Exact solution for the Hückel model of heteropolyenes

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Abstract

The Lennard–Jones equation, which determines the π electron spectrum of unsubstituted polyenes $H_2C-(CH)_{2N_d}-CH_2$, is generalized to the case of heteropolyenes $X-(CH)_{2N_d}-Y$. The closed form of the exact Hückel molecular orbitals for heteropolyenes is derived. The dependence of the local state spectrum on characteristic parameters is examined analytically for three types of heteropolyene, $X-(CH)_{2N_d}-X$, $X^+-(CH)_{2N_d}-X^-$, and $X-(CH)_{2N_d}-CH_2$. The criteria of the existence of local states and their position in the asymptotic limit are established for both signs of the alternation parameters. The results obtained predict strong and qualitatively different effects of the substitution on the optical response of the indicated types of heteropolyenes, and they can be used, therefore, in search of new compounds, which are optically active in the desired frequency region. The theory is also applied for the analysis of the dependence of all π electron levels in heteropolyenes on the electron site-energy perturbation caused by heteroatoms.

Keywords: Heteropolyene; Models; Theoretical study

1. Introduction

It is known that the Hückel Hamiltonian is the simplest and most successful parameterized one-electron Hamiltonian for describing π electron electronic structure of conjugated molecules. For heteropolyenes this model essentially includes two parameters referred to the polyene as such [1,2], namely, the number of double bonds N_d and the alternation parameter η, plus parameters of heteroatoms. The Hückel model has been elaborated in great detail for linear molecules with non-alternating bonds, see, e.g. [3–6] and Refs. therein, being thus oriented primarily on polymethine dyes, in which, as is well established experimentally, the bond alternation is absent. The case of heteropolyenes in this respect has received so far much less attention.

In the Hückel approximation, the one- and two-impurity problems in the semi-infinite alternating chains have been studied by Kventsel [7,8]. That model can be applied to heteropolyenes of the type $X-(CH)_{2N_d}-X$ and $X-(CH)_{2N_d}-CH_2$. The results obtained in [7] for the one-impurity problem have been generalized to the case of finite molecules by Castaño and Karadakov [9]. It was shown in cited works that, under certain relations between characteristic parameters, in the heteropolyene spectrum the local states can exist in the gap between the valence and conduction bands (such states do not appear in hetero-substituted polymethines).

However, the results connected with the behaviour of local states only, as was the case in [7–9], cannot be used for the direct comparison with the experiment. For example, to predict the influence of the hetero-substitution on the frequency of the maximum of the long-wave absorption, one needs to trace the dependence on heteroatom parameters of π electron energy levels that correspond to the highest occupied MO (HOMO) and lowest unoccupied MO (LUMO). A number of applications demands the knowledge of analogous dependences for other levels, e.g. HOMO $-$ 1 and LUMO $+$ 1, and, apart from the spectrum data, also the molecular orbital coefficients. Moreover, in papers cited above the classification of local states has been clarified only for the case of asymmetrical polyenes and only for those that are terminated by short (double) bonds. But, as was recently found [10], the optimal geometry for ionic forms of heteropolyenes in the ground state, as well as for neutral heteropolyenes in the lowest dipole-allowed excited state, corresponds to long (single) bonds at the molecule ends. The π electron structure of heteropolyenes for the case of 'reversed' alternation is therefore of principal importance, but it is practically unstudied.

The white spots mentioned, as well as the rapidly increasing amount of experimental data, which need a simple model for quick and reliable interpretation, put forward the urgent task of further development of the Hückel model. It should be noted in this connection that using the one-electron approximation in the case of polyenes has been repeatedly

criticized in the literature, see, e.g., [11,12]. Indeed, the electron correlation has proven to be of principal importance for polyene compounds in determining their π electron spectrum. Moreover, even at the one-electron level the assumption that the alternation parameter is constant prohibits the existence of the soliton- and polaron-type states which play an important role in long polyenes and polyacetylene materials [12,13]. But at the same time, it has been convincingly demonstrated experimentally that the Hückel model with an appropriate choice of parameters gives excellent agreement with numerous spectroscopy data on the second singlet excitation (1^1B_u state). Moreover, combining this model with the inclusion of the configurational interaction in the basis of the Hückel MOs allows Kohler to reproduce quantitatively all of the 2^1A_g and 1^1B_u state 0–0 energies that have been measured in high-resolution spectroscopic experiments [14]. In our opinion, these strong sides of the Hückel model provide more than enough reasons for its further elaboration in various aspects.

In recent work of the present authors [15], the exact expressions for the Hückel MOs and HOMO–LUMO transition dipoles for a finite chain with alternating bonds have been found and applied for the detailed analysis of the charge and bond-order distributions and linear optical response in linear polyenes. In [16] the formal results of [15] have been used for the derivation of the closed form for arbitrary interband and intraband transition dipoles that make the analysis of the non-linear response of polyenes straightforward. Here we address to the full-scale solution of the Schrödinger equation for the Hückel model of heteropolyenes.

This paper is organized as follows. Section 2 and the Appendix give the general solution of the problem. In Section 3 this solution is specified for three types of heteropolyenes, X–$(CH)_{2N_d}$–X, X$^+$–$(CH)_{2N_d}$–X$^-$, and X–$(CH)_{2N_d}$–CH_2. The regularities of the local state spectrum in these heteropolyenes are examined in great detail. This section also presents analytical results in the long chain limit. In Section 4 we discuss the gross effect of substitution on the π electron spectrum in different types of heteropolyenes. Section 5 summarizes the main findings of this work.

2. General solution

Any of π electron states of a dimerized chain with $N = 2N_d + 2$ atoms can be represented by the expansion of the type:

$$\psi = \sum_{j=1}^{N} A_j \varphi_j \tag{1}$$

where φ_j is the π electron atomic orbital of the jth atom (indexes $j = 1$ and $j = N$ refer to heteroatoms), and the expansion coefficients A_j obey the Schrödinger equation:

$$\sum_{j'=1}^{N} H_{jj'} A_{j'} = E A_j \tag{2}$$

where E is the π electron energy in a hetero-substituted polyene. The matrix elements $H_{jj'} = H_{j'j} = \int \varphi_j H \varphi_{j'}$ are taken here in the commonly accepted form, namely: $H_{jj} = \epsilon_X$, ϵ_Y ($\epsilon_{X(Y)} = \alpha_{X(X)} - \alpha_C$) for $j = 1$, N, respectively, and $H_{jj} = 0$ for $j \neq 1$, N; $H_{12} = \beta_X$, $H_{N-1N} = \beta_Y$, $H_{jj+1} = \beta \exp \eta$ for $j = 3, 5, ..., N-3$; $H_{j-1j} = \beta \exp(-\eta)$ for $j = 3, 5, ..., N-1$; and $H_{j \neq j'} = 0$ for all other values of j and j'. For the given definition of resonance integrals, the positive sign of η corresponds to double bonds in the ideal polyene, $\epsilon_{X(Y)} = 0$, $\beta_{X(Y)} = \beta$. In the following, $|\beta|$ is used as the energy unit.

Excluding from Eq. (2) the coefficients A_1 and A_N:

$$A_{1(N)} = \frac{\beta_{X(Y)}}{E - \epsilon_{X(Y)}} A_{2(N-1)} \tag{3}$$

and expanding A_{j+1}, $j = 1, 2, ..., 2N_d$, over unperturbed orthonormalized solutions to Eq. (2) (i.e., with $\beta_{X(Y)} = 0$), after some algebra one easily arrives at

$$A_{j+1} = A_2 \frac{\beta_X^2}{E - \epsilon_X} \left(G_{1,j} + \frac{\beta_Y^2 G_{1,2N_d} G_{j,2N_d}}{E - \epsilon_Y - \beta_Y^2 G_{1,1}} \right) \tag{4}$$

The quantities $G_{j,j'}$ in the above equation represent the matrix elements of the Green function operator for the unperturbed problem $G = (E - \mathscr{H}^0)^{-1}$, where the Hamiltonian $\mathscr{H}^0$ describes a dimerized chain of $2N_d$ identical atoms with single bonds at its ends.

Accordingly to Eq. (4), the condition, providing for the existence of a non-zero solution of Eq. (2) is

$$\left(1 - \frac{\beta_X^2 G_{1,1}}{E - \epsilon_X}\right)\left(1 - \frac{\beta_Y^2 G_{1,1}}{E - \epsilon_Y}\right) - \frac{\beta_X^2 \beta_Y^2 G_{1,2N_d}^2}{(E - \epsilon_X)(E - \epsilon_Y)} = 0 \tag{5}$$

Eqs. (3)–(5) supplemented by the normalization condition:

$$|A_2|^{-2} = \frac{\beta_X^2}{(E - \epsilon_X)^2}\left[1 + \frac{\beta_X^2 \beta_Y^2 G_{1,2N_d}^2}{(E - \epsilon_Y - \beta_Y^2 G_{1,1})^2} \right.$$
$$\left. + \beta_X^2 \sum_{j=1}^{2N_d}\left(G_{1,j} + \frac{\beta_Y^2 G_{1,2N_d} G_{j,2N_d}}{E - \epsilon_Y - \beta_Y^2 G_{1,1}}\right)^2\right] \tag{6}$$

completely determine the π electron energy levels and corresponding molecular orbital coefficients for a dimerized finite chain with arbitrary values of alternation (η) and perturbation (ϵ_X, ϵ_Y, β_X, β_Y) parameters.

Obviously, the reformulation of the Schrödinger problem in terms of the Green function is sensible only under the condition that the latter can be found in an explicit form. Fortunately, for the case of polyenes this can be done.

Despite that the eigen functions of $\mathscr{H}^0$ are known [15,16], finding the matrix elements $G_{j,j'}$ in their standard representation (as a bilinear expansion over the molecular orbital coefficients) by direct summation is very problematic, if at all possible. Instead, we use the relation between the needed Green function for an alternating chain with the even number of atoms as that for the same chain but one atom shorter. Since the latter can be easily found, the procedure of obtaining explicit expressions for $G_{j,j'}$ is reduced to elementary algebra (see Appendix for details).

As demonstrated below, using Eqs. (3)–(6), one can examine the dependence on characteristic parameters of any desired π electron level or corresponding MO. This is not a trivial task, especially for longer heteropolyenes, when one tries to use for this purpose Eq. (2). While, in general, the quantities of physical interest for heteropolyenes can be found only numerically, the local state spectrum, which is of crucial importance for the understanding the electronic properties of heteropolyenes, can be examined analytically.

3. Local states

In order to escape cumbersome formulae, we restrict ourselves to three particular types of heteropolyenes, X–$(CH)_{2N_d}$–X, X^+–$(CH)_{2N_d}$–X^-, and X–$(CH)_{2N_d}$–CH_2, and neglect the perturbation of resonant integrals, which is usually less important. Knowing the π electron structure of the heteropolyene types indicated, one can oversee the effects of substitution of the end C atoms by heteroatoms with arbitrary parameters.

3.1. Molecules of the type X–$(CH)_{2N_d}$–X

Setting in Eq. (5) $\epsilon_X = \epsilon_Y = \epsilon$ and $\beta_X = \beta_Y = \exp \eta$, and using explicit expressions (A10) and (A12) for the Green function matrix elements appearing in the secular equation, the latter can be transformed to the form:

$$\exp(-\eta)Z^{-1}[\sin((N_d+2)\xi) + (\exp(-2\eta)-2E\epsilon)$$
$$\sin((N_d+1)\xi)] + \epsilon^2 = 0 \tag{7}$$

where $E = \pm [2(\cosh 2\eta + \cos \xi)]^{1/2}$, $Z = \exp(-\eta)$ $\sin((N_d+1)\xi) + \exp \eta \sin(N_d\xi)$. Note that a quite different (and much more complex) form for the secular equation has been derived in [8].

The normalizing factor of the MO coefficients can be also significantly simplified by noting that with account to Eq. (7):

$$K \equiv (\sin \xi)^{-1}[E \exp(-\eta) \sin((N_d+1)\xi) - \epsilon Z]$$
$$= \pm 1 \tag{8}$$

where the choice of the sign depends on which of the following equations:

$$Z^{-1}[E \exp(-\eta) \sin((N_d+1)\xi) - \sin \xi] = \epsilon$$
$$Z^{-1}[E \exp(-\eta) \sin((N_d+1)\xi) + \sin \xi] = \epsilon \tag{9}$$

is used to determine the π electron energy: plus in Eq. (8) corresponds to the upper equation, and minus to the lower one. It is easy to verify that the set (9) is equivalent to Eq. (7).

Performing in Eq. (6) the summation and using identity (8) one gets the following expression for $|A_2|^2$:

$$\frac{(E-\epsilon)^2}{[2 \exp(2\eta) |A_2|^2]} - 1$$
$$= [\epsilon \exp \eta - K \cos((N_d+1)\xi)][EN_d \sin \xi$$
$$+ K \sin(N_d\xi) (\exp(-\eta)$$
$$+ \exp \eta \cos \xi)]/[\sin \xi \sin((N_d+1)\xi)Z] \tag{10}$$

The secular equations for more simple models, which have been extensively used previously in discussions of electronic properties of linear conjugated molecules, can be easily obtained from Eq. (7) as particular cases. For $\epsilon = 0$, Eq. (7) reduces to the Lennard–Jones equation [1]:

$$\frac{\sin((N_d+1)\xi)}{\sin((N_d+2)\xi)} = -\exp(2\eta) \tag{11}$$

In the limit $|\epsilon| \to \infty$, it is easy to see from Eq. (7) that apart from two levels with $E \sim \epsilon$, there exist $2N_d$ levels with finite energies, which are again determined by Eq. (11), where $N_d + 1$ should be replaced by N_d, and η by $-\eta$.

Finally, in the case of an undimerized chain, $\eta = 0$, one readily obtains from Eq. (7):

$$\frac{\cos((N+1)\xi/4)}{\cos((N-1)\xi/4)} = \epsilon; \quad \frac{\sin((N+1)\xi/4)}{\sin((N-1)\xi/4)} = \epsilon \tag{12}$$

where ξ is related to the π electron energy by $E = 2\cos(\xi/2)$. In this limit, the form of the secular equation is independent of the parity of N, and Eqs. (12) are valid for chains with even and odd number of atoms in the chain. Various analytical representations of the solution to this equation in the long chain approximation have been found in [3,4,6].

The analysis of Eq. (7) (or set (9)) shows that there can be $N = 2N_d + 2$ roots within the interval $0 \leq \xi \leq \pi$. These correspond to extended or band-like π electron states, the energies of which are within two intervals defined as $2 \sinh |\eta| < |E| < 2 \cosh \eta$. However, the number of real solutions which give different energies can be less than N. In this case, there appear complex roots, i.e., Eq. (7) has non-trivial solutions for δ and (or) δ' related to ξ by $\xi = i\delta$ and $\xi = \pi + i\delta'$. The energy of corresponding π electron levels is either outside the above indicated intervals, if there are solutions for δ (out-of-band levels with $|E| > 2 \cosh \eta$), or in the gap between these intervals if there are solutions for δ' (in-gap levels with $|E| < 2 \sinh |\eta|$). In both cases the corresponding electron states are local, as can be seen from the definition of their molecular orbitals. In the limit $\eta \to 0$, the in-gap local states do not exist (see Eq. (12)).

The manifestation of local states in heteropolyenes that are terminated by short ($\eta > 0$) and long ($\eta < 0$) bonds is qualitatively different. Therefore, these two cases are examined below separately.

$\eta > 0$. In the unsubstituted polyene, $\epsilon = 0$, all N states are band-like and the energies of these $N_d + 1$ valence and $N_d + 1$ conduction states, which are determined by Eq. (11), are located symmetrically below and above zero, respectively. In

the opposite limit $|\epsilon| = \infty$, the finite part of the energy spectrum includes $2N_d$ levels, the position of which is also determined by Eq. (11) but with the negative sign in the exponent and $N_d + 1$ replaced by N_d. Formally, this corresponds to a dimerized chain with single bonds at its ends. In such a system, under the condition:

$$\eta > \frac{1}{2} \ln \frac{N_d + 1}{N_d} \qquad (13)$$

there are two levels, which correspond to electron local states placed symmetrically just below and above zero.

Suppose first that inequality (13) is held. Then, as it can be easily proved by using Eq. (7), there are no local states in a hetero-substituted polyene, if

$$|\epsilon| < \epsilon_{cr}^{(1)} = \exp(-\eta) \qquad (14)$$

there is one in-gap state and one out-of-band local state, if

$$\epsilon_{cr}^{(1)} \le |\epsilon| < \epsilon_{cr}^{(2)} = \exp(-\eta) + \frac{2}{2N_d \cosh \eta + \exp(-\eta)} \qquad (15)$$

there are two out-of-band states and one in-gap state, if

$$\epsilon_{cr}^{(2)} \le |\epsilon| < \epsilon_{cr}^{(3)} = \left| \exp(-\eta) + \frac{2}{2N_d \sinh \eta - \exp(-\eta)} \right| \qquad (16)$$

and finally, if

$$|\epsilon| \ge \epsilon_{cr}^{(3)} \qquad (17)$$

in the spectrum of the given type of the hetero-substituted polyenes there exist two in-gap and two out-of-band local levels.

Note that at $|\epsilon| = \epsilon_{cr}^{(1)}$ for $\epsilon > 0$ ($\epsilon < 0$) the HOMO (LUMO) state executes the transformation from the band-like to the local state, and correspondingly, at $|\epsilon| = \epsilon_{cr}^{(3)}$ the same transformation occurs with the HOMO -1 (LUMO $+1$) state. Shifting with the increase of $|\epsilon|$, the HOMO_ (or LUMO) level crosses zero at $|\epsilon| = \epsilon_0 = \exp(\eta(2N_d + 1))$. This result is valid also for $\eta < 0$.

Under the condition:

$$\eta < \frac{1}{2} \ln \frac{N_d + 1}{N_d} \qquad (18)$$

the behaviour of the local electron states with the increases of $|\epsilon|$ differs from that just described above only in that, at $|\epsilon| = \epsilon_{cr}^{(3)}$, the HOMO (LUMO) state executes the reverse transformation from the local to the band-like state. As a consequence, for $|\epsilon| \ge \epsilon_{cr}^{(3)}$, there exist only two out-of-band local states. One can conclude therefore that, provided condition (18) is fulfilled, an arbitrary large perturbation is insufficient for the creation of two in-band local states. This property of the spectrum of symmetrical heteropolyenes (if $\eta > 0$) was first noticed by Kventsel [8].

Thus, in the given type of heteropolyenes, the regularities of the appearance and disappearance of local states in the

spectrum of hetero-substituted polyenes, both in-gap and out-of-band local states, are completely determined by relations (13)–(18), which directly follow from the exact secular Eq. (7). It is worth emphasizing that for $\eta > 0$ there can exist two, three, four or no local levels. The presence of only one local state in the π electron spectrum of the structure X–(CH)$_{2N_d}$–X with $\eta > 0$ is impossible.

In [8], the conditions of the appearance of in-gap local states have been obtained (only for $\eta > 0$) in some asymptotic limit. Probably for this reason the corresponding results of the cited paper, which pretend to be valid for finite values of N_d, turn out to be correct only in the limit $N_d \to \infty$, when inequalities (14)–(17) reduce to one.

$\eta < 0$. This case has not been previously investigated. The reason was that real polyenes have double bonds at their ends, i.e., that $\eta > 0$. However, as already mentioned in the Introduction, it is expected [10] that the optimal geometry of the lowest dipole allowed excited state in neutral heteropolyenes and of the ground state of ionic heteropolyene forms corresponds to single bonds at the chain ends. Besides, studying this case for large $|\epsilon|$ is helpful for the understanding properties of heteropolyenes with $\eta > 0$.

Similarly to the above consideration, four regions can be distinguished by using Eq. (7). If inequality:

$$|\eta| > \frac{1}{2} \ln \frac{N_d + 2}{N_d + 1} \qquad (19)$$

is held, the critical values of $|\epsilon|$, at which changes in the number of the in-gap or (and) out-of-band local states occur, are now determined by the following relations:

$$\epsilon_{cr}^{(1)} = \left| \exp(|\eta|) - \frac{2}{2N_d \sinh|\eta| + \exp(|\eta|)} \right|$$

$$\epsilon_{cr}^{(2)} = \exp(|\eta|) \qquad (20)$$

$$\epsilon_{cr}^{(3)} = \exp(|\eta|) + \frac{2}{2N_d \cosh \eta + \exp(|\eta|)}$$

Inequality (19) represents the condition of the existence of two local states (HOMO and LUMO) in an unsubstituted dimerized chain with N atoms and single bonds at its ends. These two local states are present in the spectrum until $|\epsilon| < \epsilon_{cr}^{(1)}$. The LUMO ($\epsilon > 0$) or HOMO ($\epsilon < 0$) state transforms into a state of the band-like type at $|\epsilon| = \epsilon_{cr}^{(1)}$, so that, in the region $\epsilon_{cr}^{(1)} \le |\epsilon| < \epsilon_{cr}^{(2)}$, there exists only one in-gap local state. This state disappears at $|\epsilon| = \epsilon_{cr}^{(2)}$ simultaneously with the appearance of an out-of-band local state, and at $|\epsilon| = \epsilon_{cr}^{(3)}$ the second out-of-band state appears. As a consequence, for $|\epsilon| \ge \epsilon_{cr}^{(3)}$ there exist two out-of-band local states.

If the reverse to inequality (19) is fulfilled, there are no local states for $|\epsilon| < \epsilon_{cr}^{(1)}$, i.e., the HOMO and LUMO states are of the band-like type. The HOMO state transforms into an in-gap local state at $|\epsilon| = \epsilon_{cr}^{(1)}$ and back into a band-like state at $|\epsilon| = \epsilon_{cr}^{(2)}$. The behaviour of out-of-band local states remains qualitatively unchanged. Thus, in the case of the negative sign of the alternation parameter, there can be one,

two or no local states in the π electron spectrum of molecules X–(CH)$_{2N_d}$–X.

3.2. Molecules of the type X^+–$(CH)_{2N_d}$–X^-

This case is interesting not only because molecules of this type really exist, e.g., $X^+ = B$ ($\epsilon = 1$), $X^- = N$ ($\epsilon = -1$), but also as the model of molecular quantum wires, where the electron site energies of the end atoms are shifted oppositely due to the contact with external positive and negative electrodes. Therefore, the dependence of the π electron spectrum dependence on ϵ can be helpful for the understanding of the molecular wire response to the applied potential — currently, one of most challenging issues in the field of molecular electronics [17].

Setting $\epsilon_X = -\epsilon_Y = \epsilon$ and $\beta_{X(Y)} = \exp \eta$ in Eqs. (5) and (6), one obtains for the normalizing factor:

$$\frac{(E-\epsilon)^2}{2\exp(2\eta)\,|A_2|^2}$$

$$= E[\,(2N_d+3-\sin((2N_d+3)\xi)\,\sin^{-1}\xi)$$

$$\times (\exp(-2\eta)+\cos\xi)/2$$

$$-\epsilon^2\exp\eta\,Z\sin((N_d+1)\xi)\,]/$$

$$[\,(E\exp(-\eta)\,\sin((N_d+1)\xi)+\epsilon Z)Z\,] \qquad (21)$$

where ξ is determined by solutions to

$$\epsilon^2 = \exp(-2\eta)Z^{-1}[\exp\eta\,\sin((N_d+2)\xi)+\exp(-\eta)$$

$$\sin((N_d+1)\xi)\,]\,|_{\eta\to 0} = \frac{\sin((N+1)\xi/2)}{\sin((N-1)\xi/2)} \qquad (22)$$

The N_d+1 solutions of Eq. (22), which are chosen exactly in the same way as described above, determine $2(N_d+1)$ π electron energies. Obviously, the valence and conduction levels in this system are lying symmetrically below and above zero, irrespective of the sign and value of ϵ. Due to this fact, the calculation of the π electron spectrum is considerably simplified.

The regions with the different number of local states are now determined by

$$\epsilon_{cr}^{(1)} = \exp(-\eta)\begin{cases} \left(1+\dfrac{2\exp\eta}{2N_d\cosh\eta+\exp(-\eta)}\right)^{1/2}, & \eta>0 \\[3ex] \left(1+\dfrac{2\exp\eta}{2N_d\sinh\eta-\exp(-\eta)}\right)^{1/2}, & \eta<0 \end{cases}$$

$$\epsilon_{cr}^{(2)} = \exp(-\eta)\begin{cases} \left(1+\dfrac{2\exp\eta}{2N_d\sinh\eta-\exp(-\eta)}\right)^{1/2}, & \eta>0 \\[3ex] \left(1+\dfrac{2\exp\eta}{2N_d\cosh\eta+\exp(-\eta)}\right)^{1/2}, & \eta<0 \end{cases}$$

$$(23)$$

For $\eta > 0$ and $\epsilon < \epsilon_{cr}^{(1)}$ there are no local states, if condition (13) is fulfilled (this is similar to the case of symmetrical heteropolyenes). Two symmetrical out-of-band states appear at $\epsilon = \epsilon_{cr}^{(1)}$, which are the only local states in the region $\epsilon_{cr}^{(1)} \le \epsilon < \epsilon_{cr}^{(2)}$. And at values of $\epsilon \ge \epsilon_{cr}^{(2)}$ there exist two in-gap and two out-of-band local states.

A sound distinction from the case considered in the preceding subsection is that in-gap local states cannot be induced in the structure X^+–$(CH)_{2N_d}$–X^- by arbitrary large perturbation, if condition (18) is valid.

For the negative sign of η and under condition (19), two in-gap local states exist until $\epsilon < \epsilon_{cr}^{(1)}$. The π electron spectrum does not contain local states, if $\epsilon_{cr}^{(1)} \le \epsilon < \epsilon_{cr}^{(2)}$, and in the region $\epsilon \ge \epsilon_{cr}^{(2)}$ it contains two out-of-band local states. If the inequality reversed to (19) is fulfilled, in-gap states cannot exist at any value of $|\epsilon|$. Thus, under the condition:

$$|\eta| < \frac{1}{2}\ln\frac{N_d+2}{N_d+1} \qquad (24)$$

the π electron spectrum of heteropolyenes X^+–$(CH)_{2N_d}$–X^- does not contain in-gap local states independent of the sign of the alternation parameter and the absolute value of the Coulomb integral of heteroatoms.

It is also worth emphasizing that due to the fact that in the given type of heteropolyenes, both HOMO and LUMO states can be local, their optical response, in particular, its dependence on the chain length, is expected to be substantially different from that in symmetrical heteropolyenes.

3.3. Molecules of the type X–$(CH)_{2N_d}$–CH_2

As mentioned above, the one-impurity problem in finite polyenes has been addressed by Castaño and Karadakov [9], and by Kventsel [7] in the case of the semi-infinite chain with alternating bonds. But the behaviour of local states in the case of the negative sign of the alternation parameter has not been properly examined in those papers.

The normalization factor and the π electron spectrum are now determined by Eqs. (5) and (6), where $\epsilon_X = \epsilon$, $\epsilon_Y = 0$, and $\beta_{X(Y)} = \exp\eta$, i.e., by

$$\frac{(E-\epsilon^2)}{\exp(2\eta)\,|A_2|^2}$$

$$= 1+\frac{\exp(2\eta)}{2E^2\sin^2((N_d+1)\xi)}((E^2+\exp(2\eta))[E^2(N_d+1)$$

$$-E^2\sin((N_d+1)\xi)\,\cos(N_d\xi)\,\sin^{-1}\xi$$

$$+2\sin(N_d\xi)\,\sin((N_d+2)\xi)$$

$$\times(1+\exp(-2\eta))\,]+2\sin^2\xi) \qquad (25)$$

and

$$\epsilon = \frac{\exp(-2\eta)\ \sin((N_{\mathrm{d}}+1)\xi) + \sin((N_{\mathrm{d}}+2)\xi)}{E\ \sin((N_{\mathrm{d}}+1)\xi)}\Bigg|_{\eta \to 0}$$

$$= \pm \frac{\sin((N+1)\xi/2)}{\sin(N\xi/2)} \qquad (26)$$

respectively.

For $\epsilon = 0$ Eq. (26) coincides with the Lennard–Jones Eq. (11), whereas in the limit $|\epsilon| \to \infty$, the finite part of the spectrum corresponds to a dimerized chain consisting of $2N_{\mathrm{d}}+1$ C atoms, that is (see Appendix): $E = 0$, $E_k^{0v(c)} = +(-)[2[\cosh(2\eta) + \cos(\pi k/(N_{\mathrm{d}}))]]^{1/2}$, where k takes positive integer values, $1, 2, ..., N_{\mathrm{d}}$. One of π electron levels is infinitely distant, $E \sim \epsilon$.

For finite perturbations the analysis of Eq. (26) again has to be carried out separately for positive and negative signs of η, since the dependence of local levels on ϵ in these two cases is substantially different.

$\eta > 0$. As distinct from the case of symmetrical hetero-polyenes, there exist only three regions, which are determined by

$$\epsilon_{\mathrm{cr}}^{(1)} = \exp(-\eta) + \frac{1}{2(N_{\mathrm{d}}+1)\cosh \eta}$$

and

$$\epsilon_{\mathrm{cr}}^{(2)} = \exp(-\eta) + \frac{1}{2(N_{\mathrm{d}}+1)\sinh \eta} \qquad (27)$$

and which are distinguished from one another by the number of local states: no local states, if $|\epsilon| < \epsilon_{\mathrm{cr}}^{(1)}$, one out-of-band local state, if $\epsilon_{\mathrm{cr}}^{(1)} \le |\epsilon| < \epsilon_{\mathrm{cr}}^{(2)}$, and one out-of-band and one in-gap local state, if $\epsilon \ge \epsilon_{\mathrm{cr}}^{(2)}$. These conditions coincide with those obtained in [9].

Unlike the case of two heteroatoms, the qualitative behaviour of the spectrum is independent of the particular relation between the chain length and the value of the alternation parameter. It can also be concluded from the analysis of Eq. (26) that the HOMO level cannot be raised above zero (or the LUMO level be lowered below zero) by an arbitrary large perturbation of only one end atom.

$\eta < 0$. In this case, the qualitative behaviour of the spectrum becomes dependent on the relation between the chain length and alternation parameter. Precisely, if inequality (19) is fulfilled, i.e., the HOMO and LUMO states in the unperturbed chain are local, they remain as the local type until

$$|\epsilon| < \epsilon_{\mathrm{cr}}^{(1)} = \exp |\eta| - \frac{1}{2(N_{\mathrm{d}}+1)\sinh |\eta|} \qquad (28)$$

At $|\epsilon| = \epsilon_{\mathrm{cr}}^{(1)}$ the LUMO (if $\epsilon > 0$) or HOMO (if $\epsilon < 0$) state transforms into a band-like state. The spectrum contains one in-gap local state in the interval:

$$\epsilon_{\mathrm{cr}}^{(1)} \le |\epsilon| < \epsilon_{\mathrm{cr}}^{(2)} = \exp |\eta| + \frac{1}{2(N_{\mathrm{d}}+1)\cosh \eta} \qquad (29)$$

and at $|\epsilon| = \epsilon_{\mathrm{cr}}^{(2)}$ an out-of-band local state appears. So, in

region $|\epsilon| > \epsilon_{\mathrm{cr}}^{(2)}$ there exist one in-gap and one out-of-band local state. As $|\epsilon| \to \infty$, the energy of the former tends to zero, whereas the energy of the latter goes to infinity.

As it can be shown from Eq. (26), if inequality (24) is fulfilled, the above definition of critical values $\epsilon_{\mathrm{cr}}^{(i)}$, $i = 1, 2$, changes in the following way:

$$\epsilon_{\mathrm{cr}}^{(1)} = \begin{cases} \dfrac{1}{2(N_{\mathrm{d}}+1)\sinh |\eta|} - \exp |\eta|, & |\eta| > \dfrac{1}{4}\ln \dfrac{N_{\mathrm{d}}+2}{N_{\mathrm{d}}+1}, \ \mathrm{a} \\[3mm] \dfrac{1}{2(N_{\mathrm{d}}+1)\cosh \eta} + \exp |\eta|, & |\eta| < \dfrac{1}{4}\ln \dfrac{N_{\mathrm{d}}+2}{N_{\mathrm{d}}+1}, \ \mathrm{b} \end{cases}$$

$$\epsilon_{\mathrm{cr}}^{(2)} = \begin{cases} \dfrac{1}{2(N_{\mathrm{d}}+1)\cosh \eta} + \exp |\eta|, & |\eta| > \dfrac{1}{4}\ln \dfrac{N_{\mathrm{d}}+2}{N_{\mathrm{d}}+1}, \ \mathrm{a} \\[3mm] \dfrac{1}{2(N_{\mathrm{d}}+1)\sinh |\eta|} - \exp |\eta|, & |\eta| < \dfrac{1}{4}\ln \dfrac{N_{\mathrm{d}}+2}{N_{\mathrm{d}}+1}, \ \mathrm{b} \end{cases}$$

$$(30)$$

Now there are no local states for $|\epsilon| < \epsilon_{\mathrm{cr}}^{(1)}$. At $|\epsilon| = \epsilon_{\mathrm{cr}}^{(1)}$, depending on the relation between N_{d} and $|\eta|$, either an in-gap (a) or out-of-band (b) local state appears (see Eq. (30)) which remains the only local state in the region $\epsilon_{\mathrm{cr}}^{(1)} \le |\epsilon| < \epsilon_{\mathrm{cr}}^{(2)}$. And the second local state, either an out-of-band (a) or in-gap (b) state appears at $|\epsilon| = \epsilon_{\mathrm{cr}}^{(2)}$, so that in region $\epsilon \ge \epsilon_{\mathrm{cr}}^{(2)}$ two local states of both types are present in the spectrum.

The effect of a single impurity on the π electron spectrum of a semi-infinite alternating chain has been examined by Kventsel [7]. His results related to the case $\eta < 0$ need some comments. First, the crucial role of the relation between N_{d} and $|\eta|$ in determining the spectrum of local states has not been recognized. In the other words, the conditions (19), (24), and (30a,b), which determine the above-discussed different types of the local state spectrum have been overlooked. Second, it has been concluded in [7] that "... for arbitrary value $\Delta \alpha$ (here ϵ) there is one and only one 'surface' (i.e. local) level". This statement is obviously not correct.

Summarizing, the character and evolution of the local state spectrum in structures $X-(CH)_{2N_{\mathrm{d}}}-CH_2$ with $\eta < 0$ in response to changes of ϵ are substantially dependent on the relation between N_{d} and $|\eta|$. Under condition (19), there are two in-gap local states, if $|\epsilon| < \epsilon_{\mathrm{cr}}^{(1)}$, one in-gap state in region $\epsilon_{\mathrm{cr}}^{(1)} \le |\epsilon| < \epsilon_{\mathrm{cr}}^{(2)}$, and one in-gap and one out-of-band state, if $|\epsilon| \ge \epsilon_{\mathrm{cr}}^{(2)}$. Under condition (24) there are no local states in the first of the indicated regions. The relation between N_{d} and $|\eta|$ in this case also determines which of local states, the in-gap or out-of-band, appears first at $|\epsilon| = \epsilon_{\mathrm{cr}}^{(1)}$ (see Eq. (30)). For values of $|\epsilon| \ge \epsilon_{\mathrm{cr}}^{(2)}$ there always exist one in-gap and one out-of-band state independent of the sign and magnitude of the alternation parameter.

3.4. Asymptotic limit

To conclude this section we consider energies of the frontier MOs in the asymptotic limit $N_{\mathrm{d}} \to \infty$. In this case, the

Table 1
Frontier MO energies in the asymptotic limit

Heteropolyene type	State	Energy (in units $|\beta|$)			
		$\eta > 0$		$\eta < 0$	
		$\epsilon > 0$	$\epsilon < 0$	$\epsilon > 0$	$\epsilon < 0$
X–(CH)$_{2N_d \to \infty}$–X	LUMO+1	$2\sinh\eta$	E_{in}^∞	$2\sinh|\eta|$	$2\sinh|\eta|$
	LUMO	$2\sinh\eta$	E_{in}^∞	E_{in}^∞	$-E_{\text{in}}^\infty$
	HOMO	$-E_{\text{in}}^\infty$	$-2\sinh\eta$	E_{in}^∞	$-E_{\text{in}}^\infty$
	HOMO−1	$-E_{\text{in}}^\infty$	$-2\sinh\eta$	$-2\sinh|\eta|$	$-2\sinh|\eta|$
X$^+$–(CH)$_{2N_d \to \infty}$–X$^-$	LUMO+1	$2\sinh\eta$	$2\sinh\eta$	$2\sinh|\eta|$	$2\sinh|\eta|$
	LUMO	E_{in}^∞	E_{in}^∞	E_{in}^∞	E_{in}^∞
	HOMO	$-E_{\text{in}}^\infty$	$-E_{\text{in}}^\infty$	$-E_{\text{in}}^\infty$	$-E_{\text{in}}^\infty$
	HOMO−1	$-2\sinh\eta$	$-2\sinh|\eta|$	$-2\sinh\eta$	$-2\sinh|\eta|$
X–(CH)$_{2N_d \to \infty}$–CH$_2$	LUMO+1	$2\sinh\eta$	$2\sinh\eta$	$2\sinh|\eta|$	$2\sinh|\eta|$
	LUMO	$2\sinh\eta$	E_{in}^∞	E_{in}^∞	0
	HOMO	$-E_{\text{in}}^\infty$	$-2\sinh\eta$	0	$-E_{\text{in}}^\infty$
	HOMO−1	$-2\sinh\eta$	$-2\sinh\eta$	$-2\sinh|\eta|$	$-2\sinh|\eta|$
Ideal polyene H$_2$C–(CH)$_{2N_d \to \infty}$–CH$_2$	LUMO+1	$2\sinh\eta$	$2\sinh\eta$	$2\sinh|\eta|$	$2\sinh|\eta|$
	LUMO	$2\sinh\eta$	$2\sinh\eta$	0	0
	HOMO	$-2\sinh\eta$	$-2\sinh\eta$	0	0
	HOMO−1	$-2\sinh\eta$	$-2\sinh\eta$	$-2\sinh|\eta|$	$-2\sinh|\eta|$

secular equation has analytical solutions for the energies of local states, providing a helpful estimate of the hetero-substitution effect on the relative position of the frontier MO energies, which is of particular interest for the comparison with experiment.

It can be shown that three secular equations considered above, i.e., Eqs. (7), (22) and (26), give the same solution for δ and δ':

$$\exp\delta = \frac{1}{2}\{[(\epsilon^2 - \exp(-2\eta))^2 + 4\epsilon^2 \exp(2\eta)]^{1/2}$$
$$- \exp(-2\eta) + \epsilon^2\} \tag{31}$$

and

$$\exp\delta' = \frac{1}{2}\{[(\epsilon^2 - \exp(-2\eta))^2 + 4\epsilon^2 \exp(2\eta)]^{1/2}$$
$$+ \exp(-2\eta) - \epsilon^2\} \tag{32}$$

which determine non-zero energies of local states.

The in-gap local state energies for all three types of heteropolyenes are summarized in Table 1, where we use the notation:

$$E_{\text{in}}^\infty = \left(2\cosh(2\eta) - 2\cosh\left[\ln\frac{1}{2}([(\epsilon^2 - \exp(-2\eta))^2 \right.\right.$$
$$\left.\left. + 4\epsilon^2 \exp(2\eta)]^{1/2} + \exp(-2\eta) - \epsilon^2)\right]\right)^{1/2}$$

In the asymptotic limit, the conditions of the existence of in-gap local states reduce to the following ones: $|\epsilon| > \exp(-\eta)$, if $\eta > 0$, and $|\epsilon| < \exp(|\eta|)$, if $\eta < 0$.

The energy of out-of-band local states is determined by the following quantity:

$$E_{\text{out}}^\infty = \left(2\cosh(2\eta) + 2\cosh\left[\ln\frac{1}{2}([(\epsilon^2 - \exp(-2\eta))^2 \right.\right.$$
$$\left.\left. + 4\epsilon^2 \exp(2\eta)]^{1/2} - \exp(-2\eta) + \epsilon^2)\right]\right)^{1/2}$$

In structures X–(CH)$_{2N_d \to \infty}$–X, the energy of the out-of-band local state is equal to $+(-)E_{\text{out}}^\infty$ for $\epsilon > 0$ ($\epsilon < 0$) (it corresponds to a double degenerate state); in X$^+$–(CH)$_{2N_d \to \infty}$–X$^-$ to $\pm E_{\text{out}}^\infty$ for two levels below and above the continuous spectrum; and in X–(CH)$_{2N_d \to \infty}$–CH$_2$ there exists the same but non-degenerate out-of-band local state as in the symmetrical heteropolyene. The condition of the existence of out-of-band local states is $|\epsilon| > \exp(-\eta)$.

As seen from Table 1, the relative position of the frontier MOs is substantially influenced by the substitution of end C atoms and, additionally, it is very sensitive to the type of substitution.

In real (finite) heteropolyenes, the dependence of the energy difference between the π electron states responsible for the most intense optical transitions (e.g. $E_{\text{LUMO}} - E_{\text{HOMO}}$) on $|\epsilon|$ is far more complex than that presented in Table 1. Because of this and also because of its importance, it deserves special discussion that will be given in a forthcoming publication.

4. π-Electron spectrum

In this section we discuss the dependence of the full π electron spectrum of heteropolyenes on the perturbation introduced by the presence of heteroatoms. The effects of hetero-substitution are exemplified by two representative
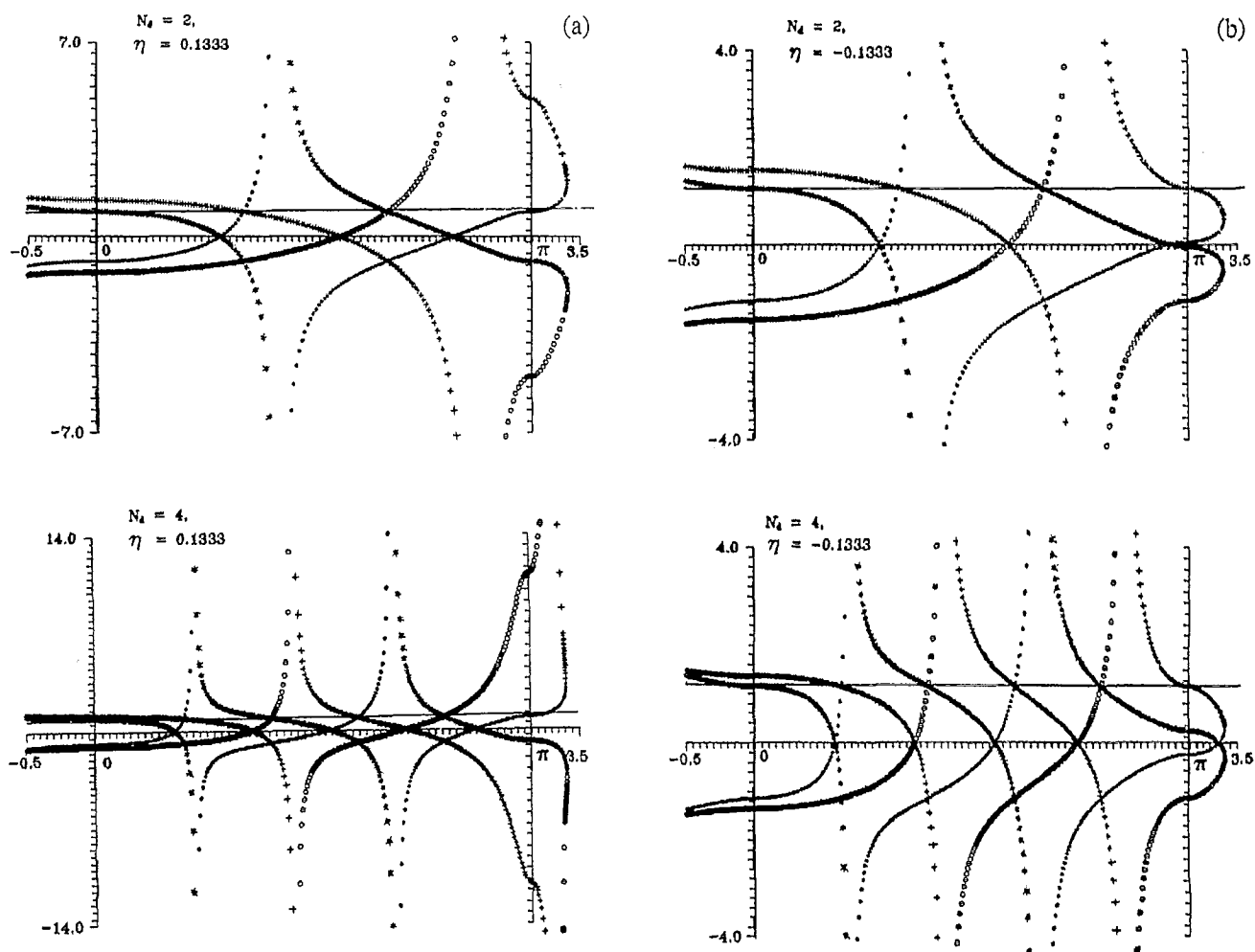
Fig. 1. Graphical solution of Eqs. (9) for $|\eta| = 0.1333$, the experimental value [17], and N_d chosen to fulfill conditions (13), (19) ($N_d = 2$), and (18), (24) ($N_d = 4$). Curves $*$ and $+$ ($\bullet$ and $\circ$) correspond to the dependence of the left-hand side of the upper (lower) equation on x (the variable defined in the text) for $E > 0$ and $E < 0$, respectively. The horizontal lines correspond to $\epsilon = \epsilon_{cr}^{(1)} = 0.87$ ($\eta = 0.1333$) and $\epsilon = \epsilon_{cr}^{(2)} = 1.14$ ($\eta = -0.1333$). The solutions are given by the x coordinate of intersections of curves $*$, $+$, $\bullet$, and $\circ$ with the horizontal line.

cases of hexatriene ($N_d = 2$) and decapentatriene ($N_d = 4$), calculated for the typical value of the alternation parameter, $|\eta| \approx 0.13$ [18]. It is worth emphasizing that the π-electron spectrum transformations in response to changes of the perturbation 'visualized' below for $N_d = 4$ remain qualitatively similar in longer chains. Therefore, we take a comparatively small value of N_d in order to make transparent graphical illustrations. Using Eq. (9), (12), or (26), one can easily obtain the exact π electron spectrum practically for an arbitrary chain length. The asymptotic limit $N_d \to \infty$ can be described analytically (see Section 3.4).

Consider first symmetrical substitution, in which case inequality (13) is valid for the heterodecapentatriene, whereas (18) for the heterohexatriene. A useful look at the heteropolyene π electron spectrum is provided by the graphical solution of Eq. (7). In practice, it is more convenient to use for this purpose Eqs. (9). The analysis of these equations shows that they have real roots for $0 < \xi < \pi$, $\delta < 0$ ($\xi = i\delta$), and $\delta' \leq 2\eta$ ($\xi = \pi + i\delta'$), which determine $2N_d + 2$ π electron energies. Therefore, the intersections of curves, which represent the dependence of the left-hand side of Eqs. (9) on

x ($x = \delta$ for $x < 0$, $x = \xi$ for $0 < x < \pi$, and $x = \delta'$ for $\pi < x \leq 2\eta$) with the horizontal line at the value of ϵ in the ordinate axis, give all desired solutions of Eqs. (9). The dependence of the left-hand side of Eqs. (9) on x is shown in Fig. 1: curves $*$ and $+$ ($\bullet$ and $\circ$) correspond to the left-hand side of the upper (lower) equation for $E > 0$ and $E < 0$, respectively. The horizontal line corresponds to $\epsilon = \epsilon_{cr}^{(1)}$ in Fig. 1(a) ($\eta = 0.1333$) and $\epsilon = \epsilon_{cr}^{(2)}$ in Fig. 1(b) ($\eta = -0.1333$).

In this representation of solutions to Eqs. (9), the intersections with the ϵ-line occurred within intervals $x < 0$, $0 \leq x \leq \pi$ and $\pi < x \leq 2\eta$, and correspond to energies of out-of-band local states, band-like states and in-gap local states, respectively. Hence, the critical values of $|\epsilon|$ defined in Eqs. (14)–(17) are determined by intersections of curves shown with vertical lines $x = 0$ and $x = \pi$. For the given choice of parameters and $\eta > 0$ these critical values, $\epsilon_{cr}^{(i)}$, $i = 1, 2, 3$, are equal to 0.87, 1.28, 5.0 for hexatriene, and to 0.87, 1.1, 11.2 for decapentatriene. In the case $\eta < 0$, then the critical values of $|\epsilon|$ are: $\epsilon_{cr}^{(i)} = 0.05$, 1.14, 1.53 ($N_d = 2$) and 0.24, 1.14, 1.36 ($N_d = 4$) for $i = 1, 2, 3$, respectively. Intersections of
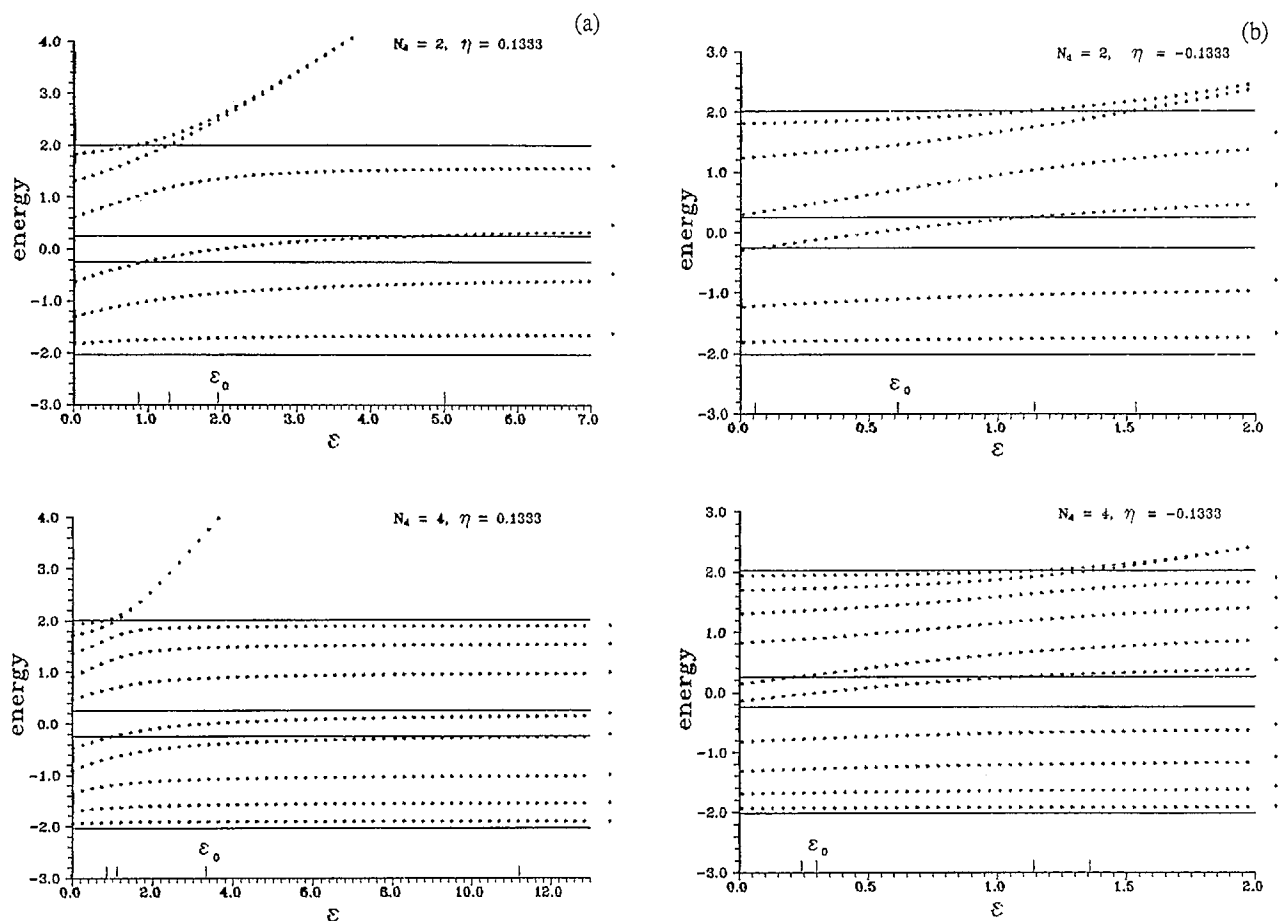
Fig. 2. Dependence of the position of π electron levels in heteropolyenes of the type X–(CH)$_{2N_d}$–X on $\epsilon = \alpha_X - \alpha_C$, the difference in the Coulomb integrals between the guest (X) and host (C) atoms. The heteropolyene parameters are the same as in Fig. 1. The edges of the spectrum of band-like states correspond to $|E| = 0.2674$, 2.0178, the horizontal lines. The last points on the right show the level positions in the limit $\epsilon = \infty$. The critical values of $|\epsilon|$ (see definitions in Eqs. (14)–(16) and (20)) are marked by vertical strokes in the ϵ-axis from left to right: $\epsilon_{cr}^{(1)} = 0.87$ (a, $N_d = 2$, 4), 0.05 (b, $N_d = 2$), 0.24 (b, $N_d = 4$); $\epsilon_{cr}^{(2)} = 1.28$ (a, $N_d = 2$), 1.1 (a, $N_d = 4$), 1.14 (b, $N_d = 2$, 4); $\epsilon_{cr}^{(3)} = 5.0$ (a, $N_d = 2$), 11.2 (a, $N_d = 4$), 1.53 (b, $N_d = 2$), 1.36 (b, $N_d = 4$). The value of ϵ_0 ($E_{HOMO}(\epsilon_0) = 0$) is equal to 1.95 (a, $N_d = 2$), 3.35 (a, $N_d = 4$), 0.51 (b, $N_d = 2$), and 0.30 (b, $N_d = 4$).

curves with each other at $\epsilon = \epsilon_{cr}^{(1)}$ indicate that, at this value of $|\epsilon|$, N_d valence and N_d conduction band-like states are placed symmetrically below and above zero.

Note that if inequality (13) is fulfilled (as for $N_d = 4$) and $\eta > 0$, the last curve to the right intersects with the vertical line $x = \pi$ twice (see Fig. 1(a)). This corresponds to the transformation of the HOMO (if $\epsilon > 0$) or LUMO (if $\epsilon < 0$) state into an in-gap local state at a smaller value of $|\epsilon|$ and to the reverse transformation into a band-like state at a larger value of $|\epsilon|$. Under condition (18) (as for $N_d = 2$ and same value of η), two curves intersect with line $x = \pi$. This indicates that, with the increase of $|\epsilon|$, first the HOMO or LUMO state and then the HOMO -1 or LUMO $+1$ state execute transformation from the band-like to the local state. The behaviour of the last curves to the right in Fig. 1(b) ($\eta < 0$) can be interpreted in a similar way.

From the practical point of view it is interesting to note that the magnitude of $|\epsilon|$ needed for the appearance (disappearance) of in-gap local states is quite moderate. Therefore, the change in the nature of the HOMO or LUMO state in real polyenes under the substitution of end C atoms by possible

substitutors, for which the value of $|\epsilon|$ usually varies from 1 to 3, is very likely. In particular, it is seen from Fig. 1(a) that, in hexatriene and decapentatriene, the substitution of end carbon atoms by boron ($\epsilon = 1$) should result in the transformation of the HOMO state into an in-gap local state. The same transformation but with the LUMO state is expected in the case of the substitution by nitrogen ($\epsilon = -1$) or oxygen ($\epsilon = -1$, -2) atoms.

The overall changes of the spectrum in response to the increase of ϵ (> 0) are displayed in Fig. 2. The critical values $\epsilon_{cr}^{(i)}$, $i = 1$, 2 and 3 are marked by vertical strokes on the ϵ-axis from the left to right. Besides, the values of $\epsilon_0 = \exp(\eta(2N_d + 1))$, at which the HOMO (LUMO) level crosses zero, are also indicated. These are: 1.95 ($\eta = 0.133$), 0.51 ($\eta = -0.133$) and 3.35 ($\eta = 0.133$), 0.30 ($\eta = -0.133$) for $N_d = 2$ and $N_d = 4$, respectively.

The appearance (disappearance) of local states in this figure corresponds to intersections of dotted curves (each represents the π electron energy dependence on ϵ) with horizontal lines which show boundaries of band-like states in the valence and conduction bands. The in-gap states are lying
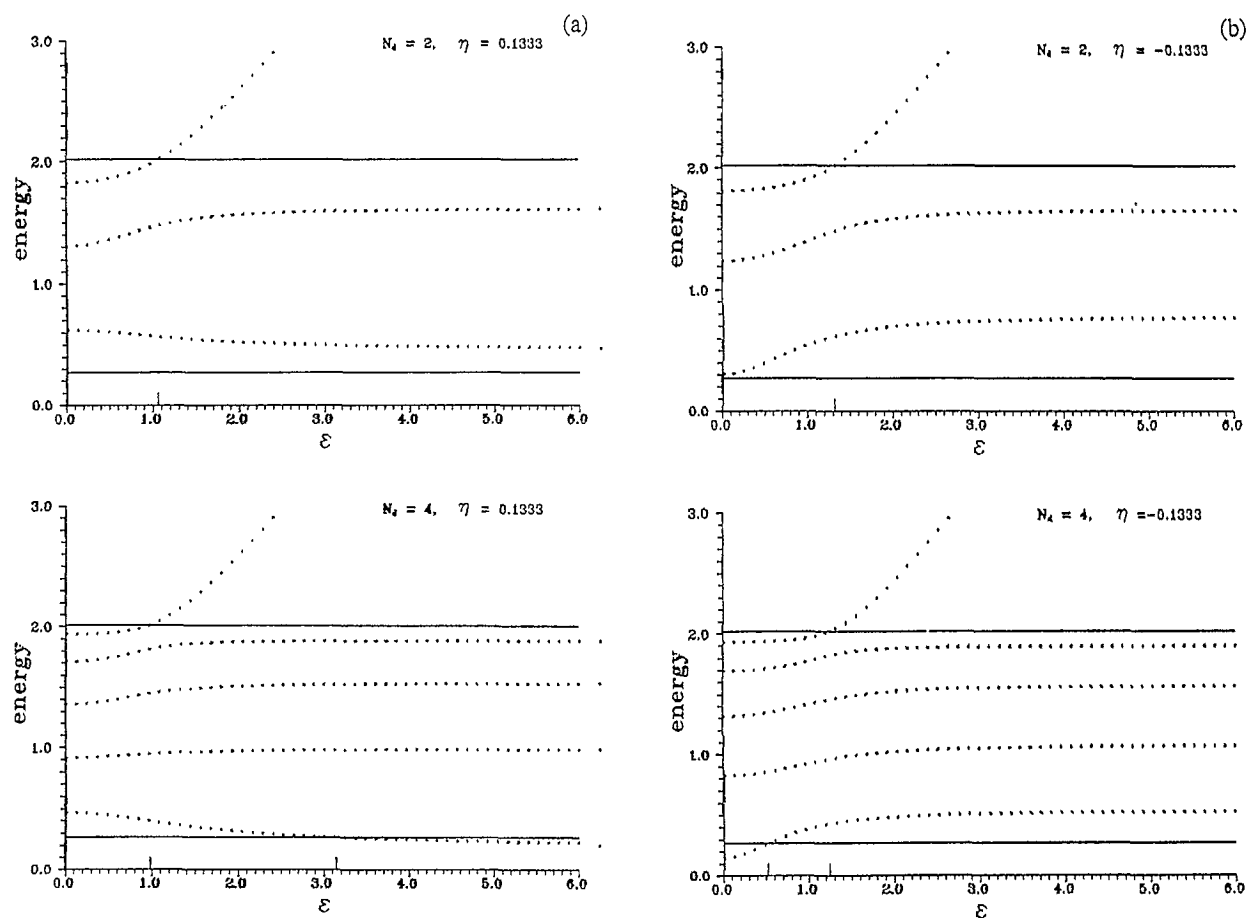
Fig. 3. Same dependence as in Fig. 2 (and same correspondence) for $X^+–(CH)_{2N_d}–X^-$. The critical values of $|\epsilon|$ (see definitions in Eq. (23)) are: $\epsilon_{cr}^{(1)} = 1.08$ (a, $N_d = 2$), 0.974 (a, $N_d = 4$), 1.32 (b, $N_d = 2$), 0.49 (b, $N_d = 4$); $\epsilon_{cr}^{(2)} = 3.12$ (a, $N_d = 4$), 1.21 (b, $N_d = 4$).

between two inner horizontal lines. The last dots to the right indicate the position of $2N_d \pi$ electron levels in the limit $\epsilon = \infty$ (two levels are infinitely distant). The HOMO and LUMO levels are represented by the $(N_d + 1)$th and $(N_d + 2)$th curves from below, respectively.

The dependences presented in Fig. 2 give a representative visual quantitative picture of the evolution of all π electron levels in symmetrical heteropolyenes with changes of the Coulomb energy of heteroatoms. In calculations, ϵ has been assumed to be positive, i.e., the electron site energy on heteroatoms to be higher than that on C atoms. For negative values of ϵ the corresponding picture can be obtained by simply replacing positive and negative energies in Fig. 2.

Now we briefly discuss the main distinctions of the π electron spectrum in heteropolyenes of the types $X^+–$ $(CH)_{2N_d}–X^-$ and $(CH)_{2N_d}–CH_2$ (Figs. 3 and 4), respectively, where the representation of the results (parameters, notations, etc.) is completely identical to that in Fig. 2.

The spectrum of $X^+–(CH)_{2N_d}–X^-$ is symmetrical with respect to zero at any value of ϵ and, therefore, only the dependence of the conduction π electron levels is shown in Fig. 3. The most remarkable feature of this dependence is that, under the positive sign of the alternation parameter, the LUMO level is lowering with the increase of $|\epsilon|$, whereas the rest of the N_d conduction levels go up. This is not so for $\eta < 0$, in which case all conduction levels are rising (all

valence levels are lowering) with $|\epsilon|$ (see Fig. 3(b)). Thus, it can be unambiguously concluded that the HOMO–LUMO gap in this type of heteropolyene is monotonically decreasing (if $\eta > 0$) or increasing (if $\eta < 0$) as a function of $|\epsilon|$, independent of the heteropolyene length. In contrast, the HOMO–LUMO gap versus $|\epsilon|$ dependence in symmetrical heteropolyenes can be qualitatively different (and also non-monotonic) in heteropolyenes of different length.

As seen from Fig. 4 (and was expected) the dependence of the π electron spectrum on $|\epsilon|$ in asymmetrical heteropolyenes is qualitatively similar to that observed in symmetrical ones. It is obviously weaker. In particular, the HOMO (LUMO) level cannot cross zero energy. There are only two critical values of $|\epsilon|$ (indicated by vertical strokes) at which certain π electron states are transformed from the band-like type to the local type and vice versa. An important distinction of this kind of heteropolyene is that, in the limit $|\epsilon| \to \infty$, the HOMO (or LUMO) state has zero energy, the property characteristic for polymethines.

5. Conclusions

Using the Green function formalism, the Hückel problem is exactly solved for the model of finite polyenes, which incorporates the bond length alternation and the possible
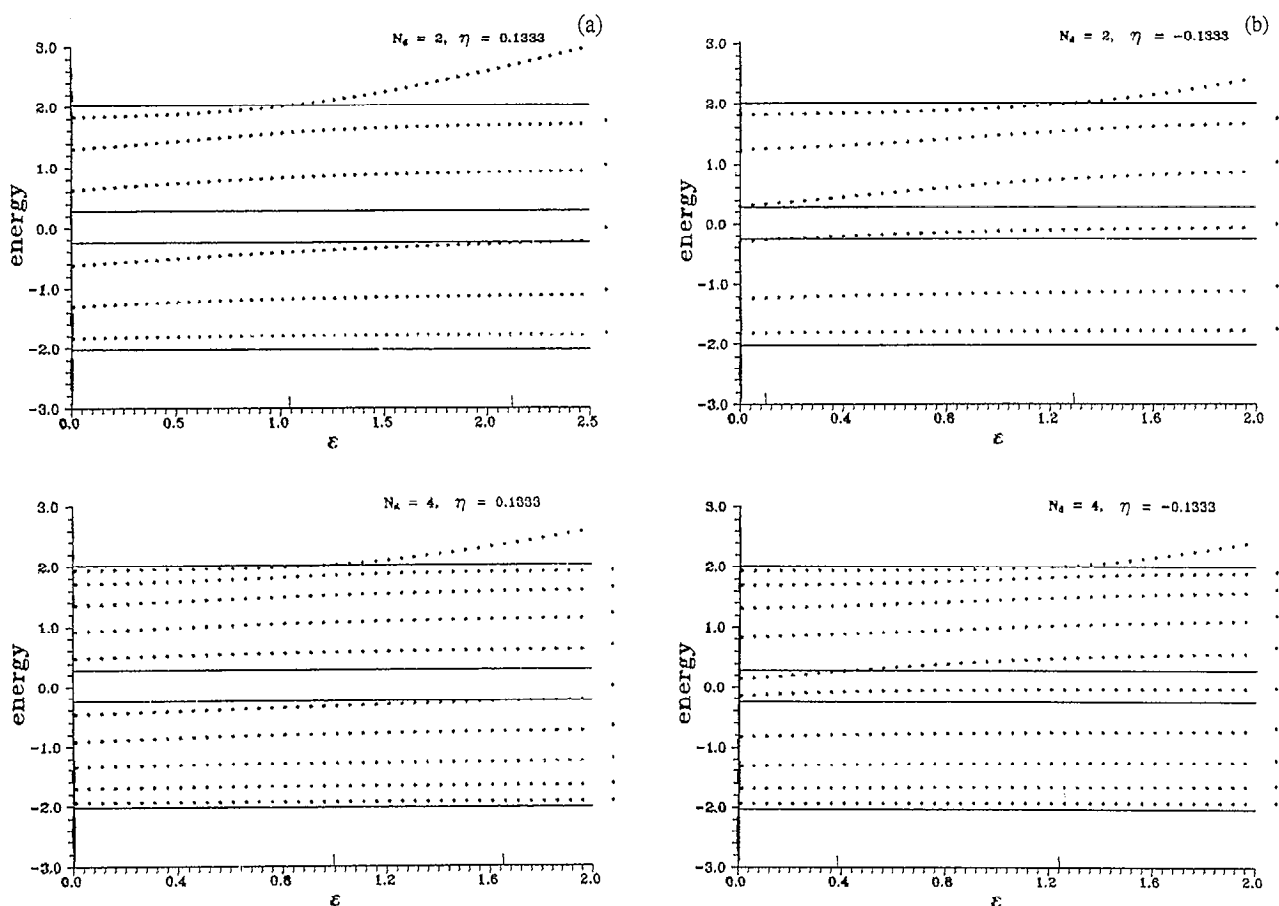
Fig. 4. Same dependence as in Fig. 2 (and same correspondence) for X–$(CH)_{2N_d}$–CH_2. The critical values of $|\epsilon|$ (see definitions in Eqs. (27)–(30)) are: $\epsilon_{cr}^{(1)} = 0.104$ (a, b, $N_d=2$), 0.974 (a, $N_d=4$), 0.395 (b, $N_d=4$); $\epsilon_{cr}^{(2)} = 2.123$ (a, $N_d=2$), 1.623 (a, $N_d=4$), 1.308 (b, $N_d=2$), 1.242 (b, $N_d=4$).

change of the Coulomb and resonance integrals produced by the substitution of end C atoms by heteroatoms. For three major types of heteropolyenes, X–$(CH)_{2N_d}$–X, X^+–$(CH)_{2N_d}$–X^-, and X–$(CH)_{2N_d}$–CH_2, the eigen-value problem, which demands solving a set of $2N_d + 2$ linear equations, is reduced to the solution of only one transcendent equation. This provides a powerful tool for studying the whole π electron spectrum as a function of characteristic parameters. The closed form of the MO coefficients in terms of solutions of the secular equation is also found. These formal results make available any desired characteristic of the indicated types of heteropolyenes for a quick and reliable analysis.

In fact, the model considered above has much wider applications. In particular, the system X^+–$(CH)_{2N_d}$–X^- obviously belongs to the type of donor/conjugated-bridge/acceptor (DBA) sequence which is intensively discussed in the literature in the context of potential molecular wires, switches, etc. (see, e.g., [19,20] and Refs. therein). The exact results presented in Section 3.2 suggest both a helpful guide for more elaborate quantum-mechanical calculations such as in [19], and a reliable test for heuristic DBA models [20]. The use of molecular orbital coefficients defined in Eqs. (3), (4) and (6) in calculations of the donor–acceptor electron transfer rate, second-harmonic generation and other quantities of interest is straightforward, but this is another story that deserves separate discussion.

In this paper we focus mainly on the local state spectrum and its dependence on characteristic parameters in both cases of double and single bonds on the heteropolyene ends. However, the relations derived in Sections 3.1–3.3 with the replacement $\epsilon \rightarrow \epsilon_{eff}$ remain valid in the case of an arbitrary end group (including the perturbation of the end C–C bonds). Of course, the effective (energy-dependent) 'parameter' ϵ_{eff} should be specified for each particular substituent. In terms of Hückel parameters this can be done for the end group of arbitrary complexity.

In the case of heteropolyenes, a number of new results as well as some corrections to previous conclusions have been presented throughout the discussion. These results establish, in particular, the relationship between the heteropolyene parameters and peculiarities of in-gap local states which are directly reflected in the optical response of heteropolyenes. Therefore, the regularities discovered can guide the search of polyene-based compounds with novel optical and electrical properties. Concrete suggestions developed on the basis of the above-presented theory are in preparation.

Acknowledgements

Appendix

Expressions for Green functions

Keeping in mind that, apart from calculations of the π electron energies and molecular orbital coefficients for heteropolyenes, the Green functions appearing in Eqs. (4)–(6) can be used in a number of other applications, e.g. studying electronic properties of branched polyenes [21], we present in this Appendix the full list of the Green function matrix elements.

The matrix elements $G_{j,j'}$, which describe an alternating chain with an even number of atoms, are connected with the Green function for a chain with an odd number of atoms (denoted below as $\tilde{G}_{j,j'}$) by the following relations:

$$G_{j,j'} = \tilde{G}_{j,j'} + \frac{\tilde{G}_{j,N-1}\tilde{G}_{N-1,j'}}{E\exp(-2\eta) - \tilde{G}_{1,1}}, \quad j,j' \neq N \tag{A1}$$

and

$$G_{N,j'} = \exp(-\eta)\frac{\tilde{G}_{N-1,j'}}{E\exp(-2\eta) - \tilde{G}_{1,1}}, \quad j' \neq N \tag{A2}$$

where the Green functions $\mathbf{G}$ and $\tilde{\mathbf{G}}$ refer to chains with $N = 2N_d + 2$ and $2N_d + 1$ atoms, respectively.

In an unperturbed polymethine chain with $2N_d + 1$ atoms, apart from N_d valence (v) and N_d conduction (c) π electron states (their MO coefficients are denoted below by $A_{jk}^{0v(c)}$, $k = 1, 2, ..., N_d$), there is an electron state with zero energy. For the MO coefficients of the latter state, the non-bonding orbital, we will use the notation A_j^0. In terms of the MO coefficients, the matrix elements of $\tilde{\mathbf{G}}$ take the form:

$$\tilde{G}_{j,j'} = \sum_{k=1}^{N_d}\left(\frac{A_{jk}^{0v}A_{j'k}^{0v}}{E - E_k^{0v}} + \frac{A_{jk}^{0c}A_{j'k}^{0c}}{E - E_k^{0c}}\right) + A_j^0 A_{j'}^0 E^{-1} \tag{A3}$$

Finding the unperturbed solution to Eq. (2) for odd values of N is elementary and gives for the bonding and anti-bonding MO coefficients:

$$A_{jk}^{0v(c)} = \left(\frac{2}{N+1}\right)^{1/2}\begin{cases}\left(\exp\eta\,\sin\frac{\pi(j+1)k}{N+1} + \exp(-\eta)\,\sin\frac{\pi(j-1)k}{N+1}\right)(E_k^{0v(c)})^{-1}, \quad j=2l-1 \\[2mm] \sin\frac{\pi jk}{N+1}, \quad j=2l\end{cases} \tag{A4}$$

where $E_k^{0v(c)} = +(-)[2[\cosh(2\eta) + \cos(\pi k/(N_d+1))]]^{1/2}$, and for the non-bonding MO coefficients:

$$A_j^0 = \begin{cases}(-1)^{(j-1)/2}\exp((j-1)\eta)\left[\dfrac{1-\exp(4\eta)}{1-\exp(2(N+1)\eta)}\right]^{1/2}, \quad j=2l-1 \\[4mm] 0, \quad j=2l\end{cases} \tag{A5}$$

Substituting Eqs. (A4) and (A5) in Eq. (A3) and performing summation, one obtains:

$$\tilde{G}_{2l,2l'} = \begin{cases}E\dfrac{\sin(l\xi)\,\sin((N_d-l'+1)\xi)}{\sin\xi\,\sin((N_d+1)\xi)}, \quad l \leq l' \\[4mm] l \leftrightarrow l', \quad l \geq l'\end{cases} \tag{A6}$$

$$\tilde{G}_{2l-1,2l'-1} = \begin{cases}\dfrac{[\sin(l\xi) + \exp(-2\eta)\,\sin((l-1)\xi)][\sin((N_d-l'+1)\xi) + \exp(-2\eta)\,\sin((N_d-l'+2)\xi)]}{E\exp(-2\eta)\,\sin\xi\,\sin((N_d+1)\xi)}, \quad l \leq l' \\[4mm] l \leftrightarrow l', \quad l \geq l'\end{cases} \tag{A7}$$

$$\tilde{G}_{2l,2l'-1} = \begin{cases} \exp\eta\,\dfrac{\sin(l\xi)\,\sin((N_d+l'+1)\xi)}{\sin\xi\sin((N_d+1)\xi)} + \exp(-\eta)\,\dfrac{\sin(l\xi)\,\sin((N_d-l'+2)\xi)}{\sin\xi\sin((N_d+1)\xi)},\ l<l' \\[2ex] l\leftrightarrow l',\ l\geq l' \\[2ex] \dfrac{\sin((N_d-l+1)\xi)\,[\sin(l\xi)+\exp(-2\eta)\,\sin((l-1)\xi)]}{\exp(-\eta)\sin\xi\sin((N_d+1)\xi)},\ l=l' \end{cases} \tag{A8}$$

Using the above equations in Eqs. (A1) and (A2) we get:

$$G_{2l,2l'} = \begin{cases} \dfrac{E\sin(l\xi)\,[\exp(-2\eta)\,\sin((N_d-l'+l)\xi)+\sin((N_d-l'+2)\xi)]}{\sin\xi\,[\exp(-2\eta)\,\sin((N_d+1)\xi)+\sin((N_d+2)\xi)]},\ l\leq l' \\[2ex] l\leftrightarrow l',\ l\geq l' \end{cases} \tag{A9}$$

$$G_{2l-1,2l'-1} = \begin{cases} \dfrac{E[\sin(l\xi)+\exp(-2\eta)\,\sin((l-1)\xi)]\,\sin((N_d-l'+2)\xi)}{\sin\xi\,[\exp(-2\eta)\,\sin((N_d+1)\xi)+\sin((N_d+2)\xi)]},\ l\leq l' \\[2ex] l\leftrightarrow l',\ l\geq l' \end{cases} \tag{A10}$$

$$G_{2l,2l'-1} = \begin{cases} \dfrac{E^2\sin(l\xi)\,\sin((N_d-l'+2)\xi)}{\sin\xi\,[\exp(-\eta)\,\sin((N_d+1)\xi)+\exp\eta\,\sin((N_d+2)\xi)]},\ l<l' \\[2ex] \dfrac{[\sin(l\xi)+\exp(-2\eta)\,\sin((l-1)\xi)]\,[\exp(-2\eta)\,\sin((N_d-l+1)\xi)+\sin((N_d-l+2)\xi)]}{\exp(-\eta)\sin\xi\,[\exp(-2\eta)\,\sin((N_d+1)\xi)+\sin((N_d+2)\xi)]},\ l=l' \end{cases} \tag{A11}$$

$$G_{2l-1,2l'} = \dfrac{[\sin(l\xi)+\exp(-2\eta)\,\sin((l-1)\xi)]\,[\exp(-2\eta)\,\sin((N_d-l'+1)\xi)+\sin((N_d-l'+2)\xi)]}{\exp(-\eta)\sin\xi\,[\exp(-2\eta)\,\sin((N_d+1)\xi)+\sin((N_d+2)\xi)]},\ l<l' \tag{A12}$$

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