A local perspective on the conjugation of double bonds in acyclic polyenes

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Abstract

The study is devoted to the elaboration of an alternative image of conjugation in acyclic polyenes as a weak and essentially local delocalization of initially-localized pairs of $\pi$-electrons of individual formally-double (C=C) bonds (instead of formation of a completely delocalized $\pi$-electron system as usual). Polyenes are modelled as sets of weakly-interacting C=C bonds, where the single (C–C) bonds represent the interaction. Expressions for the relevant non-canonical (localized) molecular orbitals (NCMOs) are derived directly without any reference to usual (canonical) MOs in the form of power series with respect to the small resonance parameter of C–C bonds. An explicit interdependence is established between the conjugation energy (CE) of polyene and the shapes of its NCMOs. As a result, a local relation follows between the constitution of the nearest environment of a certain C=C bond, delocalization pattern of the respective single pair of $\pi$-electrons and contribution of just this pair to the total CE. A simple additive scheme is deductively suggested to evaluate the CEs of polyenes in terms of essentially local increments easily found by inspection. The actual order of a C=C bond also is related to the extent of delocalization of the only pair of its $\pi$-electrons. Within a certain rough approximation, the approach yields a simplified image of acyclic conjugation in terms of shifts of separate pairs of $\pi$-electrons from C=C bonds to the nearest C–C bonds in accordance with the picture offered by the curly arrow formalism. The results are illustrated by specific examples.

Graphic abstract

Keywords    Alkenes · Electronic structures · Isomers · Conjugation · Polyenes

Introduction

Conjugation is undoubtedly among the most important and widespread phenomena in organic chemistry. An additional interaction (overlap) of 2p$_z$ orbitals of atoms of unsaturated fragments (functional groups) due to formally-single interfragmental bonds is known as its main precondition. Consequently, the compounds concerned acquire specific properties, including higher thermodynamic stabilities as compared to appropriate reference structures (e.g. sets of the relevant isolated fragments) [1, 2], shorter interfragmental bonds vs. their standard lengths [2–4], lower first ionization potentials [5], bathochromic shifts of electronic absorption bands in the UV/Vis spectra [6], etc. Although special types of this phenomenon often are distinguished and studied separately (e.g. the cross-conjugation [7–10]), the above-mentioned properties are more or less common to all conjugated molecules. That is why the term ‘the conjugation effect’ also is alternatively used. Numerous actual and potential applications of (poly)conjugated materials [1, 7, 10, 11] also deserve mention here. All these circumstances

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stimulate an interest in the very nature of the conjugation effect. General concepts and models evidently are highly desirable here.

Acyclic unsaturated hydrocarbons (polyenes) [12] are among archetypal examples of conjugated compounds. Consequences of conjugation are known to be relatively weak in polyenes [1, 2, 13, 14], especially in comparison to their cyclic (aromatic) analogues [1]. This primarily refers to properties determined by the whole system of π-electrons and referred to below as the classical ones, viz. geometry and thermodynamic stability. For example, characteristics of carbon–carbon bonds are far from being uniform over the polyene chain (cf. the so-called bond length alternation (BLA) [1, 4]), although formally-double (single) bonds are somewhat lengthened (shortened) here vs. their standard values [1–4]. The overall gain of stability also is rather insignificant in this case, i.e. conjugation energies (CEs) of polyenes are small in comparison to the relevant total π-electron energies [1]. That is why these CEs have been treated mostly in an additive manner [15–20], especially in connection with the employment of acyclic polyenes as reference systems [17–19] when studying (poly)cyclic conjugated hydrocarbons and/or their aromaticity. Nevertheless, acyclic polyenes of distinct constitutions (including isomers) exhibit different properties, e.g. the cross-conjugated (dendralene) chains are considerably less stable vs. their linearly-conjugated counterparts [1, 2, 8, 10, 20–23]. The present study addresses just the above-specified classical aspects of conjugation in acyclic polyenes.

The most popular mental image of the conjugation effect follows from the predominant approach of quantum chemistry, viz. from the standard (canonical) method of molecular orbitals (MOs). This method provides us with the representation of any molecular system by a set of double-occupied one-electron orbitals (i.e. canonical MOs (CMOs)) usually embracing the whole molecule concerned and thereby being completely delocalized. This especially refers to molecules consisting of similar fragments, such as polyenes. On this basis, the conjugation effect often is identified with the formation of an entirely delocalized system of π-electrons (see e.g. [1, 3, 4]). The success of this perspective is beyond any doubt, especially in studies of properties related to separate one-electron energy levels, such as photoelectron spectra (see e.g. [5]). In respect of classical manifestations of the same effect, however, this viewpoint is not free from important weak points: First, the drastic delocalization of CMOs when passing from isolated C=C bonds to polyene is not compatible with the above-mentioned weak (perturbational) nature of manifestations concerned. Second, the extent of delocalization of CMOs is largely independent of that of conjugation. For example, one can easily make sure that variation in relative values of resonance parameters of formally-single (C–C) bonds exerts practically no influence upon the shapes of CMOs of polyene chains in the framework of the simple Hückel model.] Finally, delocalization of CMOs is equally peculiar to both conjugated and saturated hydrocarbons in contrast to the common belief that the overall extent of delocalization grows substantially with conjugation [Besides, the very classification of hydrocarbons into saturated, conjugated aliphatic and aromatic often is grounded on qualitative differences in the relevant extents of delocalization (see e.g. [24]).] It is then no surprise that additional characteristics of (electronic) structures are introduced and used instead of CMOs themselves in comparative studies of isomers of polyenes, e.g. the conjugation length [1, 7], the topological index Z [7], graph-theoretical descriptors of branching [25], the HOMO/LUMO gap [22], etc.

Fortunately, other approaches to electronic structures of molecules also exist that are likely to offer alternative images of acyclic conjugation. These are based on the Lewis concept [26] of localized two-electron chemical bonds. Although the classical Lewis structure itself is too simple to embrace conjugation [both isolated and conjugated double bonds are treated equally here], it serves as a starting position (zero-order approximation) when looking for delocalization corrections due to interbond interaction.

The well-known valence bond (VB) theory (see e.g. [27, 28]) is an outstanding example of the above-specified approaches. Indeed, contributions of charged and radicaloid bonding schemes to the total wave function are obtainable here that are responsible for the extra delocalization vs. the relevant fundamental Rumer structure and/or Lewis structure. As for instance, analysis of MO determinants of some short conjugated compounds in terms of the VB theory [14] showed that covalent bonding schemes predominate considerably over the remaining ones in accordance with the anticipated weak delocalization. For butadiene, this conclusion has been largely supported by recent VB self-consistent field calculations [29, 30]. Analogous studies of higher linear polyenes [29], however, showed that diradicaloid bonding schemes play a more and more important role with elongation of the chain. Nevertheless, the relevant delocalization apparently is of a semi-local nature in contrast to that predicted by the CMO theory [Extinction of contributions of diradicaloid schemes is observed when the distance between the two radicaloid centers grows]. Furthermore, a unified treatment of the above-specified supplementary bonding schemes via the Dewar resonance structures has been suggested recently [2]. On this basis, a general approach to conjugation has been elaborated, wherein the number of the Dewar structures serves as a measure of delocalization and thereby of conjugation. It is also noteworthy that suppressed delocalization was found in cross-conjugated polyenes as compared to the linear ones in these studies [2, 29, 30].

Apart from the VB theory, localized approaches based on the perturbative treatment of the configuration interaction
referring to a double-occupied and a vacant (NC)MO. In its matrix form, this requirement resolves itself into a zero matrix condition for the occupied-vacant off-diagonal block (submatrix) of the total one-electron Hamiltonian (Fockian) matrix \(H\) in the basis of NCMOs being sought \([42–51, 54]\). In other words, the initial matrix \(H\) should be block-diagonalized so that its final form coincides with the direct sum of two submatrices (blocks) \(E_{\text{occ}}\) and \(E_{\text{vac}}\), referring to subspaces of double-occupied and vacant NCMOs, respectively. The transformation matrix \(C\) obtained then contains the relevant representation of NCMOs, whereas the twofold trace of the submatrix \(E_{\text{occ}}\) yields the respective total energy \((E)\) \([51, 54]\). Accordingly, the relevant charge-bond order matrix \(P\) follows after projecting to the whole subset of double-occupied (NC)MOS and is consequently expressible via submatrices of the matrix \(C\).

Comparison of the above-specified block-diagonality condition for the matrix \(H\) to the standard diagonality requirement underlying the respective secular (eigenvalue) equation \([46]\) showed the former to be a definite generalization of the latter. Indeed, multidimensional blocks \(E_{\text{occ}}\) and \(E_{\text{vac}}\) (called the eigenblocks of the matrix \(H\)) are sought instead of usual (one-dimensional) eigenvalues. It is then no surprise that more general solutions of the block-diagonalization problem proved to be obtainable via entire submatrices of the matrix \(H\) without specifying either the internal constitutions or the dimensions of the latter \([45–51, 54]\). [Solutions embrace here both the transformation matrix \(C\) and the eigenblocks of the matrix \(H\) \((E_{\text{occ}}\) and \(E_{\text{vac}}\) \([46]\).] Moreover, thanks to the well-known invariance of a matrix trace as a whole with respect to definite transformations and transpositions inside, the formalism under discussion offered new alternatives to express the total energy \((E)\), in particular, to relate the latter directly to shapes of NCMOs \([51, 54]\).

For systems consisting of a certain number of similar weakly-interacting two-center chemical bonds, solutions of the relevant block-diagonalization problem have been derived in the form of power series with respect to Hamiltonian matrix blocks representing the interbond interaction \([45–47, 51, 55]\). The resulting NCMOs (LMOs) then proved to be of the bond-orbital-and-tail constitution \([51, 55]\), i.e. these contained the main contribution of the bonding orbital of one of several interacting bonds (referred to as the parent bond of the given NCMO) and small corrections (tails) extending over the nearest neighbourhood of the latter. Accordingly, both the relevant total energies \((E)\) and the actual internal orders of formally-double \((C=C)\) bonds have been expressed in terms of the so-called delocalization coefficients of occupied NCMOs \([51, 54]\). It is evident that \(\pi\)-electron systems of acyclic polyenes also belong to the class under discussion \([56]\) provided that these hydrocarbons are modelled as sets of weakly-interacting double \((C=C)\) bonds and the single \((C–C)\) ones represent the interaction. Such a
model, in turn, is compatible with the above-described weak classical manifestations of acyclic conjugation. Additional arguments for the adequacy of this model may be found elsewhere [56–58].

In summary, the present study is devoted to the application of the above-mentioned achievements to the elaboration of an alternative viewpoint of the conjugation of double (C=C) bonds in acyclic polyenes in terms of nearly-localized MOs (NCMOs) and thereby weakly-delocalized pairs of π-electrons. In particular, we expect to find a relation between the delocalization pattern of these electrons and the local constitution of the carbon backbone. Analysis of the relevant CEs in terms of increments of separate π-electron pairs also is among our aims.

### Results and discussion

#### Expressions for NCMOs of polyenes

Let us confine ourselves to small- and medium-sized polyenes containing \( N \) formally-double (C=C) bonds and \( N - 1 \) formally-single (C=C) ones. Numbers of both carbon atoms and π-electrons then equal to \( 2N \). Besides, no need arises here for specifying either the number \( N \) or the overall constitution of the polyene concerned (linear or branched). As already mentioned, the C–C bonds are assumed to be weak as compared to the C=C ones. Accordingly, the set of \( N \) isolated C=C bonds (ethene fragments) serves as the zero order approximation (reference system) of our polyene, whereas the C–C bonds represent the interaction between the C=C bonds (perturbation).

Let us start with the \( 2N \)-dimensional basis of \( 2p_z \) atomic orbitals (AOs) of carbon atoms \( \{ \chi \} \). At the Hückel level, our polyene is representable by \( 2N \) Coulomb parameters, as well as by \( N \) and \( N - 1 \) resonance parameters (integrals) of C=C and C–C bonds, respectively. [Parameters between AOs of more remote atoms are ignored as usual [59, 60].] As an initial approximation, let these parameters be replaced by their mean values correspondingly denoted by \( a, \beta, \) and \( \gamma \). Further, the parameter \( \gamma \) is supposed to take a sufficiently small value so that it may be regarded as a first order term vs. \( \beta \). Given that the usual equalities \( a = 0 \) and \( \beta = 1 \) are accepted for convenience, a negative energy unit and thereby a positive \( \gamma \) value (\( \gamma > 0 \)) accordingly follow. Consequently, \( \gamma \) is a dimensionless quantity representing the ratio of the resonance integral of single bonds to that of double bonds.

Let us now define the bond orbitals (BOs) of double (C=C) bonds. To this end, let the initial AOs \( \{ \chi \} \) be enumerated in such a way that orbitals belonging to the same C=C bond (say, to the \( i \)th one) acquire the coupled numbers \( i \) and \( N+i \), where \( i \) here and below refers to the \( i \)th double bond (this type of numbering is exemplified in Fig. 1). Let the bonding BO (BBO) of this bond \( \phi_{(+i)} \) and its antibonding counterpart (ABO) \( \phi_{(-i)} \) be defined as a normalized sum and difference, respectively, of the above-specified two AOs, viz.

\[
\phi_{(+i)} = \frac{1}{\sqrt{2}}(\chi_i + \chi_{N+i}), \quad \phi_{(-i)} = \frac{1}{\sqrt{2}}(\chi_i - \chi_{N+i}).
\]

Since passing from the basis \( \{ \chi \} \) to \( \{ \phi \} \) actually implies taking into account resonance parameters (\( \beta = 1 \)) between AOs inside C=C bonds, all BBOs and all ABOs are ultimately characterized by one-electron energies correspondingly equal to 1 and –1 in our energy units. Accordingly, resonance parameters between BOs \( \phi_{(+i)} \) and \( \phi_{(-j)} \) (let them be called the intrabond ones) vanish for any \( i \). Further, orbitals \( \phi_{(+i)} \) and \( \phi_{(-j)} \) (\( i = 1,2,\ldots,N \)) are supposed to be double-occupied and vacant, respectively, in the zero order (reference) system. In other words, the BBOs \( \phi_{(+i)} \) (\( i = 1,2,\ldots,N \)) represent individual pairs of π-electrons of C=C bonds “before conjugation”.

Let us now dwell on analogous parameters between BOs of different C=C bonds (interbond resonance parameters). Let us introduce the following notations for the three principal types of the latter, viz.

\[
\langle \phi_{(+j)} | \hat{H} | \phi_{(+i)} \rangle = T_{ij}, \quad \langle \phi_{(-j)} | \hat{H} | \phi_{(-i)} \rangle = Q_{ij},
\]

\[
\langle \phi_{(+j)} | \hat{H} | \phi_{(-i)} \rangle = R_{ij}, \tag{2}
\]

where the BOs concerned are shown inside the bra- and ket-vectors. Since C=C bonds interact one with another via C–C ones in our model, non-zero values of parameters of Eq. (2) correspond to BOs of the former connected by a C–C bond [57] and referred to below as first-neighbouring double bonds (the relevant absolute values equal to \( \gamma /2 \)). Thus, parameters of Eq. (2) are first order terms with respect to \( \gamma \).

Our next step consists in representing the above-defined quantities in a matrix form. Let us start with collecting all BBOs \( \phi_{(+i)}, i = 1,2,\ldots,N \) and all ABOs \( \phi_{(-i)}, i = 1,2,\ldots,N \) into
two \( N \)-dimensional subsets of BOs. The relevant row and column matrices will be correspondingly denoted by ket- and bra-vectors \( |\phi_{(+)}\rangle, |\phi_{(-)}\rangle, \langle \phi_{(+)}| \) and \( \langle \phi_{(-)}| \). One-electron energies of BOs then accordingly compose \( N \times N \)-dimensional matrices \( I \) and \( -I \), where \( I \) here and below stands for the unit matrix. Finally, square matrices of the same size \( T, Q, \) and \( R \) may be defined that contain parameters of Eq. (2) as separate elements and are first order terms relatively to \( I \). Besides, diagonal elements of these matrices vanish [Note that \( R_{ij} \) coincides with the intrabond resonance parameter of the \( j \)th double bond]. An efficient procedure to construct matrices \( T, Q, \) and \( R \) for specific systems may be found in Ref. [57].

Let us now introduce a series of \( N \times N \)-dimensional matrices \( G_{(k)}, k = 1,2,3,.. \) (the so-called principal matrices of the perturbational NCMO (PNCMO) theory [47, 51, 54]) defined as follows

\[
G_{(1)} = -\frac{1}{2}R, \quad G_{(2)} = -\frac{1}{2}(TG_{(1)} - G_{(1)}Q) = \frac{1}{4}(TR - RQ), \\
G_{(3)} = -\frac{1}{2}(TG_{(2)} - G_{(2)}Q) - 2G_{(1)}G^*_{(1)}G_{(1)}. 
\]

where the superscript \( * \) here and below indicates the transposed counterpart of the matrix concerned. As is seen from Eq. (3), matrices \( G_{(k)}, k = 1,2,3,.. \) contain factors \( \gamma^k \) and are terms of the \( k \)th order with respect to \( \gamma \) as indicated by their subscripts \( (k) \). Moreover, \( G_{(k)}, k = 1,2,3,.. \) are skew-symmetric matrices in the case of polyenes [56], i.e.

\[
G^*_{(k)} = -G_{(k)}
\]

and serve as convenient terms when expressing their NCMOs as demonstrated below. Again, individual elements \( G_{(k)ij} \) of matrices \( G_{(k)} \) have a clear chemical meaning [57, 61]. Let us dwell now on this point.

The first order element \( G_{(1)ij} \) represents the direct (through-space) interaction between BOs \( \phi_{(+)} \) and \( \phi_{(+)} \). Moreover, the relevant absolute value coincides with \( \gamma/4 \) for any pair of first-neighbouring C=C bonds \( I \) and \( M \) and vanishes otherwise. Accordingly, a two-membered conjugated path [62, 63] corresponds to any significant element \( G_{(1)ij} \) and vice versa. [This path is abbreviated below by CP(2).] The second order element \( G_{(2)ij} \) in turn, is interpretable as the indirect (through-bond) interaction of BOs \( \phi_{(+)} \) and \( \phi_{(+)} \) by means of orbits of intervening C=C bonds playing the role of mediators. A non-zero value of this element is ensured if (i) \( I \) and \( M \) are second-neighbouring C=C bonds (i.e. possess a common first neighbour \( L \)) and (ii) the \( I \)-th, \( L \)-th and \( M \)-th C=C bonds are linearly-conjugated (but not cross-conjugated). In other words, coincidence of the fragment \( I-L-M \) with a three-membered conjugated path [abbreviated below by CP(3)] is required here. In addition, absolute values of significant elements \( G_{(2)ij} \) are uniform and equal to \( \gamma^2/8 \) due to similarity of all CP(3)s in polyenes. Analogously, the third order element \( G_{(3)ij} \) represents the indirect interaction of BOs \( \phi_{(+)} \) and \( \phi_{(+)} \) by means of two mediators. In contrast to elements \( G_{(2)ij} \), however, the side neighbours of either \( I \)-th or \( M \)-th C=C bonds (if any) also offer their BOs to mediate the interaction concerned [61] along with intervening bonds. Consequently, non-zero elements \( G_{(3)ij} \) generally arise not only for third-neighbouring C=C bonds but also for first-neighbouring ones.

Let us now turn to NCMOs of polyenes. Let the ket-vector (row-matrix) of double-occupied NCMOs be denoted by \[|\psi_{(+)}\rangle\]. The latter then takes the form of a linear combination of entire subsets of BOs \(|\phi_{(+)}\rangle\) and \(|\phi_{(+)}\rangle\) (see “Methods”), viz.

\[
|\psi_{(+)}\rangle = |\phi_{(+)}\rangle C_{11} + |\phi_{(+)}\rangle C_{21} 
\]

where \( C_{11} \) and \( C_{21} \) are \( N \times N \)-dimensional matrices playing the role of “coefficients”. The matrix \( C_{11} \) represents the so-called intersubset tails of double-occupied NCMOs, whilst \( C_{21} \) reflects the consequent renormalization of these orbitals and has been called the renormalization matrix [51]. Further, matrices \( C_{11} \) and \( C_{21} \) have been sought in the form of power series with respect to \( \gamma \), i.e. as sums of increments \( C_{11}^{(k)} \) and \( C_{21}^{(k)} \) of increasing orders \( k \). As a result, these increments proved to be ultimately representable via matrices \( G_{(k)} \) of Eq. (3). Thus, the first four contributions to the intersubset “coefficient” \( C_{21} \) take the following form.

\[
C_{21}^{(0)} = 0, \quad C_{21}^{(1)} = G_{(1)}, \quad C_{21}^{(2)} = G_{(2)}, \quad C_{21}^{(3)} = G_{(3)} + \frac{1}{2}G_{(1)}G^*_{(1)}G_{(1)} 
\]

Meanwhile, members of the expansion for the renormalization matrix \( C_{11} \) consist of sums of products of matrices \( G_{(k)} \) of lower orders, i.e. of \( G_{(k-1)}, G_{(k-2)} \), etc., namely.

\[
C_{11}^{(0)} = 1, \quad C_{11}^{(1)} = 0, \quad C_{11}^{(2)} = -\frac{1}{2}D^{(2)}_{(+)}, \quad C_{11}^{(3)} = -\frac{1}{2}D^{(3)}_{(+)} 
\]

where

\[
D^{(2)}_{(+)} = G_{(1)}G^*_{(1)}, \quad D^{(3)}_{(+)} = G_{(1)}G^*_{(2)} + G_{(2)}G^*_{(1)} 
\]
Delocalization coefficients of NCMOs and related quantities

Let us now turn to characteristics of NCMOs representing the extents of their delocalization [46, 47, 51]. The expression for an individual NCMO $\psi_{(+j)}$ follows straightforwardly from Eq. (5), viz.

$$\psi_{(+j)} = \sum_{(+)} \phi_{(+j)} C_{11,ij} + \sum_{(--)} \phi_{(--)m} C_{21,mi} \quad (9)$$

where sums over $(+)$ and over $(-m)$ here and below generally embrace all BBOs $\phi_{(+)}$, $j = 1, 2, \ldots N$ and all ABOs $\phi_{(--)m}$, $m = 1, 2, \ldots N$ of the given system, respectively, whereas $C_{11,ij}$ and $C_{21,mi}$ stand for elements of matrices $C_{11}$ and $C_{21}$. Let the partial (intersubset) delocalization coefficient of the NCMO $\psi_{(+)i}$. Over the ABO $\phi_{(--)m}$ be denoted by $d_{(+)(--)m}$ and defined as the square of the element $C_{21,mi}$ of Eq. (9). As with the latter, the coefficient $d_{(+)(--)m}$ also takes the form of power series with respect to $\gamma$, i.e.

$$d_{(+)(--)m} = |C_{21,mi}|^2 = \sum_{k=2}^{\infty} d_{(+)(--)m}^{k} \quad (10)$$

where $d_{(+)(--)m}^{k}$, $k = 2, 3, \ldots$ stands for the increment of the $k$th order (first order terms are absent due to the left relation of Eq. (6)). The first three members of Eq. (10) are expressible as follows [51]

$$d_{(+)(--)m}^{2} = (G_{(1)i}^{(1)})^2 > 0, \quad d_{(+)(--)m}^{3} = 2G_{(1)i}^{(1)}G_{(2)i}^{(2)}m,$$
$$d_{(+)(--)m}^{4} = 2G_{(1)i}^{(1)}G_{(3)i}^{(3)} + G_{(1)i}^{(1)}G_{(1)i}^{(1)}G_{(1)i}^{(1)}G_{(1)i}^{(1)} + (G_{(2)i}^{(2)})^2. \quad (11)$$

The notation $(G_{(1)i}^{(1)}G_{(1)i}^{(1)})^{(1)}$ here and below stands for the relevant element of the matrix product $G_{(1)i}^{(1)}G_{(1)i}^{(1)}$. The positive sign of the second order term $d_{(+)(--)m}^{(1)}$ also deserves emphasizing. Further, the skew-symmetric nature of matrices $G_{(k)}^{(k)}$ (see Eq. (4)) evidently is extendable to the matrix product $G_{(1)i}^{(1)}G_{(1)i}^{(1)}$. Consequently, all terms of Eqs. (10) and (11) referring to $m = i$ vanish including the intrabond delocalization coefficients $d_{(+)(--)m}^{(1)}$, their separate increments $d_{(+)(--)m}^{(1)}$ and individual components of the latter discussed below. Moreover, the equality $C_{21,ii}^{(1)} = 0$ follows from Eq. (6) for any $k$ for the same reason. Thus, double-occupied NCMOs $\psi_{(+)i}$ of Eq. (9) contain no increments of ABOs of their parent C=C bonds $(\phi_{(--)})$. This, in turn, implies the heads [55] of NCMOs of polyenes to be of zero polarities. Similarly, the skew-symmetric nature of matrices $G_{(k)}^{(k)}$ yields the equalities

$$d_{(+)(--)m}^{(k)} = d_{(--)(--)m}^{(k)} \quad (12)$$

for any $k$ whatever the actual mutual arrangement of the $j$th and $M$th C=C bonds. Hence, the extent of delocalization of the NCMO $\psi_{(+)}$ over the ABO of the $M$th bond $(\phi_{(--m)})$ coincides with that of the $M$th NCMO $(\psi_{(+m)})$ over the ABO $\phi_{(--m)}$. This result ensures zero charge redistribution among C=C bonds in polyenes [54] and is referred to below as the symmetry property of partial delocalization coefficients. As with vanishing intrabond terms, the symmetry property of Eq. (12) embraces also individual components of the right-hand sides of relations of Eq. (11).

Let us now define the total (intersubset) delocalization coefficient of the same NCMO $\psi_{(+)}$ over all ABOs as follows

$$D_{(+)} = \sum_{(--)} d_{(+)(--)m} \quad (13)$$

Substituting the right relation of Eq. (10) into Eq. (13) yields an expression for $D_{(+)}$ in the form of an analogous power series, i.e.

$$D_{(+)} = \sum_{k=2}^{\infty} D_{(+)}^{(k)} \quad (14)$$

where

$$D_{(+)}^{(k)} = \sum_{(-m)} d_{(+)(--)m}^{(k)} \quad (15)$$

Besides, members $D_{(+)}^{(k)}$ of Eq. (14) coincide with respective diagonal elements $D_{(+)}^{(k)}$ of the intersubset delocalization matrices $D_{(+)}^{(k)}$ of Eq. (8). Positive signs of second order members $(D_{(+)}^{(2)} > 0)$ also deserve mention here. Finally, the extent of (intersubset) delocalization of all double-occupied NCMOs $\psi_{(+)}, i = 1, 2, \ldots N$ may be characterized similarly. The analogues of Eqs. (13)–(15) are then as follows

$$D_{(+)} = \sum_{(+)i} D_{(+)}^{(i)}, D_{(+)} = \sum_{k=2}^{\infty} D_{(+)}^{(k)} D_{(+)}^{(k)} = \sum_{k=2}^{\infty} \sum_{(-m)} d_{(+)(--)m}^{(k)} \quad (16)$$

where $D_{(+)}$ has been called the complete delocalization coefficient of double-occupied NCMOs. It is also evident that members of the expansion concerned $(D_{(+)}^{(k)})$ coincide with traces of matrices $D_{(+)}^{(k)}$ of Eq. (8).

Total energies of polyenes (E) also are representable as sums of increments $(E_{(k)}^{(i)}, k)$ of an increasing order $(k)$ with respect to $\gamma$ [51, 54, 57, 58, 64] (see Methods). The zero order member of this series $(E_{(1)}^{(i)})$ coincides with the total energy of N isolated double bonds equal to 2 $N$ in our energy units, whereas the first order term $(E_{(1)}^{(1)})$ vanishes [51, 54, 64]. Meanwhile, members $E_{(k)}^{(i)}$ of higher orders $(k = 2, 3, \ldots)$ have been expressed via increments of the same order to the above-defined (intersubset) delocalization coefficients of NCMOs, viz.
where \( \Delta E \) here and below stands for the trace of a certain matrix. Thus, a positive increment to delocalization (either \( d^{(k)}_{(+i),(-jm)}>0 \) or \( p^{(k)}_{(+i)}>0 \)) contributes to stabilization of the system and vice versa. Besides, the intrasubset delocalization is not contained in Eqs. (17) and (18). This result is in line with the well-known zero energetic effect of interaction of double-occupied orbitals [65], as well as with the theorem [42] about existence of non-orthogonal LMOs without intrasubset tails. The less important nature of these tails is supported also by expressibility of renormalization matrices \( C^{(k)}_{11} \) via the intersubset delocalization matrices \( D^{(k)}_{(i)d} \), as shown in Eq. (8).

Additivity of the CE of polyene \( \Delta E \) with respect to contributions of individual pairs of \( \pi \)-electrons also is among outcomes of Eqs. (17) and (18). Indeed, sums over \( k \) and over \( (+i) \) may be interchanged in these relations and we then obtain that

\[
\Delta E = \sum_{k=2}^{\infty} \sum_{(i)} \Delta E_{(k)}
\]

where the contribution of the \( i \)th pair \( \Delta E_{(k)} \) also is expressible as a sum of increments \( \Delta E_{(k)} \) of an increasing order \( (k) \) as follows

\[
\Delta E_{(k)} = \frac{4}{k-1} \sum_{(i)} D^{(k)}_{(+i)} = 4D^{(2)}_{(+i)} + 2D^{(3)}_{(+i)} + \frac{4}{3} D^{(4)}_{(+i)} + \ldots
\]

(20)

It is seen that \( \Delta E_{(k)} \) is related to the extent of (intersubset) delocalization of the respective single NCMO \( \psi_{(+i)} \). Thus, the more delocalized the \( i \)th pair of \( \pi \)-electrons becomes, the more it contributes to the total CE and vice versa. Besides, derivation of Eq. (17) [51, 54, 64] was based on transpositions of matrix factors inside the trace of the eigenblock \( E_{\text{occ}} \) (see “Methods”). That is why the coincidence of separate increments \( \Delta E_{(k)} \) with respective diagonal elements of this eigenblock generally is not ensured. Again, Eqs. (18)–(20) offer us a direct relation between the CE of polyene and the shapes of its NCMOs with no reference to one-electron energies of the latter [Note that the usual way of the derivation of total energies consists in finding the energies of individual double-occupied NCMOs (LMOs) followed by summing them up in the NCMO method too [52], whereas interrelations between energies and shapes of NCMOs are known hitherto as anticipations only [52, 66]]. If we recall now that any double-occupied NCMO \( \psi_{(+i)} \) possesses a parent double (C=C) bond (viz. the \( i \)th one), the increment \( \Delta E_{(k)} \) of Eq. (20) is alternatively interpretable as the contribution of the \( i \)th C=C bond to the total CE \( \Delta E \). Hence, additive schemes for CEs of polyenes [17–20] acquire an additional support.

Finally, an analogous expansion deserves attention for the actual bond orders \( (p_{(i)}) \) of formally-double (C=C) bonds (see “Methods”). The point is that proportionality has been established [54] between corrections \( p_{(i)} \) to the initial bond order \( (p_{(0)}) = 1 \) inside the \( i \)th formally-double (C=C) bond, on the one hand, and members of the power series of Eq. (14) for the total delocalization coefficient of the respective NCMO \( \psi_{(+i)} \), on the other hand, viz.

\[
p_{(i)} = -2D^{(k)}_{(+i)}
\]

(21)

Thus, a positive (negative) term of the expansion of Eq. (14) is accompanied by a negative (positive) increment to the internal order of the \( i \)th C=C bond and thereby contributes to weakening (strengthening) of the latter as compared to an isolated C=C bond. In other words, more delocalized pairs of \( \pi \)-electrons refer to weaker C=C bonds and vice versa. Finally, the combination of relations of Eqs. (20) and (21) indicates that weaker C=C bonds provide higher contributions to the CE and vice versa.

Therefore, application of the NCMO method allows the acyclic conjugation to be described not only by the total CE \( \Delta E \) as usual but also by characteristics associated with individual C=C bonds, such as the partial contributions \( \Delta E_{(k)} \) to the total CE and the actual internal bond orders \( (p_{(i)}) \). Moreover, these characteristics are interrelated for any (\( i \)th) C=C bond and determined by the total delocalization coefficient \( (D_{(i)}^{(k)}) \) of the respective single NCMO \( \psi_{(+i)} \).

Local contributions to delocalization and their relation to curly arrows

Let us now turn to the analysis of the dependence of partial and total delocalization coefficients of NCMOs upon the
specific constitution of the carbon backbone of the polyene concerned. This dependence evidently is contained implicitly in the expressions for $d_{(i)}^{(k)}$ of Eq. (11). Since the increments $d_{(i)}^{(k)}$ are members of the power series of Eq. (10) starting with $k = 2$, the second order terms $d_{(i)}^{(2)}$ are likely to determine the most part of delocalization in polyenes. Thus, let us begin with an analysis of just these terms along with related characteristics $D_{(+)}^{(2)}$, $E_{(+)}$, and $p_{(+)}^{(2)}$.

From the first relation of Eq. (11), we obtain

$$d_{(i)}^{(2)} = d_{(i)}^{(+)} = \frac{y^2}{16} > 0$$  \hspace{1cm} (22)

where the additional superscripts + and $f$ here and below correspondingly indicate the positive sign of the increment concerned and its relevance to first-neighbouring C=C bonds. Local and thereby transferable nature of these increments also is evident, along with their direct relation to the diagrams of Refs. [43, 44], for perturbative delocalization corrections of the first order. Second order contributions to the total delocalization coefficient of the NCBO $\psi_{(+)}$ and to related characteristics then result from Eqs. (15), (20), and (21), viz.

$$D_{(+)}^{(2)} = \frac{y^2}{16} n_i > 0, \quad E_{(+)} = \frac{y^2}{4} n_i > 0, \quad p_{(+)}^{(2)} = -\frac{y^2}{8} n_i < 0$$  \hspace{1cm} (23)

where $n_i$ is the number of first neighbours of the $i$th C=C bond. Thus, the more first neighbours the $i$th C=C bond has, the more it contributes to the total CE, the lower the actual order inside this bond becomes and the more delocalized NCBO corresponds to it. Alternatively, the increments of Eq. (23) represent all C=C bonds attached to the $i$th C=C bond and thereby all CP(2)s embracing the latter. Consequently, these increments always take non-zero values because each C=C bond is connected with the remaining part of the molecule via at least a single C=C bond (i.e. $n_i \neq 0$). This implies an increased delocalization of any pair of $\pi$-electrons in polyenes as compared to that of ethene (in accordance with previous conclusions [52]), as well as weaker double bonds in the former case.

Further, a clear parallelism exists between the above-exhibited local increments to delocalization and the well-known curly arrow formalism (arrow pushing) [67–69] based an assumption about shifts (displacements) of electron pairs from broken bonds to newly-formed ones (just these shifts are depicted by curly arrows). To discuss this point, let us return to the expression for the NCBO $\psi_{(+)}$ of Eq. (9) and represent the latter in terms of three components associated with the own BBO ($\phi_{(+)}$), other BBOs ($\phi_{(+)}$; $i \neq j$) and ABOs ($\phi_{(-)}$), respectively, viz.

$$\psi_{(+)} = \phi_{(+)}(1 - \frac{1}{2} D_{(+)}^{(2)} - \frac{1}{2} D_{(+)}^{(3)} + ...)$$

$$+ \sum_{(+)} \phi_{(+)} \left( -\frac{1}{2} D_{(+)}^{(2)} - \frac{1}{2} D_{(+)}^{(3)} - ... \right)$$

$$+ \sum_{(-)} \phi_{(-)} (G_{(1)}^{(i)} + G_{(2)}^{(i)})$$  \hspace{1cm} (24)

where Eqs. (6), (7), and (8) also are invoked. Notations $D_{(+)}^{(k)}$ stand here for off-diagonal elements of the intersubset delocalization matrices $D_{(+)}^{(k)}$ of Eq. (8), whereas the restriction $m \neq i$ of the last term is due to Eq. (4).

Let us take first the simplest conjugated $\pi$-electron system of butadiene $(N = 2)$ as an example and consider its NCBO $\psi_{(+)}$ ascribed to the bond $C_1 = C_3$ (Fig. 1). As discussed already, second order elements $G_{(2)}^{(i)}$ and $G_{(2)}^{(i)}$ of Eq. (24) vanish for butadiene. The NCBO $\psi_{(+)}$ then takes the following approximate form

$$\psi_{(+)} = \phi_{(+)}(1 - \frac{1}{2} D_{(+)}^{(2)}) + \phi_{(-)} G_{(+)}^{(2)}$$  \hspace{1cm} (25)

where $D_{(+)}^{(2)}$ coincides with $d_{(+)}^{(2)}$ (see Eq. (15)) and $G_{(+)}^{(2)} > 0$ [57] [Terms to within $k = 2$ are included here]. Thus, the NCBO $\psi_{(+)}$ contains a bonding combination of AOs $\chi_3$ and $\chi_2$, referring to the formally-single bond $C_3 - C_2$ and an antibonding combination of AOs $\chi_1$ and $\chi_4$ embracing the remaining double bond (C$_3$ = C$_4$). At the same time, the increment of the own BBO ($\phi_{(+)}$) is lowered proportionally to square of the same element $G_{(+)}^{(2)}$. Thus, the three-center bonding combination of AOs $\chi_1$, $\chi_2$, and $\chi_4$ actually arises instead of the former BBO $\phi_{(+)}$ due to conjugation. This reshaping of the orbital concerned may be interpreted as a local shift (displacement) of the initially-localized pair of $\pi$-electrons of the formally-double bond C$_1 = C_3$ to the formally-single bond C$_3$ = C$_2$ and depicted by a usual curly arrow starting from the former and ending on the latter. The remaining pair of $\pi$-electrons (i.e. that of the bond C$_2$ = C$_4$) also is accordingly shifted to the same intervening single bond (C$_1$ = C$_2$). It is also evident that the partial delocalization coefficient $d_{(+),(-)}^{(2)}$ (and/or $d_{(+),(-)}^{(2)}$) serves as a qualitative measure of these displacements. Thus, the arrows of butadiene may be formally associated just with these coefficients. The symmetry property for the latter (see Eq. (12)) then ensures similarity between these arrows.

An analogous simple picture is preserved also when passing to more extended polyenes provided that the nearest-neighbour approximation is additionally invoked (i.e. increments of second-neighbouring C=C bonds (such as $D_{(+)}^{(2)}$ and $G_{(+)}^{(2)}$ are ignored). As a result, the relevant
approximate expression for an NCMO $\psi_{(+i)}$ resembles that of Eq. (25) except for the sum over ABOs ($\phi_{(-j)l}$) of all first neighbours (M) of the $i$th C=C bond arising instead of the only $\phi_{(-2)}$-containing term. If we ascribe a curly arrow to each partial delocalization coefficient $d_{(+i)}^{(2)}$ as previously and recall the additive form of the relevant total coefficient $D^{(2)}_{(+i)}$ (see Eq. (15)), the latter will be accordingly represented by the whole set of arrows starting from the $i$th C=C bond. Hence, the more arrows start from a certain $(i)$th formally-double bond, the weaker the latter becomes due to conjugation. Thus, we actually arrive at a simplified image of the acyclic conjugation in terms of uniform shifts of individual pairs of $\pi$-electrons.

Let us now turn to analysis of members of higher orders of our expansions that are expected to give rise to distinctions among C=C bonds characterized by the same nearest environment (i.e. by uniform $n_I$ values).

**Environment-dependent contributions to delocalization**

As opposed to the above-discussed contribution $d_{(+i)}^{(2)}$ the definition of its third order analogue $d_{(+i)}^{(3)}$ (see Eq. (11)) contains also the element $G_{(2)im}$ of the second order matrix $G_{(2)}$, shown in Eq. (3). As already mentioned, the element $G_{(2)im}$ takes a non-zero value for second-neighbouring C=C bonds. Since no pairs of C=C bonds are present in acyclic polyenes that are both first and second neighbours simultaneously, the increments $d_{(+i)}^{(3)}$ vanish. The same then refers also to third order contributions both to total delocalization coefficients of NCMOs and to CEs of polyenes [57].

Let us now turn to increments of the fourth order to partial delocalization coefficients, viz. to $d_{(+i)}^{(4)}$ defined by the last relation of Eq. (11). Let the orbitals $\phi_{(+j)}$ and $\phi_{(-j)}$ belong to first-neighbouring C=C bonds I and M. The first order element $G_{(1)im}$ then takes a non-zero value, whereas the second order one ($G_{(2)im}$) vanishes. Further, the third order element $G_{(3)im}$ may be easily eliminated from Eq. (11) by substituting the last relation of Eq. (3). The resulting expression for $d_{(+i)}^{(4)}$ then consists of two components, viz.

$$d_{(+i)}^{(4)} = d_{(+i)}^{(+4)} + d_{(+i)}^{(-4)}$$

(26)

where

$$d_{(+i)}^{(+4)} = -G_{(1)im}(TG_{(2)} - G_{(2)Q})_{im}$$

(27)

$$d_{(+i)}^{(-4)} = -3G_{(1)im}(G_{(1)}G_{(1)}'G_{(1)})_{im}$$

(28)

and the superscripts + and – specify the signs of these components established below. Given that I and M are second neighbours, a non-zero value of the element $G_{(2)im}$ is allowed but not of $G_{(1)im}$. We then obtain

$$d_{(+i)}^{(+4)} = (G_{(2)im})^2 > 0,$$

(29)

where the superscript $s$ indicates the relevance of increments concerned to second-neighbouring C=C bonds. Finally, $d_{(+i)}^{(2)}$ vanish for more distant C=C bonds, as both $G_{(1)im}$ and $G_{(2)im}$ take zero values in this case. Let us now consider the increments of Eqs. (26)–(29) separately.

Let us start with the component $d_{(+i)}^{(+4)}$ representable as follows

$$d_{(+i)}^{(+4)} = -G_{(1)im} \sum_{(+j)l} T_{ij} G_{(2)jm} + G_{(1)im} \sum_{(-j)l} G_{(2)jl} Q_{lm}$$

(30)

where sums over $(+j)$ and over $(-j)$ correspondingly embrace BBOs and ABOs except for orbitals of the $i$th and $M$th C=C bonds (viz. $\phi_{(+j)}$, $\phi_{(+jm)}$ and $\phi_{(-j)}$, $\phi_{(-jm)}$, respectively). The exception is due to the zero diagonal (intrabond) elements of matrices $T$, $Q$, and $G_{(2)}$. Moreover, the sum over $(+j)$ actually embraces BBOs of only first neighbours of the $i$th C=C bond (except for the $M$th one) because of zero values of off-diagonal elements of the matrix $T$ for more distant C=C bonds. Similarly, the second sum of Eq. (30) concerns ABOs of first neighbours (L) of the $M$th bond, where $L \neq I$. Let the $J$th and $L$th bonds be called the side neighbours of the $i$th and $M$th one, respectively. Again, the elements $G_{(2)jm}$ and $G_{(2)jl}$ of Eq. (30) do not vanish if BOs $\phi_{(+j)}$ and $\phi_{(-j)}$, as well as $\phi_{(+jl)}$ and $\phi_{(-jl)}$ belong to second-neighbouring C=C bonds that are terminals of at least a single CP(3) in addition. This implies that the above-specified side neighbours contribute to the component $d_{(+i)}^{(+4)}$ if fragments $J$–$I$–$M$ and/or $I$–$M$–$L$ coincide with CP(3). For example, the bonds both $C_1 = C_5$ and $C_4 = C_8$ of the linear octatetraene I($N=4$) contribute to $d_{(+i)}^{(+4)}$, due to their participation in CP(3)s $C_1 = C_5$–$C_2$ = $C_6$–$C_3$ = $C_7$ and $C_2 = C_6$–$C_3$ = $C_7$–$C_4$ = $C_8$, respectively (Fig. 1). Additivity of the overall component $d_{(+i)}^{(+4)}$ with respect to increments of several CP(3)s (if any) also easily follows from Eq. (30). Finally, similarity of CP(3)s in polyenes ensures uniform contributions of individual representatives of these paths coinciding with $r^4/64$. This implies the positive sign of the component concerned as indicated by the superscript +. After substituting into the first relation of Eq. (17), this component certainly yields a positive energetic increment and thereby contributes to stabilization of the given system.

Let us now consider other components of Eq. (26), namely $d_{(+i)}^{(-4)}$ defined by Eq. (28). Let $n_I(\neq M)$ and $n_M(\neq I)$ stand for numbers of side neighbours of the $i$th and $M$th C=C bond, respectively, where $n_I(\neq M) = n_I - 1$ and
and is a negative quantity contributing to destabilization of the system. Moreover, the component \( d_{(+),(-)m}^{(4)} \) of Eq. (31) takes a non-zero value for any pair of first-neighbouring C=C bonds \( I \) and \( M \) in contrast to the former one \( d_{(+),(+),(-)m}^{(4)} \), where participation of the \( Ith \) and \( Mth \) C=C bonds in a certain CP(3) was additionally required. Hence, the component \( d_{(+),(-)m}^{(4)} \) represents a certain universal repulsion of \( \pi \) - electron pairs of first-neighbouring C=C bonds in analogy with the ideas underlying the VSEPR model [70, 71]. It is also seen that the component \( d_{(+),(-)m}^{(4)} \) grows with increasing numbers of side neighbours of the bonds concerned.

As a result, the overall fourth order increment \( d_{(+),(+),(-)m}^{(4)} \) to the partial delocalization coefficient of the NCMO \( \psi_{(+)} \) of the \( Ith \) bond over the ABO of the first-neighbouring (\( Mth \) bond (\( \psi_{(-)m} \)) generally consists of two contributions of opposite signs and of comparable absolute values (see Eq. (26)). Moreover, the above-established dependence of components both \( d_{(+),(+),(-)m}^{(4)} \) and \( d_{(+),(-)m}^{(4)} \) upon constitutions of first neighbourhoods of C=C bonds concerned (\( I \) and \( M \)) is extendable also to the total increment \( d_{(+),(-)m}^{(4)} \) and thereby ensures a semi-local nature of the latter.

By contrast, pairs of second-neighbouring C=C bonds (\( I \) and \( M \)) are characterized by the only a priori positive increment to delocalization \( d_{(+),(+),(-)m}^{(4)} \) defined by Eq. (29). The latter takes a non-zero value \( y^4/64 \) and contributes to an additional stabilization of the system concerned, if the \( Ith \) and \( Mth \) C=C bonds coincide with terminals of a CP(3), e.g. of \( I-L-M \). For example, this condition is met for bonds \( C_1 = C_5 \) and \( C_5 = C_7 \) of the linear octatetraene \( R(N=4) \) (Fig. 1). Moreover, the underlying indirect interaction \( G_{(+),(+),(-)m}^{(2)} \) is mediated by BOs of the intervening (\( Lth \)) C=C bond only (viz. \( C_7 = C_6 \) of our example), whilst the relevant side neighbours (e.g. \( C_4 = C_8 \), respectively) do not participate in the formation of \( d_{(+),(+),(-)m}^{(4)} \).

As a result, this contribution is related to the diagrams of perturbative delocalization corrections [43, 44] of the second order.

The fourth order increment \( D^{(4)}_{(+)} \) to the total delocalization coefficient \( D_{(+)} \) of the NCMO \( \psi_{(+)} \), in turn, follows from Eq. (15), where the sum over \( (-)m \) embraces ABOs of only first and second neighbours of the \( Ith \) C=C bond (but not the more distant ones). It is also evident that contributions \( d_{(+),(+),(-)m}^{(4)} \), \( d_{(+),(-)m}^{(4)} \) and \( d_{(+),(+),(-)m}^{(4)} \) can be summed up separately and independently. As a result, the overall correction \( D^{(4)}_{(+)} \) also is expressible as a sum of two components of opposite signs defined as follows

\[
D^{(4)}_{(+)} = \sum_{(+)m} d^{(+)}_{(+)m,(-)m} + \sum_{(+)m} d^{(+)}_{(+)m,(+)m} \quad D^{(4)}_{(+)} = \sum_{(+)m} d^{(+)}_{(+)m,(-)m}
\]

Obviously, the positive component \( D^{(4)}_{(+)} \) is related to the participation of the \( Ith \) C=C bond in CP(3)s. Moreover, the contribution of a certain second neighbour (say, of the \( Lth \) one) to \( D^{(4)}_{(+)} \) depends only on whether the first neighbouring of the \( Ith \) bond ensures at least a single CP(3) between the \( Ith \) and \( Lth \) bonds. Hence, the component \( D^{(4)}_{(+)} \) actually is determined by constitutions of only first and second neighbourhoods of the parent (\( Ith \) bond). Meanwhile, the negative component \( D^{(4)}_{(+)} \) represents the overall repulsion undergone by the \( Ith \) pair of \( \pi \)-electrons due to the presence of its first neighbours. After the employment of Eq. (31) we obtain that

\[
D^{(4)}_{(+)} = -\frac{\gamma^4}{256} \left[ n^2_I + \sum_M n^2_{M,(\neq I)} \right]
\]
representing particular aspects of delocalization of \(\pi\) electrons.

**Analysis of specific examples**

Let us start with the simplest polyenes of the regular constitution, viz. with linear (I) and cross-conjugated (II) chains (Fig. 1), where \(N=2,3,\ldots,6\). Second and fourth order increments to partial delocalization coefficients of the relevant NCMOs are shown in Table 1 [Note that I(\(N=2\)) coincides with II(\(N=2\)). It is seen that uniform positive second order increments \((r^2/16)\) correspond to all pairs of first-neighbouring C=C bonds (denoted by \(f\)) of both chains in accordance with Eq. (22). Moreover, the coincidence of increments \(d_{(+i,-m)}^{(2)}\) for isomers I(\(N\)) and II(\(N\)) follows from the comparison of the sixths columns of Table 1 referring to the same \(N\) value. This result is due to similar first neighbourhoods (adjacencies) of C=C bonds in both chains.

Analogous conclusions may be also drawn in respect of negative fourth order corrections \(d_{(+i,-m)}^{(-4)}\). Indeed, the latter also refers to first-neighbouring (\(f\)) pairs of C=C bonds only and are transferable when passing from a linear polyene to its cross-conjugated isomer for the same reason (i.e. similar adjacencies of C=C bonds). In contrast to former corrections \((d_{(+i,-m)}^{(2)}\), however, the present ones \((d_{(+i,-m)}^{(-4)}\) are no longer uniform for distinct pairs of first-neighbouring C=C bonds. Moreover, the relevant absolute values \(d_{(+i,-m)}^{(-4)}\) grow with increasing numbers of other first neighbours of the C=C bonds concerned in accordance with Eq. (31). For example, \(d_{(+1,1)}^{(-4)}\) grows when passing from butadiene (\(N=2\)) to more extended polyenes (\(N>2\)). Similarly, \(d_{(+6,1)}^{(-4)}\) exceeds \(d_{(+1,1)}^{(-4)}\) for \(N=4,5,6\), etc.

By contrast, the positive fourth order corrections \((d_{(+i,-m)}^{(4)}\) and \(d_{(+i,(-m)}^{(+4)}\) of Table 1 refer to both first- (\(f\)) and second-neighbouring (\(s\)) pairs of C=C bonds. As discussed already, these corrections depend upon the presence of CP(3)s in the polyene concerned and thereby upon the type of conjugation. That is why the positive corrections are different for isomers (I(\(N\)) and II(\(N\)) and depend on the number of C=C bonds (\(N\)) in addition. The same then consequently refers also to total fourth order corrections \((d_{(+i,-m)}^{(4)}\) of the last column of Table 1. In this respect, individual polyenes of Fig. 1 deserve a comparative discussion.

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**Table 1** Separate increments to partial delocalization coefficients of NCMOs for simplest linear (I) and cross-conjugated (II) polyene chains

| Nr. comp | \(N\) | \((+i)\) | \((-m)\) | \(f\) | \(s\) | \(d_{(+i,(-m)}^{(2)}\) | \(d_{(+i,-m)}^{(4)}\) | \(d_{(+i,(-m)}^{(+4)}\) | \(d_{(+i,-m)}^{(-4)}\) | \(d_{(+i,(-m)}^{(+4)}\) |
|----------|------|---------|---------|-----|-----|-----------------|-----------------|-----------------|-----------------|-----------------|
| I        | 2    | 1       | 2       | \(f\) | \(s\) | \(\gamma^2/16\) | \(-\)             | \(-3\gamma^4/256\)| \(-3\gamma^4/256\)| \(-\)             |
| I        | 3    | 1       | 2       | \(f\) | \(s\) | \(\gamma^2/16\) | \(4\gamma^4/256\) | \(-6\gamma^4/256\)| \(-2\gamma^4/256\)| \(4\gamma^4/256\) |
| I        | 4    | 1       | 2       | \(f\) | \(s\) | \(\gamma^2/16\) | \(4\gamma^4/256\) | \(-6\gamma^4/256\)| \(-2\gamma^4/256\)| \(4\gamma^4/256\) |
| I        | 5    | 1       | 2       | \(f\) | \(s\) | \(\gamma^2/16\) | \(8\gamma^4/256\) | \(-9\gamma^4/256\)| \(-\gamma^4/256\) | \(4\gamma^4/256\) |
| I        | 6    | 1       | 2       | \(f\) | \(s\) | \(\gamma^2/16\) | \(4\gamma^4/256\) | \(-6\gamma^4/256\)| \(-2\gamma^4/256\)| \(4\gamma^4/256\) |
| II       | 3    | 1       | 2       | \(f\) | \(s\) | \(\gamma^2/16\) | \(-\)             | \(-6\gamma^4/256\)| \(-6\gamma^4/256\)| \(-\)             |
| II       | 4    | 1       | 2       | \(f\) | \(s\) | \(\gamma^2/16\) | \(-\)             | \(-9\gamma^4/256\)| \(-9\gamma^4/256\)| \(-\)             |
| II       | 5    | 1       | 2       | \(f\) | \(s\) | \(\gamma^2/16\) | \(-\)             | \(-9\gamma^4/256\)| \(-9\gamma^4/256\)| \(-\)             |
| II       | 6    | 1       | 2       | \(f\) | \(s\) | \(\gamma^2/16\) | \(-\)             | \(-6\gamma^4/256\)| \(-6\gamma^4/256\)| \(-\)             |
Due to the absence of CP(3)s in butadiene \((N=2)\), the negative term \(d_4^{(4)}\) is the only contribution to the relevant correction \(d_2^{(+1)}\), so that the latter also is a negative quantity. When passing to the linear hexatriene \((N=3)\), a single CP(3) arises already which embraces all the three C=C bonds of this chain. Consequently, additional positive contributions \(d_4^{(+2)}\) and \(d_4^{(+1)}\) emerge along with the former negative increments. As a result, the absolute value of the total (negative) fourth order correction \(d_2^{(+1)}\) and \(d_2^{(+2)}\) (and/or \(d_2^{(+2)}\) lower for hexatriene as compared to that of butadiene in spite of the above-discussed growing contribution \(d_2^{(+3)}\) with elongation of the chain. This implies higher ultimate values of partial delocalization coefficients \(d_2^{(+1)}\) and \(d_2^{(+2)}\) in hexatriene vs. the analogous coefficient \(d_2^{(+1)}\) of butadiene [Note that a partial coefficient \(d_2^{(+1)}\) follows after summing up a large positive second order increment \(d_2^{(+2)}\) and a relatively small fourth order correction \(d_2^{(+4)}\)]. In addition, the pair of terminal C=C bonds \((C_1=C_4\) and \(C_3=C_6)\) of hexatriene is characterized by a positive partial delocalization coefficient \(d_2^{(+2)}\). In summary, better conditions for delocalization of NCMOs (and thereby of \(\pi\)-electron pairs) are peculiar to the linear hexatriene as compared to butadiene and this outcome causes little surprise.

Similar trends are preserved also when passing to the linear octatetraene \((N=4)\). Presence of two CP(3)s now gives rise to a two-fold positive increment \(d_2^{(+1)}\) \(d_2^{(+2)}\). Referring to the internal pair of double bonds \((C_2=C_6\) and \(C_3=C_7)\) participating in both of these paths. As a result, the absolute value of the relevant fourth order contribution \(d_2^{(+1)}\) \(d_2^{(+4)}\) is even lower. Meanwhile, the corrections \(d_2^{(+2)}\) \(d_2^{(+3)}\) of octatetraene coincide with those of the linear hexatriene. This result illustrates the primary role of the nearest neighbourhood of the C=C bonds concerned in the formation of partial delocalization coefficients of NCMOs. It is then no surprise that the correction \(d_2^{(+1)}\) (referring to a terminal pair of C=C bonds) exhibits no subsequent alterations also when passing to longer linear polyenes \((N=5,6)\) in spite of growing numbers of CP(3)s. Therefore, the extinction of the enhancement of delocalization conditions is actually observed with further elongation of the linear polyene chain.

By contrast, no CP(3)s are present in the cross-conjugated polyenes (II), whatever the number of C=C bonds \(N\). This implies the negative term \(d_2^{(+1)}\) to make the only contributions to total fourth order corrections \(d_2^{(+1)}\) for all chains II. As a result, the relevant corrections \(d_2^{(+1)}\) always are of negative signs and of considerably higher absolute values as compared to those of the respective linear isomers. It is evident that the ultimate partial delocalization coefficients of NCMOs \(d_2^{(+1)}\) then take lower values.

This distinction especially refers to the internal areas of the chains under comparison. Finally, delocalization is expected to be of a more local nature in cross-conjugated chains due to absence of long-range increments \(d_2^{(+1)}\).

Let us now turn to a comparison of total delocalization coefficients \(D^{(+1)}\) of separate NCMOs \(\psi^{(+1)}\). Second and fourth order increments to these coefficients are shown in Table 2. As an example of related local characteristics, contributions of individual \(\pi\)-electron pairs and/or C=C bonds \((\Delta E_I)\) to the relevant CEs \((\Delta E_I)\) are displayed along with the two principal members of the underlying power series \((E_{2/2})\) and \((E_{4/4})\). It deserves recalling here that higher contributions \(\Delta E_I\) correspond to weaker C=C bonds and vice versa.

As discussed already, the second order increments \((E_{2/2})\) and \((E_{4/4})\) are determined by numbers \((N)\) of first neighbours of respective \((lth)\) double bonds. Uniform values of these numbers inside chains under comparison then ensure coinciding increments \((E_{2/2})\) \((E_{4/4})\) for any couple of isomers \((N)\) \((N)\). Again, the increments concerned take doubly lower values for terminal C=C bonds \((N=1)\) as compared to the internal ones \((N=2)\) for both linear (I) and cross-conjugated (II) polyenes. Due to the primary importance of second order members in general in the formation of any characteristic, both total delocalization coefficients of terminal NCMOs \((D^{(+1)}\) \(D^{(+1)}\) and \(D^{(+3)}\) \(D^{(+3)}\) and the relevant contributions to the CE \((\Delta E_I)\) \((\Delta E_I)\) also are accordingly lower. Hence, considerably suppressed delocalization of terminal \(\pi\)-electron pairs and thereby their reduced participation in conjugation is the principal common feature of both chains. Meanwhile, the relevant fourth order corrections \((E_{2/2})\) \((E_{4/4})\) are likely to determine possible distinctions between individual C=C bonds and/or separate \(\pi\)-electron pairs of the same nearest environment and thereby between the chains I and II. Thus, let us now dwell just on these corrections.

Let us start with linear polyenes I. It is seen that the corrections \((E_{2/2})\) \((E_{4/4})\) associated with the chain C=C bond grow when passing from butadiene \((N=2)\) to higher polyenes \((N=3,4\ldots)\). The same refers also to the remaining corrections ascribed to internal C=C bonds. Thus, the above-concluded enhancement of delocalization conditions with elongation of the linear polyene is additionally corroborated. Moreover, this trend is especially striking in the middle area of the chain concerned. For example, the correction \((E_{2/2})\) (referring to the third C=C bond) exceeds considerably that of the second bond \((E_{2/2})\) in polyenes \((N=5)\) and \((N=6)\). As a result, it is the central part of the chain that ensures most of the CE of a linear polyene. Accordingly, the bond length alternation (BLA) also was found to be diminished just in the middle areas of longer polyene chains [1, 2, 4, 13].

The cross-conjugated polyenes (II) offer us an entirely opposite case in the same respects. Indeed, the corrections
Table 2 Second and fourth order increments to total delocalization coefficients of NCMOs \(D_{+i}^{2(2)}\) and \(D_{+i}^{4(4)}\) along with the related energetic characteristics \(E_{+i}^{2(2)}\) and \(E_{+i}^{4(4)}\), as well as contributions of individual C=C bonds (\(\Delta E_I\)) to total CEs of polyenes I–VIII (numerical values refer to \(r = 0.5\), where \(r\) coincides with the ratio of the resonance integral of single bonds to that of double bonds. Energies are expressed in the units of the resonance integral of double bonds)

\[
\begin{array}{cccccccc}
\text{Nr. comp} & N & (+i, I) & D_{+i}^{2(2)} & D_{+i}^{4(4)} & E_{+i}^{2(2)} & E_{+i}^{4(4)} & \Delta E_I \\
\hline
\text{III} & 5 & 1 & 7\gamma/16 & 2\gamma/256 & 0.1250 & 0.0007 & 0.0653 \\
& & 2 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0002 & 0.1207 \\
& & 3 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0000 & 0.1253 \\
& & 4 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0003 & 0.1209 \\
& & 5 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0003 & 0.1253 \\
\text{IV} & 5 & 1 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0020 & 0.0655 \\
& & 2 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0000 & 0.1253 \\
& & 3 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0000 & 0.1253 \\
& & 4 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0003 & 0.1253 \\
& & 5 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0003 & 0.1253 \\
\text{V} & 5 & 1 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0000 & 0.1253 \\
& & 2 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0000 & 0.1253 \\
& & 3 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0000 & 0.1253 \\
& & 4 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0000 & 0.1253 \\
& & 5 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0000 & 0.1253 \\
\text{VI} & 5 & 1 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0000 & 0.1253 \\
& & 2 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0000 & 0.1253 \\
& & 3 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0000 & 0.1253 \\
& & 4 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0000 & 0.1253 \\
& & 5 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0000 & 0.1253 \\
\text{VII} & 5 & 1 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0000 & 0.1253 \\
& & 2 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0000 & 0.1253 \\
& & 3 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0000 & 0.1253 \\
\text{VIII} & 5 & 1 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0000 & 0.1253 \\
& & 2 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0000 & 0.1253 \\
& & 3 & \gamma/2/256 & \gamma/256 & 0.1250 & 0.0000 & 0.1253 \\
\end{array}
\]

\(D_{+i}^{4(4)}\) and \(E_{+i}^{4(4)}\) take lower values when passing from butadiene to more extended chains II. The same refers also to corrections ascribed to internal C=C bonds, viz. these exhibit an evident decrease with the increasing number of C=C corrections ascribed to internal C=C bonds, viz. these exhibit an evident decrease with the increasing number of C=C bonds (\(N\)), as well as when moving towards the middle of the chain. Thus, suppression of delocalization of \(\pi\) electrons with elongation of the cross-conjugated polyene follows and this effect also is more conspicuous in the central areas. The relevant bond length alternation also was shown to become stronger [30].

On the whole, delocalization coefficients \(D_{+i}^{+4(4)}\) of all NCMOs \(w_{+i}^{+4(4)}\) take lower values for cross-conjugated polyenes as compared to their linear isomers. Obviously, the same refers also to contributions of separate \(\pi\)-electron pairs (\(\Delta E_I\)) to the relevant CEs (\(\Delta E\)). This outcome is in line with predictions of other approaches concerning
delocalization [2, 23, 29, 30], as well as with the well-known lower stabilities (CEs) of cross-conjugated chains vs. the linear ones [1, 2, 8–10, 20–23, 57].

The above-discussed essentially the local origin of both second and fourth order contributions to total delocalization coefficients of NCMOs allows us to expect similar rules to govern the delocalization patterns also in polyenes of the less regular constitution including those possessing branched carbon backbones. To discuss this point, let us include the isomers III–VIII (Fig. 2) of decapentaene (N=5) into our set of examples.

It evident that branching sites are characterized by increments $D^{(2)}_{(+i)}$ and $E^{(2)}_{(i)}$ of relatively higher values because of increased numbers of first neighbours of the relevant C=C bonds ($n_I$). In our case, this refers to the third and second C=C bond of isomers III and VI, respectively, where $n_I = 3$. At the same time, both second order energies ($E^{(2)}_{(i)}$) and the related contributions to the complete delocalization coefficients of double-occupied NCMOs ($D^{(2)}_{(+i)}$) have been established to be uniform for isomers of polyenes [57, 61] including our decapentaenes I($N=5$), II($N=5$) and III–VIII. This seeming contradiction is easily resolved by observing that isomers III and VI contain three more localized (terminal) $\pi$-electron pairs in contrast to only two pairs of this type present in the remaining decapentaenes. The consequent reduction of the overall delocalization then compensates for its former increase due to branching so that the above-mentioned transferability of total corrections $D^{(2)}_{(+i)}$ and $E^{(2)}_{(i)}$ arises [Indeed, addition of five corrections $D^{(2)}_{(+i)}(i=1,2...5)$ yields $\gamma^2/2$ and the equality $E^{(2)}_{(i)} = 2\gamma^2$ then results from Eq. (17) for all decapentaenes]. Thus, quantitatively the same overall second order delocalization is distributed differently among separate C=C bonds within individual isomers. In particular, this distribution is less homogeneous in the branched isomers III and VI as compared to the remaining ones.

In respect of the relevant fourth order terms, the overall state of things also is rather similar: On the one hand, relative values of individual corrections $D^{(4)}_{(+i)}$ and $E^{(4)}_{(i)}$ depend on constitutions of nearest neighbourhoods of double bonds concerned in accordance with the above-revealed trends. Indeed, C=C bonds belonging to cross-conjugated fragments of isomers III–VIII generally are characterized by negative corrections $D^{(4)}_{(+i)}$ and $E^{(4)}_{(i)}$, e.g. the bonds under numbers 3, 4, 5 and 1, 2, 3 of isomers III and IV, respectively. Meanwhile, the same corrections prove to be increased (or even take positive values) for C=C bonds of linear fragments, especially for those participating in two CP(3)s. For example, higher positive values of corrections $D^{(4)}_{(+i)}$ and $E^{(4)}_{(i)}$ of isomers III and VI, respectively, may be traced back to the participation of the C=C bonds concerned in two CP(3)s. On the other hand, the relevant total corrections $D^{(4)}_{(i)}$ and $E^{(4)}_{(i)}$ take coinciding values [61] for couples of isomers III and VI, IV and VII, as well as V and VIII so that the latter are isoenergetic systems to within $k=4$ inclusive, e.g. $D^{(4)}_{(i)}$ correspondingly equal to $0$, $-12\gamma^4/256$ and $-36\gamma^4/256$. As is seen, these uniform corrections also are distributed differently among separate C=C bonds inside isoenergetic couples.

If we recall now the above-mentioned coincidence of second order energies ($E^{(2)}_{(i)}$) for isomers and confine

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![Fig. 2](https://example.com Fig. 2 Selected isomers of decapentaene (III–VIII). Numberings of C=C bonds also are shown)
ourselves to terms up to \( k = 4 \), the overall stabilities (CEs) of decapentaenes meet the following order [61]

\[ I(N = 5) > \text{III, VI > IV, VII > V, VIII > II(N = 5)} \]

that is in line with results of other approaches [12, 72]. The relevant contributions of separate C=C bonds and/or \( \pi \) -electron pairs (\( \Delta E_i \)) to CEs are displayed in the last column of Table 2. It is seen that the reduced stability of branched isomers III and VI vs. the linear one \( I(N = 5) \) goes together with increased contributions of the third and second C=C bond, respectively. Meanwhile, the remaining part of the above-exhibited order of stability of isomers is accompanied by a gradual decrease of contributions \( \Delta E_i \) of all C=C bonds.

**Conclusion**

Application of the non-canonical method of MOs offers us an alternative viewpoint of conjugation in acyclic polyenes. Accordingly, the effect of the conjugation of \( N \) double (C=C) bonds manifests itself in a weak and essentially local delocalization of respective \( N \) initially-localized pairs of \( \pi \)-electrons. The relevant conjugation energy (CE) then coincides with the total delocalization energy of all these pairs. Analogously, the relative stability of a certain polyene depends upon the extent of the underlying delocalization.

The above-formulated interrelation between the extents of delocalization and stabilization is valid also for each pair of \( \pi \)-electrons separately. Indeed, the CE of any acyclic polyene is expressible as a sum of \( N \) contributions, each of them representing an individual pair of \( \pi \)-electrons and directly related to the total delocalization coefficient of the respective single non-canonical (localized) MO. This implies that the more delocalized the \( I \)th pair of \( \pi \)-electrons becomes, the more it contributes to the total CE and vice versa. Again, the total delocalization coefficient of the \( I \)th non-canonical MO determines the extent of reduction of the internal order of the respective parent (\( I \)th) formally-double (C=C) bond when building up the polyene concerned. Consequently, more delocalized pairs of \( \pi \)-electrons correspond to weaker double bonds and vice versa. In summary, weaker (stronger) formally-double bonds make higher (lower) contributions to the total CEs of polyenes.

The extents of delocalization of individual pairs of \( \pi \)-electrons, in turn, are determined by two structural factors of local nature: First, delocalization of a certain pair is induced by the participation of the respective parent C=C bond in both two- and three-membered conjugated paths. Evidently, constitutions only of the first and of the second neighbourhoods of the parent bond are of importance here. Second, each pair of \( \pi \)-electrons undergoes a definite repulsion from all pairs of first-neighbouring C=C bonds that depends also on the relevant number of second-neighbouring bonds and inhibits the delocalization concerned. Thus, a local relation may be concluded between the constitution of the nearest environment of the \( I \)th C=C bond and delocalization pattern of the \( I \)th pair of \( \pi \)-electrons.

Comparison of linear (I) and cross-conjugated (II) polyene chains shows that the reduced relative stabilities (CEs) of the latter are accompanied by decreased extents of delocalization of all pairs of \( \pi \)-electrons contained. Moreover, the distinction concerned is especially striking for pairs of \( \pi \)-electrons ascribed to central areas and becomes more and more pronounced with elongation of the chain. The underlying reason lies in absence of three-membered conjugated paths in the cross-conjugated chains (II) in contrast to the linear ones (I). Meanwhile, lower CEs of branched polyenes as compared to respective linear isomers go together with increased delocalization of pairs of \( \pi \)-electrons pertinent to C=C bonds at the branching sites having three or four first neighbours. This exclusive delocalization is due to the participation of the relevant parent C=C bonds in a higher number of two-membered conjugated paths.

Therefore, the local perspective on acyclic conjugation succeeds in describing the classical manifestations of the effect in polyenes, such as increased thermodynamic stabilities and reduced bond orders inside the formally-double bonds. Moreover, it is this perspective that provides us with the above-summarized simple interrelations between different aspects of the effect.

**Methods**

Let us start with the direct method of derivation of NCMOs. The block-diagonalization problem determining the latter takes the following form [42–51, 54]

\[
C^{-1}HC = \begin{pmatrix}
E_{\text{occ}} & 0 \\
0 & E_{\text{vac}}
\end{pmatrix}, \quad C^* C = I
\]  

(34)

where \( H, E_{\text{occ}}, \) and \( E_{\text{vac}} \) stand for the initial Hamiltonian matrix and its eigenblocks, respectively. The transformation matrix \( C \) coincides with the NCMO representation matrix under our interest and contains the relevant coefficients in its columns. The unitarity requirement for this matrix (i.e. the right relation of Eq. (34)) serves to reduce the ambiguity of NCMOs [47] and ensures their orthogonality. Both the matrix \( C \) and the eigenblocks \( E_{\text{occ}} \) and \( E_{\text{vac}} \) are quantities being sought.

The BOs \( \{ \phi \} \) of Eq. (1) have been chosen as the initial basis functions in our case. The total Hamiltonian matrix \( (H) \) of any polyene is then expressible as a sum of the zero order member \((H_{(0)})\) and of the first order one \((H_{(1)})\)
correspondingly containing one-electron energies of BOs and the interbond resonance parameters of Eq. (2) and thereby referring to our reference system and its perturbation. Using the above-introduced matrices $I$, $T$, $R$ and $Q$, we then obtain

$$H = H_{(0)} + H_{(1)} = \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix} + \begin{bmatrix} T & R \\ R^* & Q \end{bmatrix}$$ \hspace{1cm} (35)$$

Again, both the total matrix $H$ and its components ($H_{(0)}$ and $H_{(1)}$) consist of four $N \times N$-dimensional submatrices (blocks): Diagonal positions of the matrix $H$ are occupied by submatrices embracing terms of both zero ($I$) and first order ($T$ and $Q$) with respect to $\gamma$. These blocks correspond to subsets of BBOs and of ABOs, respectively. Meanwhile, the off-diagonal submatrices $R$ and $R^*$ are first order terms vs. the former.

As with BOs $\{\phi\}$, the NCMOs $\{\psi\}$ also are divisible into two $N$-dimensional subsets of double-occupied and vacant orbitals. The total matrix $C$ can be then initially represented via four $N \times N$-dimensional square blocks $C_{11}$, $C_{12}$, $C_{21}$ and $C_{22}$ so that the latter may be sought as “indivisible” quantities. Moreover, the constitution of our initial Hamiltonian matrix of Eq. (35) in terms of zero ($I$) and first order blocks ($T$, $Q$, and $R$) allowed the submatrices of the matrix $C$ to be sought in the form of power series with respect to $\gamma$. The convergence of this series was found to be rather rapid [56], especially for short polyene chains. For example, the series converges even for $\gamma = 1$ in the cases of butadiene ($N = 2$) and hexatriene ($N = 3$).

The $N \times N$-dimensional eigenblocks $E_{\text{occ}}$ and $E_{\text{vac}}$ also are expressible in the form of an analogous power series [51, 54, 73], i.e. as sums over $k$ of increments $E_{\text{occ}}^{(k)}$ and $E_{\text{vac}}^{(k)}$, the latter consisting of products of our principal matrices $R$, $G_{(1)}$, $G_{(2)}$, etc. Taking the twofold trace of the eigenblock $E_{\text{occ}}$ (i.e. $2Tr E_{\text{occ}}$) then yields the relevant total energy ($E$), the $k$th order member of the expansion for the latter ($E_{(k)}$) coinciding with $2Tr E_{\text{occ}}^{(k)}$. Finally, cyclic transpositions of matrix factors (i.e. of $R$, $G_{(1)}$, $G_{(2)}$, etc.) inside the trace signs of formulæ for $E_{(k)}$ allowed the latter to be expressed via the inter-subset delocalization matrices of Eq. (8) and, subsequently, in terms of partial and total delocalization coefficients of NCMOs as shown in Eq. (17) [51].

The common charge-bond order (CBO) matrix of polyenes ($P$) also is among characteristics resulting from our principal problem of Eq. (34). Indeed, the one-electron density matrix coincides with a projector to the subset of double-occupied MOs of any type [31], including NCMOs. Thus, the relevant CBO matrix $P$ may be constructed using the NCMO representation matrix $C$ [51]. Moreover, the coincidence of the zero order double-occupied NCMOs with BBOs ensures a rather simple interrelation between matrices $P$ and $C$ [47, 51, 54] and thereby proportionality between $P_{(k,i)}$ and $D^{(k)}$ shown in Eq. (21).

Let us now dwell on the derivation of the compact formula of Eq. (31) for the negative (suppressive) component $d_{(+i,(-j)m)}$ of Eq. (26) defined by Eq. (28). The element $(G_{(1)} G_{(1)}^* G_{(1)})_{im}$ of this definition may be alternatively represented as follows

$$\langle G_{(1)} G_{(1)}^* G_{(1)} \rangle_{im} = \sum_{l \neq m} \langle G_{(1)} G_{(1)}^* G_{(1)} \rangle_{il} \equiv \sum_{l \neq m} G_{(1)l} G_{(1)}^* G_{(1)}_{im}$$ \hspace{1cm} (36)$$

With this in mind, the relation of Eq. (28) may be reformulated so that it resembles Eq. (30), viz.

$$d_{(+i,(-j)m)}^{(-4f)} = -\frac{3}{2} G_{(1)im} \sum_{(+j)\neq m} \langle G_{(1)} G_{(1)}^* G_{(1)} \rangle_{jm}$$

$$-\frac{3}{2} G_{(1)jm} \sum_{(-j)\neq i} \langle G_{(1)} G_{(1)}^* G_{(1)} \rangle_{im}$$ \hspace{1cm} (37)$$

where elements of matrices $G_{(1)}$, $G_{(1)}^*$ and $G_{(1)}$ are symmetric matrices and thereby contain non-zero diagonal elements [57, 58]. In this connection, let the component $d_{(+i,(-j)m)}^{(-4f)}$ be further partitioned into two subcomponents $d_{(+i,(-j)m)}^{(-4f)a}$ and $d_{(+i,(-j)m)}^{(-4f)b}$ correspondingly expressing diagonal and off-diagonal elements of matrices $G_{(1)}$, $G_{(1)}^*$ and $G_{(1)}$, viz.

$$d_{(+i,(-j)m)}^{(-4f)a} = -\frac{3}{2} G_{(1)im}^2 \left( \langle G_{(1)} G_{(1)}^* \rangle_{ii} + \langle G_{(1)} G_{(1)}^* \rangle_{mm} \right)$$ \hspace{1cm} (38)$$

$$d_{(+i,(-j)m)}^{(-4f)b} = -\frac{3}{2} G_{(1)im} \sum_{(+j)\neq m} \langle G_{(1)} G_{(1)}^* G_{(1)} \rangle_{jm}$$

$$-\frac{3}{2} G_{(1)jm} \sum_{(-j)\neq i} \langle G_{(1)} G_{(1)}^* G_{(1)} \rangle_{im}$$ \hspace{1cm} (39)$$

where the relation of Eq. (39) acquires the above-specified restrictions.

Let us start with the subcomponent $d_{(+i,(-j)m)}^{(-4f)a}$ of Eq. (38). Diagonal elements of matrix products $G_{(1)} G_{(1)}^*$ and $G_{(1)} G_{(1)}$ are proportional to numbers of first neighbours of the C=C bonds concerned in the case of polyenes [57], e.g.

$$\langle G_{(1)} G_{(1)}^* \rangle_{ii} = \frac{3}{2} \langle 1 \rangle \cdot n_f, \quad \langle G_{(1)} G_{(1)}^* \rangle_{mm} = \frac{3}{2} \langle 1 \rangle \cdot n_M$$ \hspace{1cm} (40)$$

It is evident that the $M$th C=C bond and the $l$th one necessarily are included when counting the first neighbours of the $l$th and $M$th C=C bonds, respectively. Consequently, a definite “own” increment of our pair of C=C bonds $I$ and $M$ arises in the relation of Eq. (38) that is twice as large as
that of any side neighbour of either \(i\)th and \(m\)th bond. We then obtain

\[
d_{(+i)(-jm)}^{(-j)+b} = \frac{3y^4}{512}(2 + n_{(i)M} + n_{M(j)})
\]

(41)

Let us now turn to the subcomponent \(d_{(+i)(-jm)}^{(-j)+b}\) of Eq. (39) and continue its comparison to Eq. (30). In contrast to elements of the matrix \(G^{(2)}\) determining the latter, the off-diagonal elements of matrix products \(G^{(1)}G^{(1)}_+\) and \(G^{(1)}_+G^{(1)}\) take non-zero values for any pair of second-neighbouring C=C bonds (irrespective of their type of conjugation) [57]. It is evident that any side neighbour \((L)\) of the \(M\)th C=C bond automatically is a second neighbour of the \(i\)th C=C bond. The same refers also to the \(i\)th side neighbour of the \(i\)th C=C bond. Moreover, contributions of these side neighbours to \(d_{(+i)(-jm)}^{(-j)+b}\) take uniform values. Consequently, the expression for the subcomponent \(d_{(+i)(-jm)}^{(-j)+b}\) coincides with that of Eq. (41) except for absence of the “own” increment (2) within the braces. The whole component \(d_{(+i)(-jm)}^{(-j)+b}\) then takes the form shown in Eq. (31).

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