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Note on the Coulson integral formula

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Let P be a polynomial of degree n, whose zeros $\lambda_1, \lambda_2, \ldots, \lambda_n$ are real-valued. The Coulson integral formula (first reported in 1940) is an expression for the sum of the positive–valued zeros of P, in terms of P. We show that the Coulson formula holds if and only if the condition $\lambda_1+\lambda_2+\cdots+\lambda_n = 0$ is obeyed. We also show how the formula has to be modified, so that it be applicable in the case when $\lambda_1 + \lambda_2 + \cdots + \lambda_n \neq 0$.

KEY WORDS: Coulson integral formula, total π-electron energy, HMO theory

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1. Introduction

In molecular orbital theory the sum of the energies of all electrons, i.e., the sum of all occupied MO energy levels, plays a significant role. In the simple Hückel molecular orbital (HMO) model [1,2] this sum is interpreted as the total π-electron energy. For many (but not for all) molecules to which the HMO model is applicable, within the study of total π-electron energy and the numerous quantities derived from it (bond orders, polarizabilities, resonance energies, ...), one encounters the sum of the positive zeros of a certain polynomial, usually referred to as the characteristic polynomial [3,4].

In the early days of molecular orbital theory, Coulson [5] discovered a formula that makes it possible to compute the latter sum without knowing the zeros of the characteristic polynomial. According to Coulson [5], if $P(x)$ is a polynomial of degree n, whose zeros $\lambda_1, \lambda_2, \ldots, \lambda_n$ are real-valued, then

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$$\sum_{+} \lambda_k = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \left[n - \frac{ix\, P'(ix)}{P(ix)} \right] \mathrm{d}x, \tag{1}$$

where $\sum_{+}$ indicates the sum of those λ_k , $k = 1, 2, \ldots, n$, that are positive-valued, P' stands for the first derivative of the polynomial $P(x)$ with regard to the variable x , and $i = \sqrt{-1}$. In formula (1) and throughout this paper, all expressions of the form $\int_{-\infty}^{+\infty} f(x)\, \mathrm{d}x$ pertain to the proper value of the respective integral.

Formula (1) was eventually much investigated and found a variety of applications. Of these the classical results by Coulson and Longuet-Higgins [6–8] were the first, followed by studies of the dependence of total π-electron energy on molecular structure [9–12], resonance energy [13,14], cyclic conjugation and the Hückel $(4m+2)$-rule [15–19], free valence, bond order, change density, and superdelocalizability [20–23], magnetic susceptibility [24,25], molecular graphs with extremal energy [26,27], to mention just a few; for more details and additional references see the book [28], the reviews [29–31], and the historical survey [32].

In view of these numerous works – that cover a period longer than 60 years – it is somewhat surprising that a simple, but essential, restriction to the applicability of formula (1) seems to be never (explicitly) mentioned. In this paper we point out this restriction and show how it can be overcome.

We first briefly repeat the original idea leading to the Coulson integral formula (1)

2. Deducing the Coulson formula

Let, as before, $i = \sqrt{-1}$ be the imaginary unit, and let a complex number z be written in the form $z = x + iy$. Then z can be presented as a point in the (x, y)-plane of a Descartes coordinate system (cf. figures 1 and 2), the so-called complex plain. The two starting points of our considerations are the following:

(1) Let Γ be a simple, positively oriented, contour in the complex plain, and z_0 be a complex number. Then, according to the well known Cauchy formula (see, for instance [33–35]),

$$\frac{1}{2\pi i} \oint_{\Gamma} \frac{\mathrm{d}z}{z - z_0} = \begin{cases} 1 & \text{if } z_0 \in \mathrm{int}(\Gamma), \\ 0 & \text{if } z_0 \in \mathrm{ext}(\Gamma), \end{cases} \tag{2}$$

where $z_0 \in \mathrm{int}(\Gamma)$ and $z_0 \in \mathrm{ext}(\Gamma)$ indicate that z_0 lies inside and outside the contour Γ , respectively.

(2) Let $P(z)$ be a polynomial of degree n in the (complex) variable z , and let $\lambda_1, \lambda_2, \ldots, \lambda_n$ be its zeros. Then

$$P(z) = \prod_{k=1}^{n} (z - \lambda_k)$$

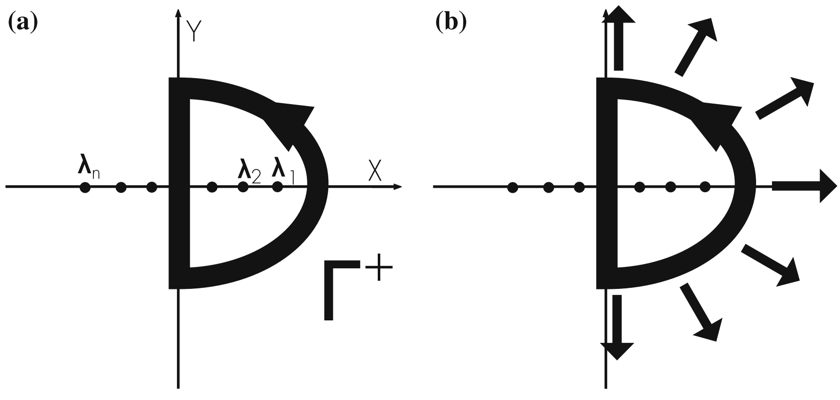

Figure 1. (a) A simple, positively oriented, contour Γ^+ in the complex plain, embracing all the positive zeros of the polynomial $P(z)$. The vertical part of Γ^+ lies on the y-axis. (b) Parts of Γ^+ are shifted to infinity, so that its vertical part remains on the y-axis.

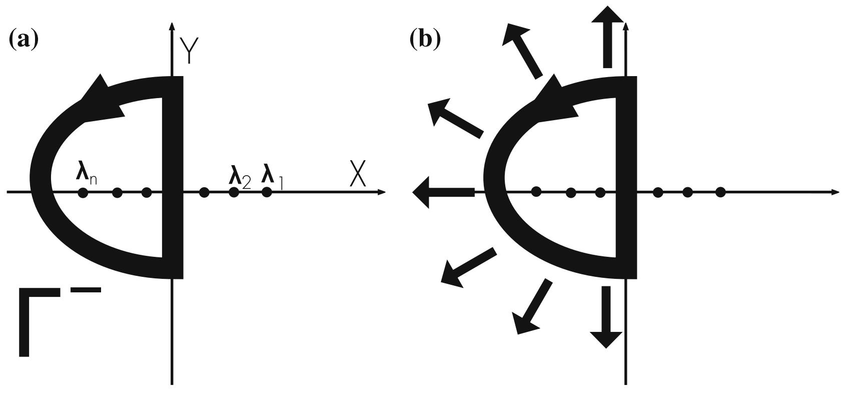

Figure 2. (a) A simple, positively oriented, contour Γ^- in the complex plain, embracing all the negative zeros of the polynomial $P(z)$. The vertical part of Γ^- lies on the y-axis. (b) Parts of Γ^- are shifted to infinity, so that its vertical part remains on the y-axis.

and, consequently,

$$P'(z) = (z-\lambda_2)(z-\lambda_3)\cdots(z-\lambda_n) + (z-\lambda_1)(z-\lambda_3)\cdots(z-\lambda_n) + \cdots + (z-\lambda_1)(z-\lambda_2)\cdots(z-\lambda_{n-1}),$$

from which follows

$$\frac{P'(z)}{P(z)} = \sum_{k=1}^{n} \frac{1}{z-\lambda_k}. \tag{3}$$

In our considerations we shall need the relation

$$\frac{z\,P'(z)}{P(z)} - n = \sum_{k=1}^{n} \frac{\lambda_k}{z-\lambda_k}, \tag{4}$$

that is readily obtained from (3). Because, evidently,

$$\frac{\lambda_k}{z-\lambda_k} \to 0 \quad \text{for} \quad |z| \to \infty$$

holds for all $k = 1, 2, \ldots, n$, from (4) we get

$$\left[\frac{z\,P'(z)}{P(z)} - n\right] \to 0 \quad \text{for} \quad |z| \to \infty. \tag{5}$$

Note that for the validity of the relations (3)–(5) it is not necessary that the zeros of the polynomial $P(z)$ be mutually distinct. As a consequence, also the Coulson formula (1) and its generalizations (14), (16), and (17) hold irrespective of the degeneracy of the zeros of the underlying polynomial.

In what follows we assume that all λ_k, $k = 1, 2, \ldots, n$, are real numbers different from zero. We denote by $\sum_+ \lambda_k$ and $\sum_- \lambda_k$ the sum of those λ_k that are positive and negative, respectively. Then, of course,

$$\sum_{+} \lambda_k + \sum_{-} \lambda_k = \sum_{k=1}^{n} \lambda_k .$$

Consider now the contour Γ^+ shown in figure 1a.

In view of the relations (2) and (4) we have

$$\frac{1}{2\pi i} \oint_{\Gamma^+} \left[\frac{z\,P'(z)}{P(z)} - n\right] \mathrm{d}z = \frac{1}{2\pi i} \oint_{\Gamma^+} \sum_{k=1}^{n} \frac{\lambda_k}{z-\lambda_k}\,\mathrm{d}z$$

$$= \sum_{k=1}^{n} \frac{\lambda_k}{2\pi i} \oint_{\Gamma^+} \frac{\mathrm{d}z}{z-\lambda_k} = \sum\nolimits_+ \lambda_k . \tag{6}$$

Because the value of the integral (7)

$$\oint_{\Gamma^+} \left[\frac{z\,P'(z)}{P(z)} - n\right] \mathrm{d}z \tag{7}$$

is independent of the actual form of the contour Γ^+ (provided it embraces all the positive-valued zeros of $P(z)$), we may inflate Γ^+ as indicated in figure 1b.

The idea behind the Coulson formula (1) is that in the limit case when Γ^+ becomes infinitely large, the only non-vanishing contribution to the integral (7) comes from integration along the y-axis. If so, then

$$\oint_{\Gamma^+} \left[\frac{z\,P'(z)}{P(z)} - n \right] \mathrm{d}z = \int_{+\infty}^{-\infty} \left[\frac{iy\,P'(iy)}{P(iy)} - n \right] \mathrm{d}(iy), \tag{8}$$

which combined with (6) straightforwardly results in formula (1).

In order that the integral over the part of the contour not lying on the y-axis vanishes, it is necessary that for $|z| \to \infty$, the integrand $z\,P'(z)/P(z) - n$ tends to zero sufficiently fast. It was sometimes believed that condition (5) suffices for the validity of the above procedure and thus for the validity of the Coulson formula (1). In what follows we show that this is not the case.

3. An apparent paradox

Using a precisely analogous reasoning as in the previous section, but integrating over the contour Γ^- shown in Figure 2a, we obtain

$$\frac{1}{2\pi i} \oint_{\Gamma^-} \left[\frac{z\,P'(z)}{P(z)} - n \right] \mathrm{d}z = \sum_{-} \lambda_k$$

a result that should be compared with formula (6). By increasing Γ^- as shown in Figure 2b, we obtain in the limit case

$$\oint_{\Gamma^-} \left[\frac{z\,P'(z)}{P(z)} - n \right] \mathrm{d}z = \int_{-\infty}^{+\infty} \left[\frac{iy\,P'(iy)}{P(iy)} - n \right] \mathrm{d}(iy) \tag{9}$$

leading to the expression analogous to (1), viz.,

$$\sum_{-} \lambda_k = -\frac{1}{2\pi} \int_{-\infty}^{+\infty} \left[n - \frac{i\,x\,P'(i\,x)}{P(i\,x)} \right] \mathrm{d}x, \tag{10}$$

that is valid under the precisely same conditions as the Coulson formula (1).

Comparing (1) and (10) we conclude that it must be

$$\sum_{+} \lambda_k = -\sum_{-} \lambda_k,$$

i.e.,

$$\sum_{k=1}^{n} \lambda_k = 0. \tag{11}$$

At the first glance condition (11) may look as a surprise, because in the derivation of the Coulson integral formula its validity was not (explicitly) required. Anyway, we have:

Proposition 1. The Coulson integral formula (1) holds if and only if the polynomial $P(z)$ has the property that the sum of its zeros is equal to zero.

If

$$\sum_{k=1}^{n} \lambda_k = h \neq 0, \tag{12}$$

then formula (1) is not valid and must not be applied. In the subsequent section we show how this difficulty can be overcome.

A more detailed analysis reveals that relation (11) is equivalent to

$$z \left[\frac{z\,P'(z)}{P(z)} - n \right] \to 0 \quad \text{for} \quad |z| \to \infty.$$

In the theory of functions of complex variables the conditions under which equalities of the type (8) and (9) are obeyed are known under the name of *Jordan Lemmas* [33–35].

4. Treating the case $\lambda_1 + \lambda_2 + \cdots + \lambda_n = h \neq 0$

The case described by equation (12) is of importance for the applications of the Coulson–type integral formulas in the theory of conjugated molecules containing heteroatoms (see, for instance [36,37]).

In order to overcome the difficulties outlined in the previous section, we introduce an auxiliary polynomial

$$\tilde{P}(z) = (z + h)\,P(z),$$

whose zeros are $\lambda_1, \lambda_2, \ldots, \lambda_n$, and $-h$. In view of relation (12), the sum of the zeros of $\tilde{P}(z)$ is equal to zero. Thus, formula (1) is applicable to $\tilde{P}(z)$.

We have to distinguish between two cases: $h > 0$ and $h < 0$.

Case 1: $h > 0$. Then $\tilde{P}(z)$ has no positive zeros other than the positive zeros of $P(z)$. Consequently,

$$\sum_{+} \lambda_k = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \left[n + 1 - \frac{ix\,\tilde{P}'(ix)}{\tilde{P}(ix)} \right] \mathrm{d}x. \tag{13}$$

Because of

$$\tilde{P}'(ix) = (ix + h)\,P'(ix) + P(ix)$$

the right-hand side of (13) is transformed into

$$\frac{1}{2\pi} \int_{-\infty}^{+\infty} \left[n - \frac{ix\,P'(ix)}{P(ix)} \right] \mathrm{d}x + \frac{1}{2\pi} \int_{-\infty}^{+\infty} \left[1 - \frac{ix}{ix + h} \right] \mathrm{d}x.$$

By direct integration we calculate

$$\frac{1}{2\pi}\int_{-\infty}^{+\infty}\left[1-\frac{ix}{ix+h}\right]\mathrm{d}x=\frac{1}{2}\,|h|,$$

which finally results in the following remarkably simple generalization of the Coulson formula:

$$\sum_{+}\lambda_k=\frac{h}{2}+\frac{1}{2\pi}\int_{-\infty}^{+\infty}\left[n-\frac{ix\,P'(ix)}{P(ix)}\right]\mathrm{d}x. \tag{14}$$

As shown below, relation (14) holds also if $h<0$.
Case 2: $h<0$. Then $-h$ is an additional positive-valued zero of $\tilde{P}(z)$ and therefore

$$\sum_{+}\lambda_k-h=\frac{1}{2\pi}\int_{-\infty}^{+\infty}\left[n+1-\frac{ix\,\tilde{P}'(ix)}{\tilde{P}(ix)}\right]\mathrm{d}x. \tag{15}$$

By an identical reasoning as in the previous case we obtain

$$\sum_{+}\lambda_k-h=\frac{1}{2}\,|h|+\frac{1}{2\pi}\int_{-\infty}^{+\infty}\left[n-\frac{ix\,P'(ix)}{P(ix)}\right]\mathrm{d}x,$$

which, by taking into account that now $|h|=-h$, leads also to formula (14).

Proposition 2. The Coulson–type integral formula (14) holds for any value of h, where h is the sum of the zeros of the underlying polynomial $P(z)$.

Evidently, the original Coulson integral formula (1) is the special case of (14) for $h=0$.

From (14) it is straightforward to deduce expressions for the sum of the negative zeros and of the absolute values of all zeros of a polynomial. We state them for the sake of completeness:

$$\sum_{-}\lambda_k=\frac{h}{2}-\frac{1}{2\pi}\int_{-\infty}^{+\infty}\left[n-\frac{ix\,P'(ix)}{P(ix)}\right]\mathrm{d}x \tag{16}$$

$$\sum_{k=1}^{n}|\lambda_k|=\frac{1}{\pi}\int_{-\infty}^{+\infty}\left[n-\frac{ix\,P'(ix)}{P(ix)}\right]\mathrm{d}x. \tag{17}$$

In parallel with (14), also the identities (16) and (17) hold for any value of h.

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