

A combined technique for computation of energy-effect of cycles in conjugated molecules

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Abstract A direct method for computation of the energy-effect (ef) of cycles in conjugated molecules is elaborated, based on numerical calculation of the (complex) zeros of certain graph polynomials. Accordingly, the usage of the Coulson integral formula can be avoided, and thus the ef -values can be calculated for arbitrary cycles of arbitrary conjugated systems.

Keywords Energy-effect of cycle · Computation of characteristic polynomial · Computation of zeros of polynomial · Chemical graph theory

Mathematics Subject Classification Primary: 65H05 · Secondary: 92E10

1 Introduction

In the 1970s, a mathematical model was elaborated [1, 2], capable of expressing the effect of an individual cycle on the total π -electron energy of a polycyclic conju-

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gated molecule. In the several dozens of papers that followed, this energy-effect was computed by means of a Coulson-integral type expression

$$ef(G, Z) = \frac{2}{\pi} \int_0^{\infty} \ln \left| \frac{\phi(G, ix)}{\phi(G, ix) + 2\phi(G - Z, ix)} \right| dx \quad (1)$$

in which $\phi(G, x)$ and $\phi(G - Z, x)$ are the characteristic polynomials of the molecular graph G and of its subgraph $G - Z$ obtained by deleting from G the cycle Z , and $i = \sqrt{-1}$. For details on Eq. (1) and its chemical applications see the review [3], the recent papers [4–8] and the references cited therein. The method for efficient numerical computation of $ef(G, Z)$ via Eq. (1) has been described in due detail [8].

The weakness of formula (1) lies in the fact that its validity is restricted to conjugated π -electron systems in which all bonding molecular orbitals are doubly occupied, and all antibonding MOs are empty. The vast majority of chemically relevant conjugated molecules (in particular, all alternant hydrocarbons in their ground state) satisfy this condition, thus making Eq. (1) a useful tool for the study of their local aromaticity. On the other hand, in the general case, Eq. (1) is not applicable to non-alternant conjugated hydrocarbons and heteroatom-containing π -electron systems. It is also not applicable in the case of ionic species and those in excited electronic states.

In order to develop a general method for computing $ef(G, Z)$, we first need to make a step back, and recall the original ideas lying in the foundation of the theory of cyclic conjugation; for some recent studies along the same lines see [9, 10].

The energy-effect of a cycle Z in a conjugated molecule is conceived [1–3] as the difference between the actual π -electron energy E_{π} and a quasi-energy E_{π}^{ref} (sometimes referred to as the “reference energy” [11]):

$$ef(G, Z) = E_{\pi} - E_{\pi}^{ref} \quad (2)$$

The quasi-energy E_{π}^{ref} is mathematically constructed by ignoring the contributions of Z to E_{π} , but retaining the contributions to E_{π} of all other (cyclic and acyclic) structural features of the underlying conjugated molecule.

Now, within the tight-binding Hückel MO model, E_{π} can be computed¹ from the characteristic polynomial $\phi(G, x)$, by calculating the roots $\lambda_1 \geq \lambda_2 \geq \dots \geq \lambda_n$ of the equation $\phi(G, x) = 0$, and by applying the formula

$$E_{\pi} = \sum_{k=1}^n g_k \lambda_k \quad (3)$$

where g_k is the occupation number of the k -th molecular orbital. In analogy to this, the quasi-energy is conceived as

¹ The quantities λ_k , $k = 1, 2, \dots, n$, are in fact the eigenvalues of the adjacency matrix. The usual way of their computation is matrix diagonalization. On the other hand, the quantities λ_k^{ref} , $k = 1, 2, \dots, n$, are not eigenvalues, and can only be obtained by calculating the zeros of the underlying polynomial.

$$E_{\pi}^{ref} = \sum_{k=1}^n g_k \lambda_k^{ref} \quad (4)$$

where λ_k^{ref} , $k = 1, 2, \dots, n$, have been shown [2] to be the roots of the polynomial $\phi^{ref}(G, Z, x) := \phi(G, x) + 2\phi(G - Z, x)$ i.e., the solutions of the equation $\phi^{ref}(G, Z, x) = 0$.

In the general case, the roots of $\phi^{ref}(G, Z, x)$ are complex-valued, $a_1 + ib_1, a_2 + ib_2, \dots, a_n + ib_n$, and we will label them so that $a_1 \geq a_2 \geq \dots \geq a_n$. In the vast majority of chemically relevant cases (e.g., for even, ground-state, closed-shell π -electron systems), the imaginary terms in the expression $\sum_{k=1}^n g_k \lambda_k^{ref}$ cancel out and E_{π}^{ref} automatically becomes real-valued. To be on the safe side, and in order to keep $ef(G, Z)$ real-valued in any case, it is purposeful to compute the reference energy via the expression

$$E_{\pi}^{ref} = \sum_{k=1}^n g_k a_k. \quad (5)$$

In what follows, we describe a procedure by means of which the quantities a_1, a_2, \dots, a_n and (if preferred) $\lambda_1, \lambda_2, \dots, \lambda_n$ can be numerically computed. Then, by employing Eqs. (2)–(5), the energy-effect of any cycle in any conjugated π -electron system can be calculated.

2 Mathematical preliminaries

2.1 Theoretical basis of the Adomian decomposition method

In this section, for the convenience of the readers, we briefly describe the main features of the Adomian decomposition method (ADM).

The ADM was developed by George Adomian (1922–1996) as a systematic and robust technique for solving both deterministic and stochastic functional equations, either linear or nonlinear [12, 13]. Quite impressively, the ADM does not rely on any unphysical or a priori restrictive assumption, such as imposed by linearization, perturbation, discretization, ad hoc assumptions, guessing the initial term or a set of basis functions, and so forth. A vast amount of literature is available on the theory of the ADM as well as its application in analyzing mathematical models of physics, chemistry, biology, mechanical engineering, chemical engineering, etc [14–25]; for a bibliography on ADM, covering the period 1961–2011, see [26]. Nevertheless, only limited effort has been made so far to exploit the ADM for solving algebraic equations [27–32].

In order to describe the basics of the ADM, consider the functional equation

$$u - N(u) = f \quad (6)$$

where N is a nonlinear operator from a Banach space $B \rightarrow B$, f is a known element of B and we are seeking $u \in B$ that satisfies Eq. (6). We assume that for every $f \in B$, Eq. (6) has a unique solution. The ADM proposes the solution u as an infinite series of the form

$$u = \sum_{i=0}^{\infty} u_i \quad (7)$$

and decomposes the nonlinear operator N as

$$N(u) = \sum_{i=0}^{\infty} A_i \quad (8)$$

where the A_i 's are called the Adomian polynomials and can be calculated through their definitional formula as [13]:

$$A_i = A_i(u_0, u_1, \dots, u_i) = \frac{1}{i!} \frac{d^i}{d\lambda^i} N\left(\sum_{k=0}^{\infty} u_k \lambda^k\right) \Bigg|_{\lambda=0}. \quad (9)$$

Substituting Eqs. (7) and (8) back into Eq. (6), we obtain

$$\sum_{i=0}^{\infty} u_i - \sum_{i=0}^{\infty} A_i = f. \quad (10)$$

Provided that the two series in Eq. (10) are convergent, we can construct the following recursion relation to generate components of the solution as

$$\begin{cases} u_0 = f \\ u_{i+1} = A_i, \quad i \geq 0 \end{cases} \quad (11)$$

Note that in certain problems, it may suffice to truncate the infinite series in Eq. (10) after their first $m \geq 1$ components, which yields an approximant of the solution of the form

$$\phi_m = \sum_{i=0}^{m-1} u_i. \quad (12)$$

The convergence of the ADM has been proven rigorously by several authors, e.g. see [33–35], and hence will be taken for granted here.

Elsewhere [36], two of the present authors developed an efficient algorithm for computation of the Adomian polynomials named *AdomPoly*, which is based on functions processing letter string elements and symbolic programming. Other algorithms for the calculation of the Adomian polynomials have also been proposed in the literature [37–39].

2.2 Two alternative algorithms for determination of the characteristic polynomial

2.2.1 The Faddeev–Leverrier algorithm

The Faddeev–Leverrier algorithm is an efficient iterative tool for calculation of the characteristic polynomial of matrices [40]. This algorithm first takes $\Lambda_1 = \Lambda$ and

$a_0 = 1$ for an n -by- n matrix Λ , and then relies on the following recursion:

$$\begin{cases} \Lambda_{i+1} = \Lambda (\Lambda_i + a_i I), & \text{for } 1 \leq i < n \\ a_i = -\frac{\text{trace}(\Lambda_i)}{i}, & \text{for } 1 \leq i \leq n \end{cases} \quad (13)$$

In this way, all of the $n + 1$ coefficients of $\phi(x) = \sum_{i=0}^n a_i x^{n-i}$, i.e. the characteristic polynomial of Λ , are found. As an additional benefit of the Faddeev–Leverrier algorithm, the inverse matrix Λ^{-1} can be obtained at no extra computational expense by means of the formula $\Lambda^{-1} = -(1/a_n) (\Lambda_{n-1} + a_{n-1}I)$.

2.2.2 Jacobson’s algorithm based on matrix minors

According to Jacobson [41], the coefficients of the characteristic polynomial of the matrix \mathbf{A} , namely

$$P(x) = \det(\mathbf{A} - x\mathbf{I}) = (-1)^n (x^n - a_1 x^{n-1} + \dots + (-1)^n a_n) \quad (14)$$

can be calculated by

$$\begin{cases} a_1 = \text{trace}(\mathbf{A}) \\ a_i = \text{sum of the } i\text{-rowed principal minors of the matrix } \mathbf{A} \text{ for } 2 \leq i \leq n - 1 \\ a_n = \det(\mathbf{A}) \end{cases} \quad (15)$$

2.3 The Shanks transform

The Shanks transform, which is due to Daniel Shanks (1917–1996), is a nonlinear transform that can dramatically accelerate the convergence of its input series [42]. The Shanks transformation $Sh(U_n)$ of the sequence U_n is defined as

$$Sh(U_n) = \frac{U_{n+1}U_{n-1} - U_n^2}{U_{n+1} - 2U_n + U_{n-1}} \quad (16)$$

Further speed-up will be achieved by successive implementation of the Shanks transformation, i.e., by the iterated Shanks transforms $Sh^2(U_n) = Sh(Sh(U_n))$, $Sh^3(U_n) = Sh(Sh(Sh(U_n)))$, etc.

Definition 2.1 Let $\mathbf{A} \in \mathbb{C}^{n \times n}$ be a complex-valued matrix with entries a_{ij} . Let $R_i = \sum_{j \neq i}^n |a_{ij}|$, for $i \in \{1, \dots, n\}$, be the sum of absolute values of the non-diagonal entries in the i -th row. Also, let $D(a_{ii}, R_i)$ be the closed disc centered at a_{ii} with radius R_i . Such a disc is known as a Gershgorin disc.

Theorem 2.1 (Gershgorin’s circle theorem) [43] *Every eigenvalue of the matrix \mathbf{A} lies within at least one of the Gershgorin discs $D(a_{ii}, R_i)$.*

Definition 2.2 (Sturm sequence) For a polynomial $P(x)$ of degree n , consider the following recursion

$$\begin{aligned}
p_0(x) &= P(x), \\
p_1(x) &= dP(x)/dx, \\
p_2(x) &= -\text{rem}(p_0, p_1), \\
&\vdots \\
p_m(x) &= -\text{rem}(p_{m-2}, p_{m-1}), \\
p_{m+1}(x) &= -\text{rem}(p_{m-1}, p_m) = 0,
\end{aligned} \tag{17}$$

where $\text{rem}(p_i, p_j)$ is the remainder of the polynomial long division of p_i by p_j and $m \leq n$. The sequence $\{p_0, p_1, \dots, p_m\}$ is called the Sturm sequence of $P(x)$.

Theorem 2.2 (Sturm) [41,44] *Let $\{p_0, p_1, \dots, p_m\}$ be a Sturm's sequence of the polynomial $P(x)$, and denote by $\sigma(\xi)$ the number of sign changes (ignoring zeroes) in the sequence $\{p_0(\xi), p_1(\xi), \dots, p_m(\xi)\}$. Then for any two real numbers $a < b$, $P(x)$ has $\sigma(a) - \sigma(b)$ distinct real roots within the interval $(a, b]$.*

3 Our combined algorithm

Due to reasons described above, we are interested in finding all the roots of the following polynomials:

$$P(x) = \phi(G, x) \tag{18}$$

$$Q(x) = \phi(G, x) + 2\phi(G - Z, x). \tag{19}$$

Since the graph $G - Z$ has fewer vertices than the graph G , we readily conclude that $Q(x)$ is monic and of degree n . Therefore, in other words, we shall solve the following type of equation both for $P(x)$ and $Q(x)$:

$$x^n + c_{n-1}x^{n-1} + \dots + c_2x^2 + c_1x + c_0 = 0 \tag{20}$$

By adopting Adomian's operator-theoretic notation, Eq. (20) is converted to

$$Lx + Nx = g \tag{21}$$

where $L = c_1$, $Nx = x^n + c_{n-1}x^{n-1} + \dots + c_2x^2$, and $g = -c_0$.

Assuming $c_1 \neq 0$, we select $L^{-1} = 1/c_1$ which yields

$$L^{-1}Lx = L^{-1}g - L^{-1}Nx \tag{22}$$

or, equivalently,

$$x = -\frac{c_0}{c_1} - \frac{1}{c_1}x^n - \frac{c_{n-1}}{c_1}x^{n-1} - \dots - \frac{c_2}{c_1}x^2. \tag{23}$$

In agreement with Adomian’s methodology, see Eq. (11), we find the first approximate real root of $P(x)$ as $\tilde{r}_1 \approx \sum_{i=0}^m x_i$, where

$$\begin{cases} x_0 = -\frac{c_0}{c_1} \\ x_{i+1} = -\frac{1}{c_1} \Theta_{(n,i)} - \frac{c_{n-1}}{c_1} \Theta_{(n-1,i)} - \dots - \frac{c_2}{c_1} \Theta_{(2,i)} \end{cases} \text{ for } i \geq 0 \tag{24}$$

with $\Theta_{(n,i)}, \Theta_{(n-1,i)}, \dots, \Theta_{(2,i)}$ denoting the respective Adomian polynomials decomposing the nonlinear terms x^n, x^{n-1}, \dots, x^2 in Eq. (23).

As pointed out in [32], other real roots of Eq. (25), can be found by polynomial deflation followed by reapplying the procedure described through Eqs. (20)–(24). For instance, the following equation

$$\begin{aligned} \frac{x^n + c_{n-1}x^{n-1} + \dots + c_2x^2 + c_1x + c_0}{x - \mu_1} &= 0 \\ &= x^{n-1} + b_{n-2}x^{n-2} + \dots + b_2x^2 + b_1x + b_0 \end{aligned} \tag{25}$$

can be examined for achieving the next remaining real root of $P(x)$ or $Q(x)$.

In the case of a diverging series generated by the recurrence relation (24), which may also imply the existence of at least two complex conjugate roots [27], the change of the variable $y = x - \alpha$ enables the calculation of the real-valued roots. Appropriate choices for α can be obtained with the aid of the Gershgorin circle theorem; in this regard, see [25,32].

Complex conjugate roots of $Q(x)$ can be calculated in a similar way via the ADM, but through the use of other equivalent canonical forms of Eq. (20), which involve even-root expressions and the choice of zero for the first solution component. Specifically, the canonical form of Eq. (20), presuming that $c_2 \neq 0$, is

$$x = \sqrt{-\frac{1}{c_2}x^n - \frac{c_{n-1}}{c_2}x^{n-1} - \dots - \frac{c_3}{c_2}x^3 - \frac{c_1}{c_2}x - \frac{c_0}{c_2}}. \tag{26}$$

Consequently, the classic ADM generates the solution components by the recurrence relation as

$$\begin{cases} x_0 = 0 \\ x_{i+1} = \Phi_i \end{cases} \text{ for } i \geq 0 \tag{27}$$

where Φ_i are the Adomian polynomials, decomposing the square-root term on the right-hand side of Eq. (26). Accordingly, $r_2 = \sum_{i=0}^\infty x_i$, or its truncated approximation $\tilde{r}_2 = \sum_{i=0}^m x_i$, corresponds to one, if any, of the complex roots of $Q(x)$. In Fig. 1 is depicted the flowchart for our new scheme, which is able to systematically calculate all the roots of a polynomial, either real or complex.

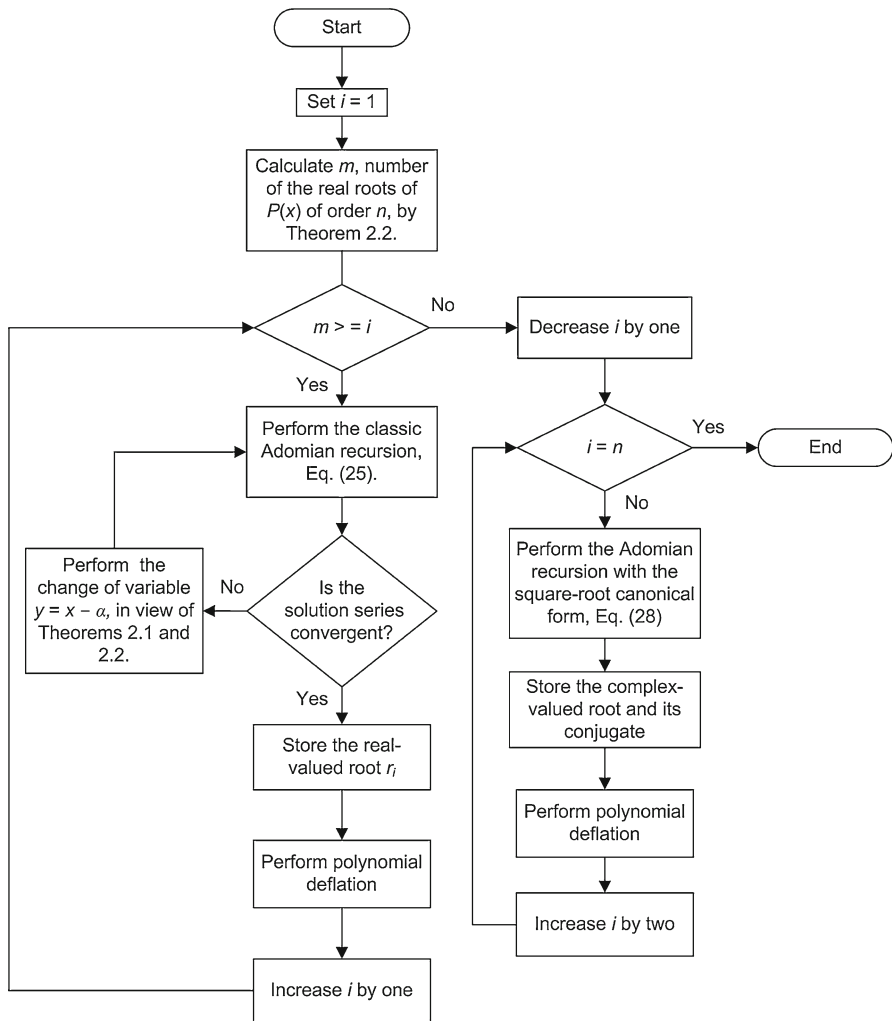


Fig. 1 Flowchart of our combined algorithm for finding real and complex roots of a polynomial

4 Illustrative examples

In order to better illustrate our algorithm, we follow step-by-step the computation of the energy-effect $ef(G, Z)$ of a particular six-membered ring Z of benzo[*a*]anthracene, cf. Fig. 2.

By means of the Faddeev–Leverrier algorithm, we first compute

$$P(x) = \phi(G, x) = x^{18} - 21x^{16} + 180x^{14} - 823x^{12} + 2203x^{10} - 3558x^8 + 3430x^6 - 1868x^4 + 505x^2 - 49$$

Fig. 2 The molecular graph of benzo[*a*]anthracene (*G*) and its cycle *Z* (indicated by shading) for which $ef(G, Z)$ is being calculated



$$Q(x) = \phi^{ref}(G, Z, x) = x^{18} - 21x^{16} + 180x^{14} - 821x^{12} + 2181x^{10} - 3472x^8 + 3280x^6 - 1752x^4 + 473x^2 - 47$$

In order to calculate the energy-effect of the cycle *Z* on the molecular graph *G*, we need to find all the roots of the polynomials $P(x)$ and $Q(x)$. By Sturm’s theorem, it is easy to find that $P(x)$ has eighteen whereas $Q(x)$ fourteen real roots in $(-\infty, +\infty)$.

Since all terms of $P(x)$ have even exponents, the variable change of $x \mapsto x^2$ would save computational time. In order to find the zeroes of $P(x)$, we apply the algorithm explained in Fig. 1 as follows:

Action on $P(x)$	Obtained root
$x^2 \mapsto x + \alpha, (\alpha = 0.5)$ & Adomian recursion formula	$r_1 = 0.71496$ $r_2 = -0.71496$
Deflate by $\prod_{i=1}^2 (x - r_i)$ & $x^2 \mapsto x + \alpha, (\alpha = 0.6)$ & Adomian recursion formula	$r_3 = 1.00000$ $r_4 = -1.00000$
Deflate by $\prod_{i=1}^4 (x - r_i)$ & $x^2 \mapsto x + \alpha, (\alpha = 0.8)$ & Adomian recursion formula	$r_5 = 1.32305$ $r_6 = -1.32305$
Deflate by $\prod_{i=1}^6 (x - r_i)$ & $x^2 \mapsto x + \alpha, (\alpha = 1)$ & Adomian recursion formula	$r_7 = 1.16563$ $r_8 = -1.16563$
Deflate by $\prod_{i=1}^8 (x - r_i)$ & $x^2 \mapsto x + \alpha, (\alpha = 1.6)$ & Adomian recursion formula	$r_9 = 1.47986$ $r_{10} = -1.47986$
Deflate by $\prod_{i=1}^{10} (x - r_i)$ & $x^2 \mapsto x + \alpha, (\alpha = 0.4)$ & Adomian recursion formula	$r_{11} = 0.45231$ $r_{12} = -0.45231$
Deflate by $\prod_{i=1}^{12} (x - r_i)$ & $x^2 \mapsto x + \alpha, (\alpha = 1.8)$ & Adomian recursion formula	$r_{13} = 1.75461$ $r_{14} = -1.75461$
Deflate by $\prod_{i=1}^{14} (x - r_i)$ & $x^2 \mapsto x + \alpha, (\alpha = 7)$ & Adomian recursion formula	$r_{15} = 2.48465$ $r_{16} = -2.48465$
Deflation by $\prod_{i=1}^{16} (x - r_i)$	$r_{17} = 2.17552$ $r_{18} = -2.17552$

Note that the polynomial deflation operation can be optionally carried out by means of appropriate commands in commercial software packages; for example “*deconv*” in MATLAB.

In a fully analogous manner, we can adopt our algorithm to obtain all roots of $Q(x)$:

Action on $Q(x)$	Obtained root
$x^2 \mapsto x + \alpha$, ($\alpha = 1.3$) & Adomian recursion formula	$r_1 = 1.17964$ $r_2 = -1.17964$
Deflate by $\prod_{i=1}^2 (x - r_i)$ & $x^2 \mapsto x + \alpha$, ($\alpha = 1.6$) & Adomian recursion formula	$r_3 = 1.31002$ $r_4 = -1.31002$
Deflate by $\prod_{i=1}^4 (x - r_i)$ & $x^2 \mapsto x + \alpha$, ($\alpha = 5$) & Adomian recursion formula	$r_5 = 2.17102$ $r_6 = -2.17102$
Deflate by $\prod_{i=1}^6 (x - r_i)$ & $x^2 \mapsto x + \alpha$, ($\alpha = 2.4$) & Adomian recursion formula	$r_7 = 1.53601$ $r_8 = -1.53601$
Deflate by $\prod_{i=1}^8 (x - r_i)$ & $x^2 \mapsto x + \alpha$, ($\alpha = 4$) & Adomian recursion formula	$r_9 = 1.81481$ $r_{10} = -1.81481$
Deflate by $\prod_{i=1}^{10} (x - r_i)$ & $x^2 \mapsto x + \alpha$, ($\alpha = 6$) & Adomian recursion formula	$r_{11} = 2.46114$ $r_{12} = -2.46114$
Deflate by $\prod_{i=1}^{12} (x - r_i)$ & $x^2 \mapsto x + \alpha$, ($\alpha = 0.1$) & Adomian recursion formula	$r_{13} = 0.46726$ $r_{14} = -0.46726$
Deflate by $\prod_{i=1}^{14} (x - r_i)$ & $x^2 \mapsto x + \alpha$, ($\alpha = 1$) & Adomian recursion formula (square-root canonical form)	$r_{15} = 0.79456 + 0.07807i$ $r_{16} = 0.79456 - 0.07807i$
Deflation by $\prod_{i=1}^{16} (x - r_i)$	$r_{17} = -0.79456 + 0.07807i$ $r_{18} = -0.79456 - 0.07807i$

Returning to the notation used in Eqs. (3) and (4), we thus have

$$\begin{aligned} \lambda_1 &= 2.48465, & \lambda_2 &= 2.17552, & \lambda_3 &= 1.75461, & \lambda_4 &= 1.47986, \\ \lambda_5 &= 1.32305, & \lambda_6 &= 1.16563, & \lambda_7 &= 1.00000, & \lambda_8 &= 0.71496, \\ \lambda_9 &= 0.45231, & \lambda_{10} &= -0.45231, & \lambda_{11} &= -0.71496, & \lambda_{12} &= -1.00000, \\ \lambda_{13} &= -1.16563, & \lambda_{14} &= -1.32305, & \lambda_{15} &= -1.47986, & \lambda_{16} &= -1.75461, \\ \lambda_{17} &= -2.17552, & \lambda_{18} &= -2.48465 \end{aligned}$$

and

$$\begin{aligned} \lambda_1^{ref} &= 2.46114, & \lambda_2^{ref} &= 2.17102, & \lambda_3^{ref} &= 1.81481, & \lambda_4^{ref} &= 1.53601, \\ \lambda_5^{ref} &= 1.31002, & \lambda_6^{ref} &= 1.17964, & \lambda_7^{ref} &= 0.79456 + 0.07807i, \\ \lambda_8^{ref} &= 0.79456 - 0.07807i, & \lambda_9^{ref} &= -0.79456 + 0.07807i, \\ \lambda_{10}^{ref} &= -0.79456 - 0.07807i, & \lambda_{11}^{ref} &= -0.71496, & \lambda_{12}^{ref} &= -1.00000, \\ \lambda_{13}^{ref} &= -1.17964, & \lambda_{14}^{ref} &= -1.31002, & \lambda_{15}^{ref} &= -1.53601, & \lambda_{16}^{ref} &= -1.81481, \\ \lambda_{17}^{ref} &= -2.17102, & \lambda_{18}^{ref} &= -2.46114. \end{aligned}$$

Now, bearing in mind that in the ground state of benzo[*a*]anthracene, $g_1 = g_2 = \dots = g_9 = 2$ and $g_{10} = g_{11} = \dots = g_{18} = 0$, we can compute $E_\pi(G)$ according to

Eq. (3), as

$$E_{\pi}(G) = 2 \times (2.48465 + 2.17552 + 1.75461 + 1.47986 + 1.32305 \\ + 1.16563 + 1.00000 + 0.71496 + 0.45231) = 25.10118$$

and, analogously, $E_{\pi}^{ref}(G, Z)$ according to Eq. (4) as

$$E_{\pi}^{ref}(G, Z) = 2 \times (2.46114 + 2.17102 + 1.81481 + 1.53601 + 1.31002 \\ + 1.17964 + 0.79456 + 0.07807i + 0.79456 - 0.07807i \\ + 0.46726) = 25.05804$$

As it is usually the case, the imaginary parts of the λ_k^{ref} 's canceled each other. Finally, by Eq. (2),

$$ef(G, Z) = 25.10118 - 25.05804 = +0.04314.$$

An identical value for $ef(G, Z)$ could have been obtained by using Eq. (1), which would require a much easier calculation procedure. On the other hand, by means of the above determined λ_k and λ_k^{ref} values, we can now calculate also the energy-effects pertaining to charged or excited forms of benzo[*a*]anthracene, which are not accessible by employing formula (1). For instance, we can calculate the following quantities.

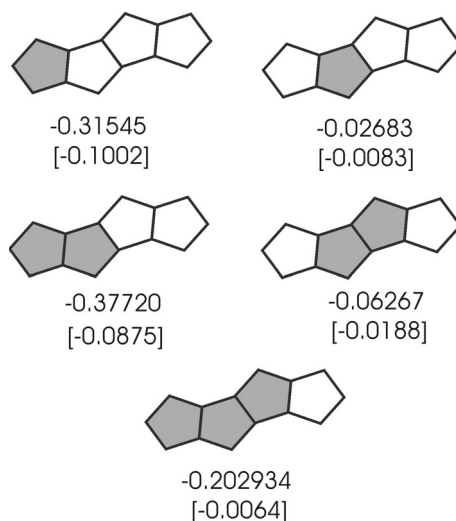
- (1) Energy-effect of cycle *Z* of benzo[*a*]anthracene monocation ($g_1 = g_2 = \dots = g_8 = 2$, $g_9 = 1$, $g_{10} = g_{11} = \dots = g_{18} = 0$):

$$E_{\pi}(G^+) = 2 \times (2.48465 + 2.17552 + 1.75461 + 1.47986 + 1.32305 \\ + 1.16563 + 1.00000 + 0.71496) + 0.45231 = 24.64887 \\ E_{\pi}^{ref}(G^+, Z) = 2 \times (2.46114 + 2.17102 + 1.81481 + 1.53601 + 1.31002 \\ + 1.17964 + 0.79456 + 0.07807i + 0.79456 - 0.07807i) \\ + 0.46726 = 24.59078 \\ ef(G^+, Z) = 24.64887 - 24.59078 = +0.05809$$

- (2) Energy-effect of cycle *Z* of benzo[*a*]anthracene dianion ($g_1 = g_2 = \dots = g_{10} = 2$, $g_{11} = g_{12} = \dots = g_{18} = 0$):

$$E_{\pi}(G^{2-}) = 2 \times (2.48465 + 2.17552 + 1.75461 + 1.47986 \\ + 1.32305 + 1.16563 \\ + 1.00000 + 0.71496 + 0.45231 - 0.45231) = 24.19656 \\ E_{\pi}^{ref}(G^{2-}, Z) = 2 \times (2.46114 + 2.17102 + 1.81481 + 1.53601 + 1.31002 \\ + 1.17964 + 0.79456 + 0.07807i + 0.79456 - 0.07807i$$

Fig. 3 Energy-effects of the cycles (indicated by *shading*) of a 4-cyclic pentagonal chain. Its molecular graph has 8 bonding and 6 antibonding MOs. In *square brackets* are the (false) *ef*-values obtained by applying Eq. (1)



$$+0.46726 - 0.46726) = 24.12352$$

$$ef(G^{2-}, Z) = 24.19656 - 24.12352 = +0.07304$$

- (3) Energy-effect of cycle Z in the second excited state of benzo[a]anthracene ($g_1 = g_2 = \dots = g_8 = 2$, $g_9 = g_{11} = 1$, $g_{10} = g_{12} = g_{13} = \dots = g_{18} = 0$):

$$E_{\pi}(G^*) = 2 \times (2.48465 + 2.17552 + 1.75461 + 1.47986 + 1.32305$$

$$+ 1.16563 + 1.00000 + 0.71496) + 0.45231$$

$$- 0.71496 = 23.93381$$

$$E_{\pi}^{ref}(G^*, Z) = 2 \times (2.46114 + 2.17102 + 1.81481 + 1.53601 + 1.31002$$

$$+ 1.17964 + 0.79456 + 0.79456) + 0.46726 - 0.79456$$

$$= 23.79622$$

$$ef(G^*, Z) = 23.93381 - 23.79622 = +0.13759$$

Note that in this latter example, the imaginary terms would not cancel out and therefore we had to apply Eq. (5).

Another group of examples where our method would be advantageous (whereas Eq. (1) is inapplicable) are the conjugated systems which in their ground states possess filled antibonding or empty bonding molecular orbitals. Such π -electron systems abound among non-alternant hydrocarbons (for details see [45]).

Characteristic representatives are pentagonal chains, in which one or more bonding MOs are empty. As an illustrative example, in Fig. 3 we provide the energy-effect of the cycles of a 4-cyclic pentagonal chain.

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