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REGULAR ARTICLE

Analytical derivation of the Hückel “4*n* + 2 rule”

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Abstract The “$4n + 2$ rule” is derived analytically at the level of the simple Hückel theory for neutral even-membered chains, their double ions, as well as cations and anions of the odd-membered chains, by determining the first order energetic effect of the ring closure. The topological background of the “$4n + 2$ rule” is also briefly discussed.

Keywords Aromaticity · Antiaromaticity · Huckel $4n + 2$ rule · Topology of MO nodes

1 Introduction

One of the basic steps in understanding the concepts of (anti)aromaticity was to put forward the question: “is *cyclic* delocalization energetically preferable (stabilizing)?”. If the answer is “yes”, we have aromaticity, if the answer is “no” or “not enough” (for instance, not enough to prevent addition reactions), then we have either antiaromaticity or simple “delocalization”.

The answer to this question is to a large extent connected to the topology (distribution of nodes) of the low lying molecular orbitals. The decisive role of the global orbital topoplogy should be assumed in order to explain why most different structures with 6 (10) electrons are energetically favourable, in both stable molecules and transition states. Therefore, the simple Hückel model [1, 2]—which just reflects the topology of the system—may still give a useful contribution to our understanding aromaticity and antiaromaticity.

According to the “$4n + 2$ rule”, usually attributed to Hückel, but probably never used by him personally [3], cyclic systems are expected to be aromatic if they have $4n + 2$ electrons and antiaromatic if they have $4n$ electrons. Otherwise, aromatic systems have twice an odd number, $2\ (2n + 1) = 4n + 2$, of electrons, while antiaromatic ones twice an even number, $2\ (2n) = 4n$, of them. (We do not consider here the aromaticity/antiaromaticity of systems with an odd number of electrons.) In the framework of the Hückel theory one usually explains this by considering the energy levels of a regular polygon and referring to our general belief that electronic configurations with closed shells are particularly stable. In fact, the electronic levels of a regular Hückel polygon with k vertices are distributed in the manner that after the total-symmetric lowest level with the eigenvalue 2β follow pairs of doubly degenerate levels (corresponding to two-dimensional irreducible representations of the symmetry group) with the eigenvalues $2\beta\cos(2\pi l/k)$, $l = 1,2,\ldots$ (We recall that the “resonance integral” $\beta < 0$ in the Hückel theory, reflecting the fact that the formation of a delocalized bonding MO between two centers leads to some energy gain.) Thus, in order to ensure that the basis functions of each irreducible representation are either completely occupied or completely empty, we have to fill an odd number of levels; as two electrons of opposite spin can be put on each level, this requires twice an odd number, i.e., $4n + 2$ of electrons. However, the stability of closed shells, although fulfilled in most cases, cannot be derived in a truly general form, thus referring

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Dedicated to Dr. Sándor Suhai on the occasion of his 65th birthday and of our nearly 40 years of acquaintance.

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to it may be considered insufficient for a true explanation of the "$4n + 2$ rule".

Furthermore, it is not the stability of the cyclic system in itself which is of true importance. If one considers basic criteria of aromaticity, then the dichotomy of addition versus substitution reactions depends on the energy gain which can be connected with the cyclic π-electron delocalization; to judge about this, one has to compare the open-ended and the closed Hückel chains of the same length. Thus we propose to start considering the problem by using the known solutions for the open-ended chains.

In papers [4, 5] the problem of polyenes and annulenes was considered from a wide perspective; analytical expressions were derived for the different bond orders of neutral systems and different aspects of their aromaticity/antiaromaticity were discussed (as e.g., the mechanisms of polyene thermo- and photoelectrocyclic reactions) even if not explicitly from the point of view of the energetic effect of the cyclic delocalization mentioned above.[1] Among others, it has been demonstrated that the Coulson bond orders between the two ends in the "$4n$" and "$4n + 2$" polyenes are of opposite signs which permitted to categorize them as Hückel-type and Möbius-type systems, respectively [5]. This has some close relationship to our energetic approach discussed below.

Coulson had solved analytically the problem of linear Hückel chain (see e.g., in [6]). For an open-ended linear chain of the length $m = 2k$, the MO coefficients are given by his formula

$$C_{jr} = \sqrt{\frac{2}{2k+1}}\sin\left(\frac{jr\pi}{2k+1}\right) \tag{1}$$

where j is the index of the carbon atom and r of the MO (or vice versa—matrix $\mathbf{C}$ is both orthogonal and symmetric).

Now we close the ring by introducing the respective $H_{1m} = H_{m1} = 1$ matrix elements (in $\beta < 0$ units). According to the known relationship between the Hückel energy and Coulson's bond orders $E = Tr(\mathbf{HD})$ the first order energy change will be

$$\Delta E^{(1)} = 2D_{1m} \tag{2}$$

That means that the Coulson's bond order between the ends of an open chain predicts the first order effect on the ring closure. It is stabilizing if $D_{1m} > 0$ and destabilizing if $D_{1m} < 0$. This point has already been noted by Dewar [7].[2]

Using the coefficients in Eq. 1, one could calculate this bond order analytically, and it shows a characteristic sign alternation and leads to the "$4n + 2$ rule" in all cases.

2 Neutral polyene of length $m = 2k$

$$D_{1(2k)} = \frac{(-1)^{(k+1)}}{2k+1}\left[2\cos^2\frac{\pi}{4k+2} + \mathrm{tg}\frac{\pi}{2k+1}\sin\frac{\pi}{2k+1}\right] \tag{3}$$

All the angles are less than $\pi/2$, so the expression in the braces is positive.[3] Therefore, Eq. 3 predicts that the ring closure is stabilizing if k is an odd number, and destabilizing k is even. The number of π-electrons is $N = m = 2k$, i.e., we get stabilization (possible aromaticity) if the number of electrons is twice an odd number, an destabilization (antiaromaticity) if it is twice an even number. Thus we have derived the "$4n + 2$ rule" for the neutral chains.

In agreement with this general result, one gets for butadiene ($k = 2$) a negative value, $D_{14} = -0.4472...$ (can be expressed analytically through $\sqrt{5}$), for hexatriene positive, and so on, predicting cyclobutadiene to be antiaromatic and benzene aromatic.

3 Double ions of chains with length $m = 2k$

The double ions can be either cations or anions—the results coincide due to the pairing properties of π-orbitals of alternating hydrocarbons:[4]

$$D_{1(2k)} = (-1)^k\frac{2}{2k+1}\cos\frac{\pi}{4k+2}\cos\frac{3\pi}{4k+2}\Big/\cos\frac{\pi}{2k+1} \tag{4}$$

All the trigonometric functions are again positive, so Eqs. 3 and 4 are always of opposite sign with respect to each other: $D_{1(2k)}$ is now positive if k is even. The number of π-electrons is $N = m \pm 2 = 2(k \pm 1)$, so again the ring closure is stabilizing if it equals twice an odd number. Thus, we have derived the "$4n + 2$ rule" for the double ions of even-membered chains.

This result means that the diions of cyclobutadiene are expected to be aromatic and those of benzene to be antiaromatic.

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[1] The author is grateful to a Referee for calling his attention to Refs. [4, 5].

[2] The author is indebted to a Referee for calling his attention to Ref. [7].

[3] In Ref. [5] the even more compact, but of course equivalent, form $D_{1(2k)} = \frac{(-1)^{(k-1)}}{2k+1}\left(1 + \sec\frac{\pi}{2k+1}\right)$ was given (in our notations). In Eq. 3 we kept the formula as it was obtained by us.

[4] In the positive ion we omit some terms as compared with the neutral molecule, for the negative ion we add the same term once more but with opposite sign, as the two ends necessarily belong to different subsets (starred and not starred) of carbons.

4 Ions of radicals (odd-membered chains) of length $m = 2k + 1$

For the (single) ions of odd-membered polyenes of length $m = 2k + 1$ one has

$$D_{1(2k+1)} = \pm\frac{(-1)^{k+1}}{k+1} \tag{5}$$

Sign "+" corresponds to positive ions (cations), sign "−" to negative ones (anions). This simplicity is due to a theorem according to which the Hückel matrix elements between atoms of the same (starred or not starred) subset of atoms vanish in the neutral species. The ending atoms of an odd-membered chain belong to the same set, therefore, in the ion all the contributions cancel except that from the non-bonding orbital—one either takes away the electron from it or adds another one to it. Now, the non-bonding orbital is known to have zero expansion coefficients on the atoms with even numbers while all its coefficients on the odd numbered atoms have the absolute value of $1/\sqrt{k+1}$ and alternating signs.

The number of π-electrons is $2k$ for the cations and $2k + 2 = 2(k + 1)$ for the anions. $D_{1(2k+1)}$ is positive for the cations if k is odd, while for the anions k should be even for that purpose; thus we get again for both cases that the ring closure is stabilizing if the number of electrons is twice an odd number. Thus, we have derived the "$4n + 2$ rule" for the ions of odd-membered chains.

A remarkable special case of this point is that for the pentadienyl anion one gets the value $D_{15} = 1/3$, which is even greater than D_{16} for hexatriene (0.3014...), in full accord with the known aromaticity of cyclopentadienyl anion having six π-electrons.

5 Discussion

Second order energy corrections to the ground state energy are always negative [8] and in our case that is valid to the sum of the second and higher energy corrections, too—see Fig. 1. They exhibit only a moderate alternation, and for systems not fulfilling the Hückel "$4n + 2$ rule" these negative energy contributions are not sufficient to compensate the significant positive energy component observed at the first order, and the total energy change of ring closure is either positive (cyclobutadiene) or is not sufficient to compensate for the fact that the number of the σ bonds decreases by one when closing the ring. (The energy lowering due to the ring closure is $0.139|\beta|$ and $0.336|\beta|$—ca. 8 and 19 kcal/mol—for the octatetraene and dodecahexaene cases, respectively.)

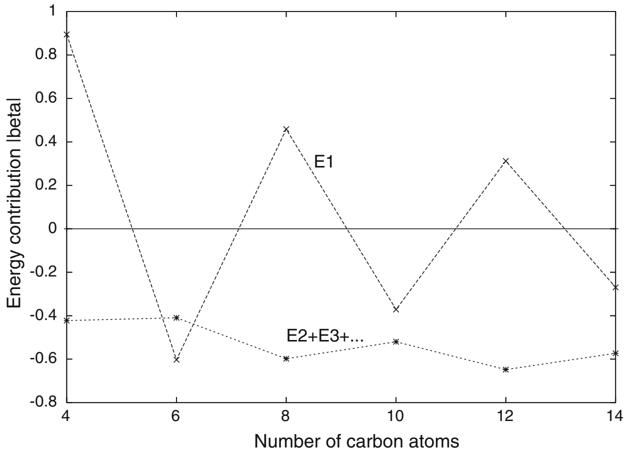

Fig. 1 The first order and higher order energy contributions taking place when a Hückel chain is closed

Finally, we shall briefly discuss the topological source of these strong alternations. It is known that the lowest energy level has no nodes, the second has one, the third two, and so on. Thus, for the first level the coefficients at the two ends of the chain are of the same sign, giving a positive contribution to the density matrix elements D_{1m}, for the second level these coefficients are of opposite sign and give a negative contribution, the third again gives a positive one etc. Thus, in butadiene there are two contributions of opposite sign. Simple considerations show that the negative must have a larger absolute value. In fact, the conjugation (delocalization) in open-ended butadiene chain leads to an energy lowering if and only if $D_{23} > 0$. This means that for the nodeless lowest state the coefficients at the positions 2 and 3 should be greater in absolute value than those of the second level for which there is a sign change. As the orbitals are normalized, the situation for the outer coefficients must be the opposite, leading to a negative D_{14} matrix element, and destructive cyclic delocalization in the cyclobutadiene. (Therefore, it is unstable and contains two practically isolated double bonds.) In hexatriene there are two positive and only one negative contributions to D_{16}, and the former ones prevail. With the further increase of the chain we have a further alternating effect, even if with a decreasing amplitude. These qualitative considerations show that the results obtained above at the Hückel level must remain basically true for more refined schemes, as well, and should reflect the actual chemical behaviour of the systems in question.

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References

1. Hückel E, Physik Z (1931) 70:204
2. Hückel E, Physik Z (1932) 76:628
3. Schleyer PVR (2008) Girona seminar on aromaticity. Girona, Spain

4. Karadakov P, Castaño O, Fratev F, Enchev V (1981) Chem Phys Lett 78:560
5. Fratev F, Enchev V, Karadakov P, Castaño O (1984) Int J Quantum Chem 26:993
6. Daudel R, Lefebvre R, Moser C (1959) Quantum chemistry. Methods and applications. Interscience, New York
7. Dewar MJS (1969) The molecular orbital theory of organic chemistry. McGraw-Hill, New York
8. Landau LD, Lifshitz EM (1974) Kvantovaya mekhanika, 3rd edn. Nauka, Moscow