

## **Aromaticity of annulenes and annulene ions with $4\nu + 2$ electrons from the viewpoint of the theory of Hartree–Fock instabilities**

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The connection between the aromaticity of annulenes and annulene ions with  $4\nu + 2$   $\pi$ -electrons and the stability of the closed-shell restricted Hartree–Fock (RHF) solutions for these systems is discussed in the framework of the PPP-approximation. It is shown that the tendency towards an uniform electron density distribution in aromatic cycles is paralleled by the stability properties of the corresponding closed-shell RHF solutions. The stability investigations are demonstrated to provide realistic estimates of the critical ring sizes at which Hückel's  $4\nu + 2$  rule breaks down.

**Key words:** Aromaticity — Annulenes — Hartree–Fock instabilities

### **1. Introduction**

Hückel's classical  $4\nu + 2$  rule [1] has given the impetus for a number of theoretical and synthetic investigations aimed at a clarification of the phenomenon of aromaticity. The annulenes provide the oldest and most frequently discussed model in this respect, attracting much interest both from the theoretical as well as from the synthetic point of view. The attention of a number of authors [2–10] has been focused on two basic problems: (i) the search for a theoretical criterion allowing to predict the aromatic character of annulenes with  $4\nu + 2$   $\pi$ -electrons, respectively, the antiaromatic character of annulenes with  $4\nu$   $\pi$ -electrons and (ii) to test whether there exists a critical ring size limiting the validity of Hückel's

rule. As is well known (see, e.g. [11] and references therein), aromatic compounds exhibit (i) a decrease in the alternation of “single” and “double” bonds and (ii) a tendency towards an uniform electron density distribution on atoms and bonds [an obvious example for (i) and (ii) is benzene].

According to Longuet-Higgins and Salem [2], Hückel's  $4\nu+2$  rule breaks for the [18]-annulene which is indicated by the fact that at this ring size the structure with alternating bond-lengths, i.e., “single” and “double” bonds, becomes lower in energy than the corresponding structure with equal bondlengths. Later PPP-studies of Dewar and Gleicher [3] have shown that the critical ring size for the appearance of bond alternation is between the [22] and [26]-annulene. This result has also been confirmed by NMR investigations [10]. The limiting ring sizes indicated by other authors [6, 8, 9] in principle closely approach either the value given by Longuet-Higgins and Salem, or the value given by Dewar and Gleicher.

The  $[4\nu+2]$ -annulenes have been chosen by Čížek and Paldus [12–14] as a convenient  $\pi$ -electronic model in their studies of the stability of closed-shell restricted Hartree-Fock (RHF) solutions. Their PPP-investigations reveal several interesting phenomena: (i) When using the Mataga-Nishimoto parametrization [15], the closed-shell RHF solutions for annulenes with up to 26 atoms are singlet stable. The closed-shell RHF solution for the [26]-annulene is singlet unstable and in addition to this solution one can find another closed-shell HF solution with lower energy and broken spatial symmetry – the so-called off-diagonal charge-density wave (CDW) [or, bond-order alternation wave (BAW)] solution. A characteristic feature of this broken-symmetry solution is the alternation of bond-orders between starred and non-starred atoms (the even annulenes are alternant systems); (ii) when using the Pariser-Parr [16], or the theoretical [17] parametrization, the ring size for which one observes the effects described in (i) is shifted to the [18]-annulene. Obviously, there exists a very good agreement between the ring sizes limiting the validity of Hückel's  $4\nu+2$  rule and the ring sizes at which the closed-shell RHF solutions for  $[4\nu+2]$ -annulenes become singlet unstable, and there appear new solutions of the BAW type. The analysis of the  $\pi$ -electronic model of the allyl radical in the framework of the PPP-approximation performed by Paldus and Veillard [18] has demonstrated that the existence of a broken symmetry solution with different bond-orders for the equidistant structure implies an energy lowering upon a distortion of the nuclear framework in accordance with the bond-order magnitudes. Similar results for model infinite systems with nearest-neighbor Coulomb interactions have been obtained by Kondo [19] and by Fukutome and Sasai [20]. It has been observed for a number of finite and infinite systems [18–24] that the relaxation of the nuclear framework according to the bond-order distribution for a BAW solution leads to an additional decrease of the total energy. Kertész et al. [25] have argued that the nonuniform electron density distribution between atoms leads to the appearance of nonzero Hellman-Feynman forces pulling the nuclei together in the high-density region. Thus, it appears that there exists a close relationship between BAW solutions and bond alternation. In the case of annulenes this relationship is further confirmed by the fact that the geometry of the antiaromatic

cyclobutadiene optimized in the framework of the PPP-method exhibits alternating bond-lengths (see the recent review [26] and the references therein), while the authors of [27] have found for the square geometry a PPP-solution with alternating bond-orders.

For large cycles Paldus and Čížek have found [14] an additional closed-shell HF solution with broken spatial symmetry – the so-called diagonal CDW's (or, simply, CDW's) which are characterized by alternating atomic charges.

It should be mentioned that as both BAW and CDW solutions exhibit nonuniform electron density distributions, the related values of the information index of aromaticity [11] based on the charge-density and bond-order matrix should be low and corresponding to nonaromatic character. One could also make another supposition of a more speculative character, that the absence of solutions with nonuniform electron distribution for  $[4\nu+2]$ -rings of moderate size is related to their lower reactivity which is usually attributed to aromatic stabilization. In this respect one should also study the nonsinglet (or, triplet) stability of the pertinent closed-shell RHF solutions which is connected with the possible existence of spin-unrestricted HF (spin-UHF) solutions, the importance of which for the explanation of the mechanisms of radical reactions has been emphasized by Fukutome et al. (see [28] and Refs. therein). The considerations adduced above show that there should exist a connection between the aromaticity of  $[4\nu+2]$ -annulenes and the stability of the pertinent closed-shell RHF solutions. In this article we present PPP-investigations of the stability of the closed-shell RHF solutions for cycles with  $4\nu+2$  electrons, which, according to Hückel's rule, should be aromatic at least for moderate ring sizes. Calculations have been carried out not only for the  $[4\nu+2]$ -annulenes, but also for several charged systems with  $4\nu+2$  electrons – the  $[4\nu+1]^-$ -annulene anions, the  $[4\nu+3]^+$ -annulene cations, the  $[4\nu]^{2-}$ -annulene dianions and the  $[4(\nu+1)]^{2+}$ -annulene dications. By these investigations we trace the possible relationship between the stability of the closed-shell RHF solutions for cycles with  $4\nu+2$  electrons and their aromaticity.

## 2. Theory

The formalism developed by Paldus and Čížek in their investigations of the stability of the closed-shell RHF solutions for  $[4\nu+2]$ -annulenes [12–14] can straightforwardly be adapted to the cases of different closed-shell annulene ions.

It is well known that the high spatial symmetry of an  $N$ -atomic cycle with equal bondlengths (point group  $D_{Nh}$ ) completely determines the form of the pertinent RHF orbitals. Each one of these orbitals belongs to a definite one-dimensional irreducible representation of the subgroup  $C_N$  of the point group  $D_{Nh}$  and may conveniently be labelled [12–14] by its quasimomentum  $j$  ( $j=0, 1, 2, \dots, N-1$ ).

The symmetry factorization of the closed-shell stability problems in the case of  $[4\nu+2]$ -annulenes has been described in detail in [14]. A similar factorization is applied for each one of the charged cyclic systems with  $4\nu+2$  electrons in the present article. It is due to the fact that the only nonzero elements

of the matrices  $A^x$ ,  $B^x$  ( $x = s, ns$ ) participating in the singlet and nonsinglet stability problems (for definitions, see, e.g. [12]) are:

$$\begin{aligned} A_{k_p \rightarrow k_p+p, l_p \rightarrow l_p+p}^s &= A_{-k_p \rightarrow -k_p-p, -l_p \rightarrow -l_p-p}^s \\ &= \Delta(k_p) \delta_{k_p, l_p} + 2K(p) - K(k_p - l_p), \end{aligned} \quad (1a)$$

$$\begin{aligned} B_{k_p \rightarrow k_p+p, -l_p \rightarrow -l_p-p}^s &= B_{-k_p \rightarrow -k_p-p, l_p \rightarrow l_p+p}^s \\ &= 2K(p) - K(k_p + l_p + p), \end{aligned} \quad (1b)$$

$$\begin{aligned} A_{k_p \rightarrow k_p+p, l_p \rightarrow l_p+p}^{ns} &= A_{-k_p \rightarrow -k_p-p, -l_p \rightarrow -l_p-p}^{ns} \\ &= \Delta(k_p) \delta_{k_p, l_p} - K(k_p - l_p) \end{aligned} \quad (2a)$$

$$\begin{aligned} B_{k_p \rightarrow k_p+p, -l_p \rightarrow l_p-p}^{ns} &= B_{-k_p \rightarrow -k_p-p, l_p \rightarrow l_p+p}^{ns} \\ &= -K(k_p + l_p + p) \end{aligned} \quad (2b)$$

where  $p = 1, 2, \dots, n$  for even values of  $N$  ( $N = 2n$ ) as well as for odd values of  $N$  ( $N = 2n + 1$ ). In the above equations and further in the text all indices labelling orbitals should be taken modulo  $N$ . The indices  $k_p, l_p$  belong to the set  $G_p$ :

$$G_p \equiv \{\nu - p + 1, \nu - p + 2, \dots, \nu\}, \quad (3a)$$

and the indices  $-k_p, -l_p$  - to the set  $G_{N-p}$ :

$$G_{N-p} \equiv \{-\nu + p - 1, -\nu + p - 2, \dots, -\nu\}. \quad (3b)$$

The sets  $G_p, G_{N-p}$  represent subsets of the set  $G$  comprised of the indices of the occupied RHF orbitals:

$$G \equiv \{-\nu, -\nu + 1, \dots, \nu\}. \quad (4)$$

There are two exceptions from the definitions (3), namely in the case of  $[4\nu]^{2-}$ -annulene dianions

$$G_{N/2} \equiv G_n \equiv G_{2\nu} \equiv \{-\nu + 1, -\nu + 2, \dots, \nu - 1\}, \quad (5a)$$

and in the case of  $[4(\nu + 1)]^{2+}$ -annulene dication:

$$G_{N/2} \equiv G_n \equiv G_{2\nu+2} \equiv G \quad (5b)$$

It may easily be shown that the quasimomentum transfer [12] corresponding to the orbital monoexcitation  $k_p \rightarrow k_p + p$  is equal to  $p$ , while the quasimomentum transfer corresponding to the orbital monoexcitation  $-k_p \rightarrow -k_p - p$  is equal to  $N - p$ .

The quantity  $K(j)$  is given by:

(i) for even values of  $N$  ( $N = 2n$ ) [14]:

$$K(j) = N^{-1} \left[ \gamma_{00} + (-1)^j \gamma_{0n} + 2 \sum_{\mu=1}^{n-1} \gamma_{0\mu} \cos(2\pi j\mu/N) \right]; \quad (6a)$$

(ii) for odd values of  $N$  ( $N = 2n + 1$ ):

$$K(j) = N^{-1} \left[ \gamma_{00} + 2 \sum_{\mu=1}^n \gamma_{0\mu} \cos(2\pi j\mu/N) \right]. \quad (6b)$$

Here  $\gamma_{\mu\nu}$  denotes the Coulomb repulsion integral between the atomic orbitals  $\mu$  and  $\nu$ .

The quantity  $\Delta(k_p)$  stands for the difference between the orbital energies [14] of the orbitals with quasimomenta  $k_p + p$  and  $k_p$ :

$$\Delta(k_p) = 2\beta \{ \cos [2\pi(k_p + p)/N] - \cos (2\pi k_p/N) \} - \sum_{l \in G} [K(k_p + p - l) - K(k_p - l)], \quad (7)$$

where  $\beta$  represents the resonance integral between neighboring atomic orbitals.

For the sake of convenience, further in this article we shall denote the orbital monoexcitations labelling nonzero elements of the matrices  $\mathbf{A}^x$ ,  $\mathbf{B}^x$  only by the indices of the corresponding occupied orbitals, i.e. the orbital monoexcitation  $k_p \rightarrow k_p + p$  will be denoted simply by  $k_p$ , and the orbital monoexcitation  $-k_p \rightarrow -k_p - p$  by  $-k_p$ . Bearing this convention in mind, the subproblems resulting from the symmetry factorization of the singlet and nonsinglet stability problems may be represented as [note that the pair of Eqs. (8a) and (8b) defines one eigenvalue/eigenvector problem]:

$$\sum_{l_p \in G_p} [A_{k_p, l_p}^x e_{l_p}^{x,y} + (-1)^y B_{k_p, -l_p}^x e_{-l_p}^{x,y}] = \eta_p^{x,y} e_{k_p}^{x,y}, \quad (8a)$$

$$\sum_{l_p \in G_p} [(-1)^y B_{-k_p, l_p}^x e_{l_p}^{x,y} + A_{-k_p, -l_p}^x e_{-l_p}^{x,y}] = \eta_p^{x,y} e_{-k_p}^{x,y} \quad (8b)$$

$$(x = s, ns; y = 0, 1; k_p \in G_p).$$

In Eqs. (8)  $p = 1, 2, \dots, n-1$  for even values of  $N$  ( $N = 2n$ ) and  $p = 1, 2, \dots, n$  for odd values of  $N$  ( $N = 2n + 1$ ). For even values of  $N$  there appears also a  $p = n$  subproblem, the so-called maximum quasimomentum transfer subproblem [14]. This subproblem may be represented by either one of Eqs. (8a), (8b), or, alternatively, as (see also [14]):

$$\sum_{l_n \in G_n} [A_{k_n, l_n}^x + (-1)^y B_{k_n, l_n}^x] e_{l_n}^{x,y} = \eta_n^{x,y} e_{k_n}^{x,y} \quad (9)$$

$$(x = s, ns; y = 0, 1; k_n \in G_n).$$

There exist unitary transformations which allow the further factorization of the eigenvalue/eigenvector problems (8) ( $p \neq n$  for even values of  $N$ ):

$$^+ e_{k_p}^{x,y} = 2^{-1/2} (e_{k_p}^{x,y} + e_{-k_p}^{x,y}), \quad (10a)$$

$$^- e_{k_p}^{x,y} = 2^{-1/2} (e_{k_p}^{x,y} - e_{-k_p}^{x,y}). \quad (10b)$$

As a result, one obtains subproblems of a twice lower dimension:

$$\sum_{l_p \in G_p} [A_{k_p, l_p}^x + (-1)^y B_{k_p, -l_p}^x]^+ e_{l_p}^{x,y} = ^+ \eta_p^{x,y} e_{k_p}^{x,y}, \quad (11)$$

$$\sum_{l_p \in G_p} [A_{k_p, l_p}^x - (-1)^y B_{k_p, -l_p}^x]^- e_{l_p}^{x,y} = ^- \eta_p^{x,y} e_{k_p}^{x,y}. \quad (12)$$

For the sake of convenience, further in the text we shall refer to Eq. (11) as to the  $(p, x, y, +)$  stability subproblem, and to Eq. (12) – as to the  $(p, x, y, -)$  stability

subproblem. It may be easily established with the help of Eqs. (1), (2), (11), (12) that the matrices of some of the subproblems (11), (12) are identical. Such are the matrices of the  $(p, s, 0, +)$  and  $(p, s, 1, -)$  subproblems, as well as the matrices of the  $(p, ns, 0, +)$  and  $(p, ns, 1, -)$  subproblems. The matrices of the  $(p, s, 0, -)$ ,  $(p, s, 1, +)$ ,  $(p, ns, 0, -)$ ,  $(p, ns, 1, +)$  subproblems are also identical.

The  $p = n$  subproblems (9) appearing for even values of  $N$  may also be subjected to further factorization by means of the unitary transformation proposed in [14]:

$${}^+e_{0_n}^{x,y} = e_{0_n}^{x,y}, \quad (13a)$$

$${}^+e_{k_n}^{x,y} = 2^{-1/2}(e_{k_n}^{x,y} + e_{-k_n}^{x,y}) \quad (13b)$$

$${}^-e_{k_n}^{x,y} = 2^{-1/2}(e_{k_n}^{x,y} - e_{-k_n}^{x,y}). \quad (13c)$$

In Eqs. (13b), (13c)  $k_n \in G_n^>$ , where  $G_n^>$  is a subset of  $G_n$ . In the case of  $[4\nu+2]$ -annulenes

$$G_n^> \equiv G_{2\nu+1}^> \equiv \{1, 2, \dots, \nu\}, \quad (14a)$$

in the case of  $[4\nu]^{2-}$ -annulene dianions

$$G_n^> \equiv G_{2\nu}^> \equiv \{1, 2, \dots, \nu-1\}, \quad (14b)$$

and in the case of  $[4(\nu+1)]^{2+}$ -annulene dication

$$G_n^> \equiv G_{2\nu+2}^> \equiv \{1, 2, \dots, \nu\}. \quad (14c)$$

The  $(n, x, y, +)$  subproblem arising from a  $p = n$  subproblem may be represented as [the subscripts  $n$  have been omitted from Eqs. (15), (16) for the sake of convenience]:

$$[A_{00}^x + (-1)^y B_{00}^x]{}^+ e_0^{x,y} + 2^{1/2} \sum_{l \in G^>} [A_{0l}^x + (-1)^y B_{0l}^x]{}^+ e_l^{x,y} = {}^+ \eta^{x,y} e_0^{x,y} \quad (15a)$$

$$2^{1/2} [A_{k_0}^x + (-1)^y B_{k_0}^x]{}^+ e_0^{x,y} + \sum_{l \in G^>} [A_{kl}^x + A_{k,-l}^x + (-1)^y (B_{kl}^x + B_{k,-l}^x)]{}^+ e_l^{x,y} = {}^+ \eta^{x,y} e_k^{x,y}. \quad (15b)$$

There arises also a  $(n, x, y, -)$  subproblem:

$$\sum_{l \in G^>} [A_{kl}^x - A_{k,-l}^x + (-1)^y (B_{kl}^x - B_{k,-l}^x)]{}^- e_l^{x,y} = {}^- \eta^{x,y} e_k^{x,y} \quad (16)$$

The analysis of Eqs. (15), (16) shows that the matrices of the  $(n, ns, 1, +)$  and  $(n, s, 1, +)$  subproblems are identical. The same holds for the matrices of the  $(n, ns, 0, -)$  and  $(n, s, 0, -)$  subproblems and for the matrices of the  $(n, ns, 1, -)$  and  $(n, s, 1, -)$  subproblems.

### 3. Numerical results and discussion

At the beginning of this section we provide a brief description of the parameterization scheme employed in the present stability investigations. It has been assumed that the value of the resonance integral  $\beta$  is  $-2.388$  eV, while the Coulomb repulsion integrals have been calculated using the Mataga-Nishimoto formula

**Table 1.** Lowest eigenvalues of the singlet stability problem for cyclic systems with  $4\nu+2$  electrons (see text for explanations)

$\nu$	$[4\nu+2]$	$[4\nu+1]^-$	$[4\nu+3]^+$	$[4\nu]^{2-}$	$[4(\nu+1)]^{2+}$
0	—	—	7.164*	—	4.776*
1	4.179	5.340*	4.041*	4.776*	3.377*
2	1.943	3.111	2.329	3.377*	2.087
3	0.950	1.778	1.371	2.087	1.267
4	0.395	1.058	0.810	1.267	0.767
5	0.043	0.610	0.444	0.767	0.432
6	-0.198	0.305	0.187	0.432	0.193
7	-0.373	0.085	-0.003	0.193	0.015
8	-0.505	-0.081	-0.149	0.015	-0.123
9	-0.607	-0.210	-0.264	-0.123	-0.232
10	-0.689	-0.313	-0.357	-0.232	-0.321

[15];  $\gamma_{00} = 10.84$  eV. The distance between neighboring atoms has been assumed to be equal to 1.40 Å.

We have performed investigations of the stability of the closed-shell RHF solutions for  $[4\nu+2]$ -annulenes,  $[4\nu+1]^-$ -annulene anions,  $[4\nu+3]^+$ -annulene cations,  $[4\nu]^{2-}$ -annulene dianions and  $[4(\nu+1)]^{2+}$ -annulene dications with  $\nu$  taking integer values from 0 to 10. The obtained lowest eigenvalues of the singlet and nonsinglet stability problems are given in Tables 1 and 2.

The eigenvalues adduced in Table 1 (except those marked by an asterisk) originate from the following subproblems: for the  $[4\nu+2]$ -annulenes - from the  $(n, s, 1, -)$  subproblems; for the  $[4\nu+1]^-$ -annulene anions and for the  $[4\nu+3]^+$ -annulene cations - from the  $(n, s, 0, +)/(n, s, 1, -)$  subproblems; for the  $[4\nu]^{2-}$ -annulene dianions and for the  $[4(\nu+1)]^{2+}$ -annulene dications from the  $(n, s, 0, +)$  subproblems. The eigenvalues marked by an asterisk originate from the  $(1, s, 0, -)/(1, s, 1, -)$ -subproblems. The eigenvalues from Table 2 (except

**Table 2.** Lowest eigenvalues of the nonsinglet stability problem for cyclic systems with  $4\nu+2$  electrons see text for explanations)

$\nu$	$[4\nu+2]$	$[4\nu+1]^-$	$[4\nu+3]^+$	$[4\nu]^{2-}$	$[4(\nu+1)]^{2+}$
0	—	—	3.456*	—	1.532*
1	-0.201	1.753	0.624	1.532*	0.289
2	-1.475	-0.102	-0.598	0.289	-0.606
3	-2.049	-0.956	-1.226	-0.606	-1.126
4	-2.369	-1.436	-1.604	-1.126	-1.459
5	-2.568	-1.742	-1.856	-1.459	-1.688
6	-2.703	-1.954	-2.037	-1.688	-1.856
7	-2.800	-2.110	-2.173	-1.856	-1.985
8	-2.871	-2.230	-2.280	-1.985	-2.087
9	-2.926	-2.325	-2.365	-2.087	-2.170
10	-2.969	-2.402	-2.436	-2.170	-2.239

those marked by an asterisk appear in the following subproblems: for the  $[4\nu+2]$ -annulenes in the  $(n, ns, 0, +)$  subproblems; for the  $[4\nu+1]^-$ -annulene anions and for the  $[4\nu+3]^+$ -annulene cations – in the  $(n, ns, 0, +)/(n, ns, 1, -)$ -subproblems; for the  $[4\nu]^{2-}$ -annulene dianions and for the  $[4(\nu+1)]^{2+}$ -annulene dications – in the  $(n, ns, 0, +)$ -subproblems. The eigenvalues marked by an asterisk appear in the  $(1, ns, 0, +)/(1, ns, 1, -)$  subproblems.

The results about the singlet stability of the investigated cyclic systems exhibit several interesting properties. The transitions between singlet stable and singlet unstable closed-shell RHF solutions take place between the  $[22]$  and  $[26]$ -annulenes, between the  $[29]^-$  and  $[33]^-$ -annulene anions, between the  $[27]^+$  and  $[31]^+$ -annulene cations, between the  $[32]^{2+}$ ,  $[32]^{2-}$  and  $[36]^{2+}$ ,  $[36]^{2-}$ -annulene dications and dianions. These values are in very good agreement with the common concept about the limiting ring sizes at which Hückel's rule breaks (see also Introduction). It has been shown by Čížek and Paldus [12–14] that the singlet instability of the closed-shell RHF solution for  $[4\nu+2]$ -annulenes originating from the  $(n, s, 1, -)$  stability subproblem is connected with the existence of an energetically advantageous off-diagonal CDW (or, BAW) solution. For larger cycles, Paldus and Čížek have found [14] also a diagonal CDW solution associated with a singlet instability originating from the  $(n, s, 0, +)$  stability subproblem. In the case of the Mataga–Nishimoto parametrization scheme this instability is encountered first for the  $[54]$ -annulene. Thus, for  $[4\nu+2]$ -annulenes the singlet instability towards an off-diagonal CDW solution is encountered before the singlet instability towards a diagonal CDW solution. On the contrary, our results show that for the  $[4\nu]^{2-}$ -annulene dianions and for the  $[4(\nu+1)]^{2+}$ -annulene dications the first singlet instability to be encountered upon increase of the ring size originates from the  $(n, s, 0, +)$  subproblem. It may be easily demonstrated that the spatial symmetry breaking connected with this instability is of the diagonal CDW type. The analysis of the spatial symmetry breaking associated with the singlet instabilities in cycles with an odd number of atoms shows that it is connected with the existence of closed-shell Slater determinants belonging to the point group  $D_{2h}$  which correspond to lower energies than the pertinent RHF solutions.

It is not surprising that the closed-shell RHF solutions for the majority of the investigated cyclic systems are nonsinglet unstable. In fact, the nonsinglet stability of closed-shell RHF solutions in the framework of the PPP-approximation appears to be a rare phenomenon, at least for the most common parametrization schemes (see also [29]). In this respect, it is interesting to note that for the parametrization scheme adopted in the present paper, the closed-shell RHF solutions for the systems  $[3]^+$ ,  $[4]^{2+}$ ,  $[4]^{2-}$ ,  $[5]^-$ ,  $[7]^+$ ,  $[8]^{2+}$ ,  $[8]^{2-}$  are nonsinglet stable. In order to get additional insight into the nonsinglet stability properties of these systems, we have investigated the dependence of the lowest eigenvalues from the corresponding nonsinglet stability problems on the value of the resonance integral  $\beta$  while keeping all other parameters fixed. In particular, we have analytically established the critical values of  $\beta$ , namely,  $\beta_{\text{crit}}$ , separating the regions of nonsinglet stable and nonsinglet unstable closed-shell RHF solutions for the

above mentioned systems plus benzene (see Table 3)<sup>1</sup>. For  $\beta > \beta_{\text{crit}}$  the pertinent closed-shell RHF solutions are nonsinglet unstable, while for  $\beta < \beta_{\text{crit}}$  they are nonsinglet stable. In fact, the increase of  $|\beta|$  leads to an increase of the relative weight of the sum of one-electron operators in the total  $\pi$ -electronic Hamiltonian of the investigated system and vice versa. It may be easily established from Eqs. (1), (2), (6) and (7), that for large values of  $|\beta|$  the lowest eigenvalues from the singlet, as well as from the nonsinglet stability problems approach the difference between the lowest virtual orbital energy and the highest occupied orbital energy. Consequently, for large values of  $|\beta|$  the closed-shell RHF solutions for the investigated systems should be singlet, as well as nonsinglet stable. However, the  $|\beta_{\text{crit}}|$  values from Table 3 are relatively low. They are even lower (except  $|\beta_{\text{crit}}|$  for benzene) than the values recommended by the majority of the PPP-parametrization schemes. This fact suggests that the nonsinglet stability of the closed-shell RHF solutions for the systems from Table 3 (except benzene) is due not only to the effect of the one-electron part of the  $\pi$ -electronic Hamiltonian. On the other hand, the closed-shell RHF solutions for the discussed systems are also singlet stable (see Table 1). This notable stability of the closed-shell RHF solutions for  $[3]^+$ ,  $[4]^{2+}$ ,  $[4]^{2-}$ ,  $[5]^-$ ,  $[7]^+$ ,  $[8]^{2+}$ ,  $[8]^{2-}$  agrees very well with the expected aromatic character of these systems.

It is interesting to note that the lowest eigenvalues of the singlet and nonsinglet stability problems for  $[4\nu+2]$ -annulenes originate always from the maximum quasimomentum transfer subproblems (see also [12–14]). However, our results show that for the other investigated cyclic systems the lowest eigenvalues may appear also in subproblems which do not correspond to the maximum possible values of  $p$  (this is observed especially for systems of smaller size).

We can conclude from the results of the present investigations that there exists a connection between the aromaticity of cyclic  $\pi$ -electronic systems with  $4\nu+2$  electrons and the stability of the pertinent closed-shell RHF solutions. The analysis of the singlet stability of the pertinent closed-shell RHF solutions provides estimates for the limiting ring sizes at which the investigated cyclic systems become nonaromatic. The transition from aromatic to nonaromatic systems upon increase of the ring size is indicated by the appearance of a singlet instability of the closed

**Table 3.** Critical values of  $\beta$  separating regions of nonsinglet stable and nonsinglet unstable closed-shell RHF solutions for several cyclic systems.

System	$\beta_{\text{crit}}$ (eV)
$[3]^+$	-1.236
$[4]^{2+}$ , $[4]^{2-}$	-1.622
$[5]^-$	-1.687
$[6]$	-2.479
$[7]^+$	-2.087
$[8]^{2+}$ , $[8]^{2-}$	-2.221

<sup>1</sup> For small cycles as those from Table 3 it is possible to determine the value of  $\beta_{\text{crit}}$  analytically. However, for larger cycles  $\beta_{\text{crit}}$  should be determined either by interpolation, or by means of the elegant procedure recently proposed by Paldus and Chin [24]

shell RHF solutions which is associated with an energetically advantageous tendency towards a nonuniform electron density distribution. The nonsinglet stability of the closed-shell RHF solutions for the smallest cycles with  $4\nu + 2\pi$ -electrons marks the notable preference for a totally symmetric electron density distribution in these classical examples of aromatic systems.

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