - X$ ($\Delta = 2\varepsilon$). In this case, Eqs. (6) and (7) determine a set of critical values of only one perturbation parameter ε. These critical values $\varepsilon_{cr}^{(i)}$, $i = 1, 2, 3$, at which the number of in-gap and out-of-band states present in the π-electron spectrum changes, are summarized in Table I. The numbering of $\varepsilon_{cr}^{(i)}$ corresponds to the increase in critical values, i.e. $\varepsilon_{cr}^{(1)} \leq \varepsilon_{cr}^{(2)} \leq \varepsilon_{cr}^{(3)}$. Since the dependence of the set $\varepsilon_{cr}^{(i)}$ on N_d and η for different types of heteropolyenes has been already examined in many details, we restrict ourselves by few remarks, paying special attention to effects of the finite length of the bridge on the local state spectrum.

$X -(CH)_{2N_d} - CH_2$. If $\eta > 0$, there are no local states in the unperturbed polyene. The critical values of $|\varepsilon|$ needed for the appearance of an out-of-band ($\varepsilon_{cr}^{(1)}$) and an in-gap ($\varepsilon_{cr}^{(2)}$) states decrease monotonously with the increase of the chain length. In the limit $N_d = \infty$, $\varepsilon_{cr}^{(1)} = \varepsilon_{cr}^{(2)}$. Consequently, in the infinite-chain model the radius of local states will be overestimated, and the overestimation will be much more substantial for the in-gap state (one of frontier orbitals), than for the out-of-band state (deep or high lying orbitals). The conclusion just made directly follows from the fact that, as seen from the definitions of $\varepsilon_{cr}^{(1)}$ and $\varepsilon_{cr}^{(2)}$ given in Table I, the end effects play a negligible role for $\varepsilon_{cr}^{(1)}$ when $N_d \gg 1$, however, the same is true in respect of $\varepsilon_{cr}^{(2)}$ for much longer bridges, where $\eta N_d \gg 1$, since in real molecules $\eta \ll 1$.

If $\eta < 0$, two qualitatively different situations may be actual: (i) there are two in-gap local states for $|\varepsilon| < \varepsilon_{cr}^{(1)}$ and (ii) there are no local states if values of $|\varepsilon|$ obey the latter inequality. In addition, in the second case this is an in-gap

TABLE I. Critical values $\varepsilon_{cr}^{(i)}$ of the perturbation parameter $|\varepsilon|$ in heteropolyene of the type $X^+-(CH)_{2N_d}-X^-$, $X-(CH)_{2N_d}-CH_2$, and $X-(CH)_{2N_d}-X$. $\varepsilon_{cr}^{(i)}$ ($\varepsilon_{cr}^{(1)} \leq \varepsilon_{cr}^{(2)} \leq \varepsilon_{cr}^{(3)}$) dividing the $|\varepsilon|$-axis into regions with a different number of in-gap (''in'') and out-of-band (''out'') local states.

Type $\eta>0$	$4\eta < \ln\frac{(N_d+1)^2}{N_d^2+2N_d}$		$\ln\frac{(N_d+1)^2}{N_d^2+2N_d} < 4\eta < 2\ln\frac{N_d+1}{N_d}$		$2\eta > \ln\frac{N_d+1}{N_d}$		Definition of $\varepsilon_{cr}^{(i)}$
	In	Out	In	Out	In	Out	
	0	0	0	0	0	0	$\varepsilon_{cr}^{(1)}=e^{-\eta}$
X–···–X	1	1	1	1	1	1	$\varepsilon_{cr}^{(2)}=e^{-\eta}+2(2N_d \cosh\eta+e^{-\eta})^{-1}$
	0	1	1	2	1	2	$\varepsilon_{cr}^{(3)}=|e^{-\eta}+2(2N_d \sinh\eta-e^{-\eta})^{-1}|$
	0	2	0	2	2	2	$\varepsilon_{cr}^{(2)} \Leftrightarrow \varepsilon_{cr}^{(3)}$, if $4\eta<\ln\frac{(N_d+1)^2}{N_d^2+2N_d}$
	0	0	0	0	0	0	$\varepsilon_{cr}^{(1)}=e^{-\eta}\sqrt{1+2e^{\eta}(2N_d \cosh\eta+e^{-\eta})^{-1}}$
X$^+$–···–X$^-$	0	2	0	2	0	2	$\varepsilon_{cr}^{(2)}=e^{-\eta}\sqrt{1+2e^{\eta}(2N_d \sinh\eta-e^{-\eta})^{-1}}$
	0	2	0	2	2	2	if $2\eta<\ln\frac{N_d+1}{N_d}$, $\varepsilon_{cr}^{(2)}$ does not exist
	0	0	0	0	0	0	$\varepsilon_{cr}^{(1)}=e^{-\eta}+(2(N_d+1)\cosh\eta)^{-1}$
X–···–CH$_2$	0	1	0	1	0	1	$\varepsilon_{cr}^{(2)}=e^{-\eta}+(2(N_d+1)\sinh\eta)^{-1}$
	1	1	1	1	1	1	

Type $\eta<0$	$4|\eta| < \ln\frac{N_d+2}{N_d+1}$		$\ln\frac{N_d+2}{N_d+1} < 4|\eta| < 2\ln\frac{N_d+2}{N_d+1}$		$2|\eta| > \ln\frac{N_d+2}{N_d+1}$		Definition of $\varepsilon_{cr}^{(i)}$
	In	Out	In	Out	In	Out	
	0	0	0	0	2	0	$\varepsilon_{cr}^{(1)}=|e^{|\eta|}-2(2N_d \sinh|\eta|+e^{|\eta|})^{-1}|$
X–···–X	1	0	1	0	1	0	$\varepsilon_{cr}^{(2)}=e^{|\eta|}$
	0	1	0	1	0	1	$\varepsilon_{cr}^{(3)}=e^{|\eta|}+2(2N_d \cosh\eta+e^{|\eta|})^{-1}$
	0	2	0	2	0	2	
	0	0	0	0	2	0	$\varepsilon_{cr}^{(1)}=e^{|\eta|}\sqrt{1+2e^{\eta}(2N_d \sinh\eta-e^{|\eta|})^{-1}}$
X$^+$–···–X$^-$	0	0	0	0	0	0	$\varepsilon_{cr}^{(2)}=e^{|\eta|}\sqrt{1+2e^{\eta}(2N_d \cosh\eta+e^{|\eta|})^{-1}}$
	0	2	0	2	0	2	if $2\eta<\ln\frac{N_d+1}{N_d}$, $\varepsilon_{cr}^{(1)}$ does not exist
	0	0	0	0	2	0	$\varepsilon_{cr}^{(1)}=|e^{|\eta|}-(2(N_d+1)\sinh|\eta|)^{-1}|$
X–···–CH$_2$	0	1	1	0	1	0	$\varepsilon_{cr}^{(2)}=e^{|\eta|}+(2(N_d+1)\cosh\eta)^{-1}$
	1	1	1	1	1	1	$\varepsilon_{cr}^{(1)} \Leftrightarrow \varepsilon_{cr}^{(2)}$ if $4|\eta|<\ln\frac{N_d+2}{N_d+1}$

state that appears first at $|\varepsilon|=\varepsilon_{cr}^{(1)}$, if $\ln(N_d+2)/(N_d+1)<4|\eta|<2\ln(N_d+2)/(N_d+1)$, while for smaller values of $|\eta|$ an out-of-band state appears first at $|\varepsilon|=\varepsilon_{cr}^{(1)}$. It is also worth emphasizing that the definitions of $\varepsilon_{cr}^{(1)}$ and $\varepsilon_{cr}^{(2)}$ are interchanging, see Table I, when passing from $4|\eta|>\ln(N_d+2)/(N_d+1)$ to smaller values of $|\eta|$. Correspondingly, in the infinite-chain model $\varepsilon_{cr}^{(1)}$ will be overestimated while $\varepsilon_{cr}^{(2)}$—underestimated, if $4|\eta|>\ln(N_d+2)/(N_d+1)$, and vice versa, if the opposite inequality holds.

As is demonstrated in the above examples, the manifestation of end effects is substantially dependent on the parameters of the polyene chain. The infinite-chain model at most ignores this dependence. Moreover, there is no even definite correlation between predictions of the infinite- and actual length models of heteropolyenes with regard to the critical values of $|\varepsilon|$ at which the local state spectrum undergoes qualitative changes. Thus, one cannot be sure whether the effect of localization is underestimated or overestimated, since this depends on the relation between values of $|\eta|$ and N_d. The same conclusion refers to the radius of local states.

$X^+-(CH)_{2N_d}-X^-$. This model corresponds to an idealized donor/bridge/acceptor (DBA) system with the donor ($\varepsilon>0$) and acceptor ($\varepsilon<0$) levels placed symmetrically on the opposite sides of the Fermi level. Due to numerous potential applications of this type of molecule, DBA systems have been intensively studied in recent years, see Refs. 4–6 and references therein. Note also that we use the term donor (acceptor) in its usual ''physical'' meaning, while in relevant literature it is often used in the ''chemical'' sense.[14]

As to DBA type molecules, it is of interest to answer a question to what extent the conclusions made for $X-(CH)_{2N_d}-CH_2$ are applicable for $X^+-(CH)_{2N_d}-X^-$. As seen from Table I, if $\eta > 0$ there is a certain correlation between definitions of $\varepsilon_{cr}^{(1)}$—the minimal perturbation which is needed to induce out-of-band states, and $\varepsilon_{cr}^{(2)}$—the minimal perturbation at which in-gap local states appear in $X^+-(CH)_{2N_d}-X^-$, and analogous quantities for $X-(CH)_{2N_d}-CH_2$. So qualitatively, the local state spectrum

of the DBA type molecule in focus can be to an extent thought of as a result of a separate action of the donor and acceptor end groups, each of which creates not more than one out-of-band- and one in-gap local level. However, with regard to quantitative estimates of critical values of the perturbation parameter, the values of $\varepsilon_{cr}^{(1)}$ and $\varepsilon_{cr}^{(2)}$ in $X^+-(CH)_{2N_d}-X^-$ are always larger, than their respective values in $X-(CH)_{2N_d}-CH_2$. Indeed, for positive values of the alternation parameter we have

$$(\varepsilon_{cr}^{(1)})^2|_{X^+-\ldots-X^-} - (\varepsilon_{cr}^{(1)})^2|_{X-\ldots-CH_2} = \frac{2(N_d+1)\cosh\eta + \exp(\eta)}{[2N_d\cosh\eta + \exp(-\eta)]4(N_d+1)^2\cosh^2\eta} \equiv F_1(N_d,\eta),$$

$$(\varepsilon_{cr}^{(2)})^2|_{X^+-\ldots-X^-} - (\varepsilon_{cr}^{(2)})^2|_{X-\ldots-CH_2} = \frac{2(N_d+1)\sinh\eta + \exp(\eta)}{[2N_d\sinh\eta - \exp(-\eta)]4(N_d+1)^2\sinh^2\eta} \equiv F_2(N_d,\eta), \qquad (8)$$

and for $\eta < 0$

$$(\varepsilon_{cr}^{(1)})^2|_{X^+-\ldots-X^-} - (\varepsilon_{cr}^{(1)})^2|_{X-\ldots-CH_2} = F_2(N_d,\eta),$$

$$(\varepsilon_{cr}^{(2)})^2|_{X^+-\ldots-X^-} - (\varepsilon_{cr}^{(2)})^2|_{X-\ldots-CH_2} = \begin{cases} F_1(N_d,\eta), & \text{if } 4|\eta| > \ln\dfrac{N_d+2}{N_d+1}, \\[2mm] \dfrac{[2(N_d+1)\sinh|\eta| - \exp(\eta)][4(N_d+1)\exp(-2\eta)-1]}{[2N_d\cosh\eta + \exp(-\eta)]4(N_d+1)^2\sinh^2\eta}, & \text{if } 4|\eta| < \ln\dfrac{N_d+2}{N_d+1}. \end{cases}$$

$$(9)$$

Thus, as seen from Eqs. (8) and (9), the through-conjugated-bridge interaction between end groups gives quite an appreciable contribution into the localization of frontier states even in DBAs with rather long bridges, where $N_d \sim \eta^{-1}$.

Distinct from the case of positive values of the alternation parameter, for $\eta < 0$ the result of a combined action of the donor and acceptor levels on the π-electron spectrum of finite polyenes differs qualitatively from that which would produce these two levels, if each acted individually. One can see from Table I that in $X^+-(CH)_{2N_d}-X^-$ there are no local levels when $\varepsilon_{cr}^{(1)} < |\varepsilon| < \varepsilon_{cr}^{(2)}$, and there are no in-gap local states when $\varepsilon_{cr}^{(2)} < |\varepsilon|$ independent of values of $|\eta|$ and N_d. At the same time, an attempt to predict the character of the local state spectrum in $X^+-(CH)_{2N_d}-X^-$ on the basis of data obtained for $X-(CH)_{2N_d}-CH_2$, see Table I, may lead to incorrect conclusions.

$X-(CH)_{2N_d}-X$. As seen from the comparison of $\varepsilon_{cr}^{(i)}|_{X-\ldots-X}$ and $\varepsilon_{cr}^{(i)}|_{X-\ldots-CH_2}$, the infinite-bridge model (extensively used in Ref. 6 for the discussion of the push–pull polyene properties) can be especially misleading.

The above discussion shows that in general, taking into account the end effects as well as the C–C bond length alternation, which are always present in real substituted polyenes, is an important component of any useful theory.

$X-(CH)_{2N_d}-Y$. Using the data of Table I, which determine the number and type of local states present in heteropolyenes $X^+-(CH)_{2N_d}-X^-$, $X-(CH)_{2N_d}-X$, and

$X-(CH)_{2N_d}-CH_2$ for any value of ε, and Eqs. (6) and (7), where $\widetilde{\varepsilon}$ and $\widetilde{\Delta}$ are replaced by ε and Δ, respectively, one can easily answer the next question: What kind of local state spectrum is realized, if the electron site energies of end atoms in the given heteropolyene are shifted by different values?

To answer this question, apart from the data presented in Table I, it is helpful to establish the relationship between critical values of $|\varepsilon|$ for different types of heteropolyenes. In the general case, the corresponding relations depend on the sign of the alternation parameter, and also on the relationship between $|\eta|$ and N_d, see the Appendix. However, for values of $|\eta|$ that are of practical interest (~ 0.1), the following inequalities hold

$$\varepsilon_{cr}^{(1)}|_{X-\ldots-X} \le \varepsilon_{cr}^{(1)}|_{X-\ldots-CH_2} \le \varepsilon_{cr}^{(1)}|_{X^+-\ldots-X^-}$$

$$\le \varepsilon_{cr}^{(2)}|_{X-\ldots-X} \le \varepsilon_{cr}^{(2)}|_{X-\ldots-CH_2}$$

$$\le \varepsilon_{cr}^{(2)}|_{X^+-\ldots-X^-} \le \varepsilon_{cr}^{(3)}|_{X-\ldots-X}, \qquad (10)$$

which are valid, if

$$2\frac{N_d+1}{2N_d+1} < \exp(2\eta) < 3\frac{N_d+1}{N_d+2} \quad \text{(for } \eta > 0\text{)};$$

$$\exp(2|\eta|) > \sqrt{\frac{N_d+2}{N_d+1}} \quad \text{(for } \eta < 0\text{)}. \qquad (11)$$

It is obvious that at fixed value of $|\varepsilon|$, changing of Δ from $-\infty$ to ∞ will lead to the π-electron spectrum of $X-(CH)_{2N_d}-CH_2$, $X-(CH)_{2N_d}-X$, and $X^+-(CH)_{2N_d}-X^-$ at certain values of $|\Delta|$ denoted below as $\Delta_{cr}^{(i)}$. This will be accompanied by corresponding changes in the local state spectrum. Using the data of Table I and Eq. (10), one can easily trace the evolution of the local state spectrum as a function of Δ at any value of ε. The critical values $\Delta_{cr}^{(i)}$, at which the local state spectrum undergoes qualitative transformations, follow from Eqs. (6) and (7), where $\tilde{\varepsilon}$ and $\tilde{\Delta}$ are replaced by ε and Δ, respectively. Thus, being combined

two sets of critical parameters $\varepsilon_{cr}^{(i)}$ and $\Delta_{cr}^{(i)}$ completely determine the character of the local state spectrum of heteropolyenes.

As an illustrative example, we consider the case of $\varepsilon > \varepsilon_{cr}^{(3)}|_{X-\ldots-X}$ and $\eta > 0$, that is when the π-electron spectrum for $\Delta = 0$, ε, and 2ε contains the maximum possible number of local states, see Table I.

At $\Delta = 0$ there are two in-gap and two out-of-band states placed symmetrically above and below zero. With the increase of Δ from 0 to ε the upper in-gap state disappears first at

$$\Delta = \Delta_{cr}^{(1)} = \frac{\varepsilon^2[e^{-\eta}(N_d+1) - e^{\eta}N_d] - e^{-2\eta}[e^{-\eta}(N_d+1) - e^{\eta}(N_d+2)]}{\varepsilon[e^{-\eta}(N_d+1) - e^{\eta}N_d] - e^{-\eta}2\sinh|\eta|(N_d+1)}, \tag{12}$$

and then, the lower out-of-band state also disappears at

$$\Delta = \Delta_{cr}^{(2)} = \frac{\varepsilon^2[e^{-\eta}(N_d+1) + e^{\eta}N_d] - e^{-2\eta}[e^{-\eta}(N_d+1) + e^{\eta}(N_d+2)]}{\varepsilon[e^{-\eta}(N_d+1) + e^{\eta}N_d] + e^{-\eta}2\cosh\eta\,(N_d+1)}. \tag{13}$$

A further increase of Δ from ε to 2ε results in the appearance of the second out-of-band state above the conduction band at

$$\Delta = \Delta_{cr}^{(3)} = \frac{\varepsilon^2[e^{-\eta}(N_d+1) + e^{\eta}N_d] - e^{-2\eta}[e^{-\eta}(N_d+1) + e^{\eta}(N_d+2)]}{\varepsilon[e^{-\eta}(N_d+1) + e^{\eta}N_d] - e^{-\eta}2\cosh\eta\,(N_d+1)}, \tag{14}$$

and then—of the second in-gap state above the valence band at

$$\Delta = \Delta_{cr}^{(4)} = \frac{\varepsilon^2[e^{-\eta}(N_d+1) - e^{\eta}N_d] - e^{-2\eta}[e^{-\eta}(N_d+1) - e^{\eta}(N_d+2)]}{\varepsilon[e^{-\eta}(N_d+1) - e^{\eta}N_d] + e^{-\eta}2\sinh|\eta|(N_d+1)}. \tag{15}$$

Finally, at $\Delta = \Delta_{cr}^{(5)} = 2\varepsilon + \Delta_{cr}^{(1)}$ the upper in-gap state disappears, so that the spectrum of heteropolyene $X-(CH)_{2N_d}-Y$ with $\varepsilon_{X(Y)} > 0$ and $\varepsilon_Y - \varepsilon_X > \Delta_{cr}^{(5)}$ contains two out-of-band states above the conduction band and one in-gap state lying above zero energy.

The changes of Δ from 0 to $-\infty$ ($\varepsilon > \varepsilon_{cr}^{(3)}|_{X-\ldots-X}$, $\eta > 0$) will be accompanied by the disappearance of the lower in-gap state (which was present in $X^+-(CH)_{2N_d}-X^-$) at $|\Delta| = \Delta_{cr}^{(4)}$, so that the spectrum of heteropolyene $X-(CH)_{2N_d}-Y$, with $\varepsilon_X > 0$, $\varepsilon_Y < 0$ and $|\varepsilon_Y| - |\varepsilon_X| > \Delta_{cr}^{(4)}$ contains two out-of-band states above conduction and below valence bands and one in-gap state in the upper half of the forbidden zone of the ideal polyene chain.

The analysis of the local state spectrum dependence on Δ for any other value of ε ($\varepsilon < \varepsilon_{cr}^{(3)}|_{X-\ldots-X}$) is similar.

V. SOME EXAMPLES WITH THE USE OF EXPERIMENTAL DATA

To predict the local state spectrum and other properties of real end substituted polyenes, one needs to know values of the polyene chain parameters, η and N_d, as well as the end-group parameters. In the spirit of the proposed approach, the best way of practical applications of the formal results obtained above would be finding the model parameters from comparison with experiment. An alternative way is using for

this purpose numerical calculations, see, e.g., Ref. 6, but it is not our intention to discuss the latter possibility which is too special and too complex to be included in the present consideration. Instead, we address available experimental data.

Some of substituted polyenes have been already well described in the framework of the Hückel model, i.e., the values of the above mentioned parameters, which are in good agreement with a number of experimental data, are established, so that it makes sense to try them for the description of other substances and/or other properties of polyenes with same end groups. For example, as is known, an alkyl end group can be reasonably described by one filled atomic orbital. In our notations the parameters suggested in Ref. 15 of the Hückel Hamiltonian of α,ω-dialkylpolyenes are: the alternation parameter $\eta = -0.1333$ (that is the last unperturbed C–C bonds in the polyene chain are supposed to be double bonds), the Coulomb energy shift $\varepsilon_X = \varepsilon_Y = \varepsilon_{alk} = -1.4254$, and the end-bond perturbation $\beta_X = \beta_Y = \beta_{alk} = -0.5118$. According to Eqs. (2) and (4) the values of the effective perturbation to be compared with $\varepsilon_{cr}^{(i)}$ presented in Table I are $\tilde{\varepsilon}_{alk}(2\sinh\eta) = -(\beta_{alk}^{-2} - 1)2\sinh\eta + \beta_{alk}^{-2}\varepsilon_{alk}$ and $\tilde{\varepsilon}_{alk}(-2\cosh\eta) = (\beta_{alk}^{-2} - 1)2\cosh\eta + \beta_{alk}^{-2}\varepsilon_{alk}$. Since $|\tilde{\varepsilon}_{alk}(2\sinh\eta)| = 4.6889$ is larger, than $\varepsilon_{cr}^{(2)}|_{X-\ldots-X} = 1.14$, and $\tilde{\varepsilon}_{alk}(-2\cosh\eta) > 0$, we conclude that all π electron states of α,ω-dialkylpolyenes are band-like independent of the molecule length.
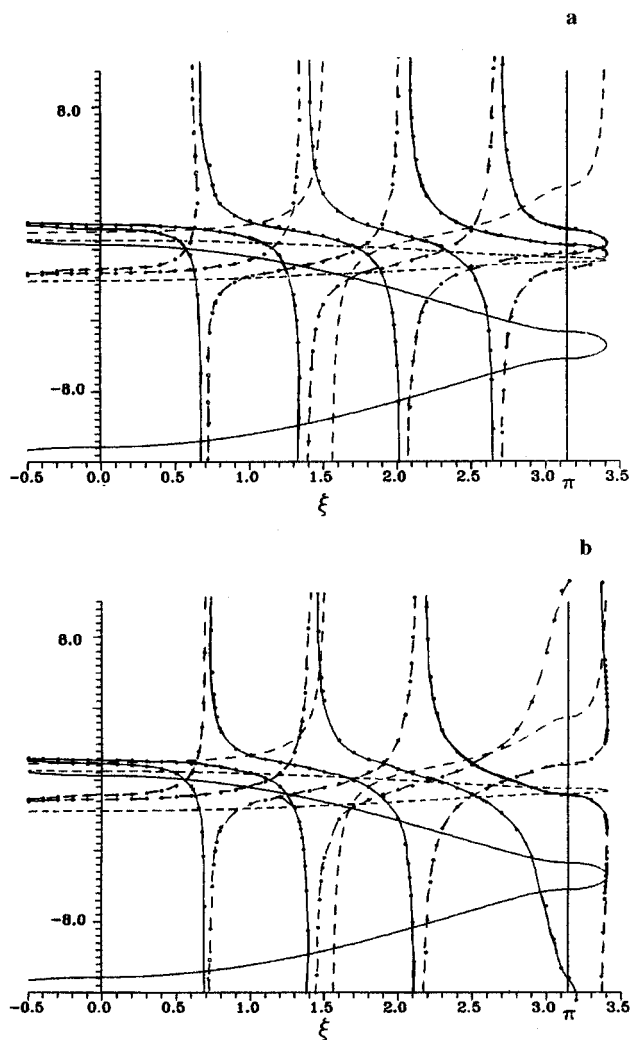
FIG. 1. Graphical solution of Eq. (3) for the cases of two alkyl and two phenyl end groups connected with a polyene chain of 8 carbons with double (a) and single (b) bonds at its ends. Solid–dotted ($E>0$) and dashed–dotted ($E<0$) curves depend only on the polyene chain parameters (here, $N_d=4$, $\eta=-0.1333$ (a), and $\eta=0.1333$ (b)). Solid, short dashed, and long dashed curves correspond to the effective perturbation defined in Eq. (2) in the case of alkyl ($\varepsilon_{alk}=-1.4254$, $\beta_X=\beta_{alk}=-0.5118$—solid curve; $\beta_X=-1.5$—short dashed curve) and phenyl ($\beta_{phen}=-0.8461$) end groups, respectively. The solutions for ξ are given by intersections of solid, short dashed and long dashed lines with solid–dotted and dashed–dotted lines as is explained in the text.

Figure 1(a) represents graphical solution of Eq. (3) for the case $N_d=4$ and the rest of parameters specified above. The solid line in this figure corresponds to the dependence $\widetilde{\varepsilon}_{alk}(E)$; positive π electron energies are determined by intersections of the lower branch of this dependence with solid–dotted curves, and negative π electron energies—by intersections of the upper branch with dashed–dotted curves. The graphical representation clarifies the role of end group parameters which determine the behavior of the effective perturbation as a function of energy. To illustrate changes in the position of π electron levels under variation of the non-diagonal perturbation, the dependence $\widetilde{\varepsilon}(E)$ is also shown (by short dashed lines) for the same diagonal perturbation

and $\beta_X=-1.5$. (Note that for $|\beta_X|>1$ the lower branch of the dependence $\widetilde{\varepsilon}(E)$ corresponds to negative energies, and the upper branch—to positive energies.) In addition, to visualize the importance of the chain geometry, we displayed in Fig. 1(b) the solution of Eq. (3) for the same parameters of the system but assuming the reversed geometry of the polyene chain (i.e., single bonds at the ends of the unperturbed polyene chain of 8 carbons). An intersection of the upper branch of the solid curve with a dashed–dotted line to the right of π indicates that in the electron spectrum of this system there is an in-gap level with nearly zero energy.

Since models of ''donor'' (e.g., NH_2, OH) and ''acceptor'' (e.g., CHO, NO_2) groups differ from that discussed above only by values of the diagonal (ε) and nondiagonal (β) perturbations, graphs of Fig. 1 give a useful insight into electronic structure of polyenes with donor (acceptor) groups at the polyene ends.

The most simple model accounting for S_2 excitation energies of a number of α,ω-diphenylpolyenes suggests that the resonance integral for carbons in a phenyl ring—the only end-group parameter—is equal to $\beta_{phen}=-0.8461$.[15] Again, the last unperturbed C–C bond in the polyene chain is supposed to be a double bond. The energy dependent effective perturbation (2) is now described by $\widetilde{\varepsilon}_{phen}(E) = 2\beta_{phen}^2(E^2-2\beta_{phen}^2)E^{-1}(E^2-3\beta_{phen}^2)^{-1}$. The behavior of this function for $E>0$ is shown in Fig. 1(a) by long dashed lines, whose intersections with solid–dotted lines represent solutions of Eq. (3) for an α,ω-diphenylpolyene with $N_d=4$ (due to the symmetry of the system only the upper part of the π electron spectrum can be considered). Changes in these solutions for the same system but with the reversed geometry can be seen from Fig. 1(b). From the definition of the effective perturbation given above it follows that, as in the case of α,ω-dialkylpolyenes, all π electron states of α,ω-diphenylpolyenes are band-like since $\widetilde{\varepsilon}_{phen}(2\sinh|\eta|)=3.5083$ is larger, than $\varepsilon_{cr}^{(2)}|_{X-..-X}$, and $\widetilde{\varepsilon}_{phen}(2\cosh\eta)=0.9736$ is less, than $\varepsilon_{cr}^{(3)}|_{X-..-X}=1.36$. However, in the chain with the reversed geometry two phenyl end groups would generate an in-gap local state, see Fig. 1(b).

It is worth emphasizing that in the above examples only knowledge of the effective perturbation was needed to conclude that there are no local states in alkyl and phenyl end substituted polyenes and thus, one can expect that the electron localization effects play a minor role in determining physical and chemical properties of these molecules in the ground state.

VI. CONCLUSION

The conditions of appearance/disappearance of local states in the π-electron spectrum of end substituted polyenes are obtained in the form of analytical relations, Eqs. (6) and (7), which determine the set of critical values of two parameters $\widetilde{\varepsilon}$ and $\widetilde{\Delta}$. By this, the problem of the classification of local state spectra in dimerized carbon chains terminated by arbitrary end groups is reduced to the same problem but for much more simple molecules—heteropolyenes, where the

end atoms differ from carbon atoms of the polyene chain only by the value of the Coulomb integrals. All details of the end-group π-electronic structure (not restricted by additional conditions) enter Eqs. (6) and (7) as only one uniquely defined (in Eq. (2)) energy dependent parameter. Its dependence on the π-electron energy is determined by the diagonal component of the end-group Green function associated with that atom which is in conjugation with the polyene bridge. For the alkyl and phenyl end groups this dependence is obtained with the use of established experimental data.

Furthermore, in view of numerous particular realizations of the local state spectrum which depend on (i) the relation between the alternation parameter and the length of the bridge, (ii) the sign of the alternation parameter, (iii) the type of substitution, and (iv) the π-electronic structure of end groups, we elaborated the standard procedure of finding two sets of critical parameters, $\tilde{\varepsilon}_{cr}^{(i)}$ and $\tilde{\Delta}_{cr}^{(i)}$, which completely determine the number and type of local states in the given heteropolyene. The corner stone of this procedure is the classification of the local state spectrum developed for heteropolyenes of the type $X-(CH)_{2N_d}-CH_2$, $X-(CH)_{2N_d}-X$, and $X^+-(CH)_{2N_d}-X^-$.

All relations necessary for practical applications of the above mentioned procedure are exact and derived in the framework of the Hückel model (or the electron part of the Su–Schrieffer–Heeger Hamiltonian). Thus, all limitations possessed by this model are transferred to the results obtained above. As mentioned in Sec. I, the model used ignores electron correlation effects though partly, they can be included in it by the appropriate choice of the characteristic parameters. Another and the most serious restriction is the assumption of the rigid geometry which prohibits self-consistent electron-phonon states such as solitons, polarons, and the like.[16,17] However, first, even solitons and polarons can be roughly described within the Hückel model as was

shown by Longuet-Higgins and Salem,[18] and Pople and Walmsley,[19] and, second, the indicated drawbacks seem to be a reasonable payment for the gained simplicity of the analytical theory which at most accounts for all principle factors that play a role in determining the π-electronic structure of a wide class of organic compounds.

It is also worth noting that the predicting power of the basic equation (1) (or (3)) is far from being exhausted by the above analysis of the local state spectrum and ranges to any quantity of physical interest related to end substituted polyenes. In this respect, possibilities of applications of more elaborated models are much more limited. In particular, by illustrative examples of Sec. V it is demonstrated how the use of Eq. (3) ''reveals'' the end group effects on all π electron energies (which remain mostly hidden when using the standard routine of numerical calculations), making ''visible'' the dependence of the π electron spectrum on the perturbation parameters. We believe therefore that the results presented above, as well as their further development, can be efficiently used as a guideline in the analysis of the electron localization and relevant phenomena that take place in conjugated molecules.

ACKNOWLEDGMENTS

APPENDIX

We present here the relationship between critical values of $|\varepsilon|$ for different types of heteropolyenes.

(I) The case $\eta > 0$. Let us introduce the following notations:

$$\eta_{cr}^{(1)} = 0.5 \ln \frac{N_d + 1 + (N_d + 1)\sqrt{1 + 8(N_d + 2)(2N_d + 1)}}{2(2N_d + 1)(N_d + 2)};$$

$$\eta_{cr}^{(2)} = 0.5\ln \frac{-(N_d + 1)^2 + (N_d + 1)\sqrt{(N_d + 1)^2 + 3N_d(N_d + 2)}}{N_d(N_d + 2)};$$

$$\eta_{cr}^{(3)} = 0.5 \ln \frac{2(N_d + 1)}{2N_d + 1};$$

$$\eta_{cr}^{(4)} = 0.5 \ln \frac{N_d + 1}{N_d}; \tag{A1}$$

$$\eta_{cr}^{(5)} = 0.5 \ln \frac{3(N_d + 1)}{N_d + 2};$$

$$\eta_{cr}^{(6)} = 0.5 \ln \frac{(N_d + 1)^2 + (N_d + 1)\sqrt{(N_d + 1)^2 + 3N_d(N_d + 2)}}{N_d(N_d + 2)};$$

$$\eta_{cr}^{(7)} = 0.5 \ln \frac{(N_d + 1)(4N_d + 7) + (N_d + 1)\sqrt{(4N_d + 7)^2 - 16(N_d + 2)}}{2(N_d + 2)}.$$

It can be shown that the following inequalities are valid:

$$\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-CH_2}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(1)}|_{X^+-\ldots-X^-}\leqslant\varepsilon_{\mathrm{cr}}^{(3)}|_{X-\ldots-X}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-CH_2}, \tag{A2}$$

if $\eta<\eta_{\mathrm{cr}}^{(1)}$,

$$\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-CH_2}\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-X}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(1)}|_{X^+-\ldots-X^-}\leqslant\varepsilon_{\mathrm{cr}}^{(3)}|_{X-\ldots-X}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-CH_2}, \tag{A3}$$

if $\eta_{\mathrm{cr}}^{(1)}<\eta<\eta_{\mathrm{cr}}^{(2)}$,

$$\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-CH_2}\leqslant\varepsilon_{\mathrm{cr}}^{(1)}|_{X^+-\ldots-X^-}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(3)}|_{X-\ldots-X}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-CH_2}, \tag{A4}$$

if $\eta_{\mathrm{cr}}^{(2)}<\eta<\eta_{\mathrm{cr}}^{(3)}$,

$$\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-CH_2}\leqslant\varepsilon_{\mathrm{cr}}^{(1)}|_{X^+-\ldots-X^-}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-CH_2}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(3)}|_{X-\ldots-X}, \tag{A5}$$

if $\eta_{\mathrm{cr}}^{(3)}<\eta<\eta_{\mathrm{cr}}^{(4)}$,

$$\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-CH_2}\leqslant\varepsilon_{\mathrm{cr}}^{(1)}|_{X^+-\ldots-X^-}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-CH_2}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X^+-\ldots-X^-}\leqslant\varepsilon_{\mathrm{cr}}^{(3)}|_{X-\ldots-X}, \tag{A6}$$

if $\eta_{\mathrm{cr}}^{(4)}<\eta<\eta_{\mathrm{cr}}^{(5)}$,

$$\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-CH_2}\leqslant\varepsilon_{\mathrm{cr}}^{(1)}|_{X^+-\ldots-X^-}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-CH_2}\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-X}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X^+-\ldots-X^-}\leqslant\varepsilon_{\mathrm{cr}}^{(3)}|_{X-\ldots-X}, \tag{A7}$$

if $\eta_{\mathrm{cr}}^{(5)}<\eta<\eta_{\mathrm{cr}}^{(6)}$,

$$\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-CH_2}\leqslant\varepsilon_{\mathrm{cr}}^{(1)}|_{X^+-\ldots-X^-}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-CH_2}\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X^+-\ldots-X^-}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(3)}|_{X-\ldots-X}, \tag{A8}$$

if $\eta_{\mathrm{cr}}^{(6)}<\eta<\eta_{\mathrm{cr}}^{(7)}$, and

$$\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-CH_2}\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-CH_2}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(1)}|_{X^+-\ldots-X^-}\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X^+-\ldots-X^-}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(3)}|_{X-\ldots-X}, \tag{A9}$$

if $\eta>\eta_{\mathrm{cr}}^{(7)}$.

(II) The case $\eta<0$. Denote:

$$\eta_{\mathrm{cr}}^{(1)}=0.5\ \ln\frac{1+\sqrt{1+8(N_d+2)(2N_d+1)}}{4(N_d+1)};$$

$$\eta_{\mathrm{cr}}^{(2)}=0.5\ \ln\frac{4N_d+7+\sqrt{(4N_d+7)^2-16(N_d+2)}}{8(N_d+1)};$$

$$\eta_{\mathrm{cr}}^{(3)}=0.25\ \ln\frac{N_d+2}{N_d+1};$$

$$\eta_{\mathrm{cr}}^{(4)}=0.5\ \ln\frac{N_d+1}{N_d}. \tag{A10}$$

In this case, the following inequalities hold:

$$\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-CH_2}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X^+-\ldots-X^-}\leqslant\varepsilon_{\mathrm{cr}}^{(3)}|_{X-\ldots-X}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-CH_2}, \tag{A11}$$

if $\eta<\eta_{\mathrm{cr}}^{(1)}$,

$$\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-CH_2}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X^+-\ldots-X^-}\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-CH_2}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(3)}|_{X-\ldots-X}, \tag{A12}$$

if $\eta_{\mathrm{cr}}^{(1)}<\eta<\eta_{\mathrm{cr}}^{(2)}$,

$$\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-CH_2}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-CH_2}\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X^+-\ldots-X^-}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(3)}|_{X-\ldots-X}, \tag{A13}$$

if $\eta_{\mathrm{cr}}^{(2)}<\eta<\eta_{\mathrm{cr}}^{(3)}$,

$$\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-CH_2}\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-X}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-CH_2}\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X^+-\ldots-X^-}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(3)}|_{X-\ldots-X}, \tag{A14}$$

if $\eta_{\mathrm{cr}}^{(3)}<\eta<\eta_{\mathrm{cr}}^{(4)}$, and

$$\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(1)}|_{X-\ldots-CH_2}\leqslant\varepsilon_{\mathrm{cr}}^{(1)}|_{X^+-\ldots-X^-}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-X}\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X-\ldots-CH_2}$$
$$\leqslant\varepsilon_{\mathrm{cr}}^{(2)}|_{X^+-\ldots-X^-}\leqslant\varepsilon_{\mathrm{cr}}^{(3)}|_{X-\ldots-X}, \tag{A15}$$

if $\eta>\eta_{\mathrm{cr}}^{(4)}$.

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