# ON A BREAKDOWN OF THE PAIRING PROPERTIES IN CONJUGATED IONS OF ALTERNANT HYDROCARBONS*

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Calculations on electronic structures of conjugated ions of naphthalene and anthracene are reported. The SCF CI method for open-shell configurations is used, together with a modified semiempirical method, based on a transformation of atomic orbitals into the Löwdin-orthogonalized atomic orbitals. An explicit breakdown of the pairing properties of the investigated alternant ions is shown.

## *Introduction*

Conjugated anions and cations of aromatic hydrocarbons display strong absorption spectra in the visible and near ultra-violet region, *cf. e. g.* [1–7], as well as the electron spin resonance (ESR) spectra with well-resolved hyperfine structure, *cf. e. g.* [8–10]. It was found, that the optical absorption spectra of both the ions — anion and cation — of the same alternant aromatic system are similar; some small differences between them are usually considered as being caused by solvent effects. On the other hand, the hyperfine structures of the ESR spectra of these ions indicate characteristic differences: the largest hyperfine splittings in the cation spectra are significantly larger than the corresponding splittings for the anions. The similarity of absorption spectra of the alternant hydrocarbon anions and cations was fully explained on the basis of the pairing properties of pi-electronic molecular orbitals in these systems [11, 12]. These properties have been revealed when using the standard PPP semiempirical method for closed-shell configurations [13, 14], as well as its open-shell analogue [15, 16]. However, taking into consideration the same pairing properties, we cannot interpret the above mentioned differences in the ESR spectra in terms of the simple McConnell's relation [17], which assumes a linear propertionality between the hyperfine splittings and the spin density on the conjugated atoms.

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One of the trends in improving the standard PPP semiempirical method is a more proper consideration of the atomic overlap integrals, as well as inclusion of all elements of the core Hamiltonian matrix, *cf. e. g.* [18–22]. These modifications result, among others, in breaking down the pairing properties of the neutral alternant molecules. In particular, the Coulson-Rushbrooke theorem [23] and the Pariser's selection rule for some electronic transitions [24], prove invalid. Hence, there arises a possibility for interpretation of the excess electronic charge on conjugated atom as some reactivity index; also more accurate results of calculations for some weak electronic transitions become available. The application of the semiempirical PPP method, modified in such a way, to the calculations for the ions of alternant hydrocarbons is very interesting just for the reason of the possible breakdown of the pairing properties. This may create a possibility of interpreting the differences in the ESR spectra in the most simple way; but it is also interesting to know, how far the theoretical similarity of the optical absorption spectra of anions and cations is retained. In this paper, the modified semiempirical method proposed by Woźnicki [21] starting from the standard SCF equations [25], is adapted to the SCF equations for open-shell configurations [26]. According to this method, the calculations have been carried out on the electronic structures of the anions and cations of naphthalene and anthracene. The configuration interaction (CI) procedure for doublet configurations has been used in the standard way [16].

*Open-shell SCF equations in atomic and orthogonalized orbital basis*

Let us assume $\Psi$ as the wave function of the system considered, belonging to certain definite values of the $\hat{S}^2$ and $\hat{S}_z$ operators, in the independent particle model. We consider the cases, in which the expectation values of the Hamiltonian

$$\hat{H} = \sum_{\xi} \hat{h}(\xi) + \sum_{\xi>\eta}\sum \frac{1}{r_{\xi\eta}}$$

have the form [26]:

$$\langle \Psi|\hat{H}|\Psi\rangle = 2\sum_{a} \mathrm{h}_a + \sum_{a,b}\sum (2\mathrm{J}_{ab} - \mathrm{K}_{ab}) +$$

$$+ f\left[2\sum_{k} \mathrm{h}_k + f\sum_{k,l}\sum (2\alpha \mathrm{J}_{kl} - \beta \mathrm{K}_{kl}) + 2\sum_{a,k}\sum (2\mathrm{J}_{ak} - \mathrm{K}_{ak})\right], \qquad (1)$$

where

$$\mathrm{h}_i = \langle \varphi_i(\xi)|\hat{h}(\xi)|\varphi_i(\xi)\rangle,$$

$$\mathrm{J}_{ij} = \langle \varphi_i(\xi)|J_j(\xi)|\varphi_i(\xi)\rangle = \left\langle \varphi_i(\xi)\varphi_j(\eta)\left|\frac{1}{r_{\xi\eta}}\right|\varphi_i(\xi)\varphi_j(\eta)\right\rangle,$$

$$\mathrm{K}_{ij} = \langle \varphi_i(\xi)|\hat{K}_j(\xi)|\varphi_i(\xi)\rangle = \left\langle \varphi_i(\xi)\varphi_j(\eta)\left|\frac{1}{r_{\xi\eta}}\right|\varphi_j(\xi)\varphi_i(\eta)\right\rangle,$$

$\hat{\mathrm{h}}$, $\hat{\mathrm{J}}_i$ and $\hat{\mathrm{K}}_i$ are the kinetic energy and nuclear attraction potential, Coulomb, and exchange operators, respectively. The subscripts $a$, $b$ denote the one-electron orbitals $\varphi$ of closed shells; $k$, $l$ are the subscripts for partially occupied orbitals constituting open shells, $0 \leqslant f \leqslant 1$

represents the fractional occupancy of these shells; $\alpha$ and $\beta$ are constants. One of the cases is the single-determinantal $\Psi$, subjected to the spin equivalence restrictions, when the open shells contain nondegenerate orbitals with parallel spins only (the half-closed shell configuration, for which $f = \frac{1}{2}$, $\alpha = 1$, $\beta = 2$). Setting $f = 0$ we obtain the well known closed-shell case [25]. The variational method, applied to (1) under the requirements of normalization and orthogonality of the orbitals, $\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$, leads to the following equations for the optimal orbitals [26]:

$$\hat{F}^{\text{open}} \varphi_i = [\hat{h} + \hat{M} - \hat{N} + \tfrac{1}{2}(\hat{P}\hat{N} + \hat{N}\hat{P})]\, \varphi_i = \varepsilon_i \varphi_i.$$

To obtain a more compact form we have introduced the operators:

$$\hat{M} = \sum_a (2\hat{J}_a - \hat{K}_a) + f \sum_k (2\hat{J}_k - \hat{K}_k),$$

$$\hat{N} = f \sum_k \left( 2\left[\frac{1-\alpha}{1-f}\right] \hat{J}_k - \left[\frac{1-\beta}{1-f}\right] \hat{K}_k \right),$$

and the one-electron spinless density operator for the wave function $\Psi$:

$$\hat{P} \equiv \hat{P}_1(\Psi, \Psi | \xi; \xi') = 2[\sum_a |\varphi_a(\xi)\rangle \langle \varphi_a(\xi')| + f \sum_k |\varphi_k(\xi)\rangle \langle \varphi_k(\xi')|], \tag{2}$$

normalized to the number of electrons (in the meaning of tr $\hat{P}$).

For molecular problems, molecular orbitals (MO) $\varphi_i$ are expanded on the (real) atomic orbitals (AO) $\chi_\mu$ (LCAO approximation):

$$\varphi_i = \sum_\mu \chi_\mu C_{\mu i}, \quad |\varphi_i\rangle = |\chi\rangle \mathbf{C}_i, \tag{3}$$

$|\chi\rangle$ is the row matrix. Thus it leads to the algebraic problem of finding the eigenvectors of the matrix $\mathbf{F}^{\text{open}}$

$$\mathbf{F}^{\text{open}} \mathbf{C}_i = \varepsilon_i \mathbf{S} \mathbf{C}_i; \tag{4}$$

$$\mathbf{F}^{\text{open}} = \mathbf{h} + \mathbf{M} - \mathbf{N} + \tfrac{1}{2}(\mathbf{SPN} + \mathbf{NPS}). \tag{5}$$

Here, $\mathbf{h} = \langle \chi | \hat{h} | \chi \rangle$ represents the $\hat{h}$ operator in the $\chi$ basis; $\mathbf{S} = \langle \chi | \chi \rangle$ is the non-orthogonality matrix for this basis, with overlap integrals as the elements. If we introduce the supermatrix $\mathbf{X}$ of two-electron integrals between the $\chi$ functions,

$$X_{\mu\nu,\varrho\tau} = \left\langle \chi_\mu(\xi)\chi_\nu(\eta) \left| \frac{1}{r_{\xi\eta}} \right| \chi_\varrho(\xi)\chi_\tau(\eta) \right\rangle \equiv (\chi_\mu\chi_\varrho | \chi_\nu\chi_\tau),$$

we obtain the following expressions for the elements of $\mathbf{M}$ and $\mathbf{N}$ matrices:

$$M_{\mu\nu} = \sum_\varrho \sum_\tau \left( X_{\mu\varrho,\nu\tau} - \frac{1}{2} X_{\mu\varrho,\tau\nu} \right) P_{\tau\varrho},$$

$$N_{\mu\nu} = \sum_\varrho \sum_\tau \left( \left[\frac{1-\alpha}{1-f}\right] X_{\mu\varrho,\nu\tau} - \frac{1}{2} \left[\frac{1-\beta}{1-f}\right] X_{\mu\varrho,\tau\nu} \right) Q_{\tau\varrho}.$$

The matrices **P** and **Q** represent the one-electron spinless (2) and spin density operators, respectively, in the basis used:

$$\mathbf{P} = 2[\sum_a \mathbf{C}_a\mathbf{C}_a^T + f\sum_k \mathbf{C}_k\mathbf{C}_k^T], \tag{6}$$

$$\mathbf{Q} = 2f\sum_k \mathbf{C}_k\mathbf{C}_k^T.$$

Diagonal elements of the super-matrix **X** can be grouped into the matrix of atomic Coulomb integrals $\boldsymbol{\gamma}$:

$$\gamma_{\mu\nu} = (\chi_\mu\chi_\mu|\chi_\nu\chi_\nu) = \mathrm{X}_{\mu\nu,\mu\nu}. \tag{7}$$

If we expand MO's on some orthogonal orbital basis, a more simple form of the $\mathbf{F}^{\mathrm{open}}$ can be reached, because the non-orthogonality matrix **S** will not be present in (5). Löwdin-orthogonalized atomic orbitals (LOAO) [27], $|\lambda\rangle = |\chi\rangle\,\mathbf{S}^{-1/2}$, are very interesting here, because they are the closest to the original atomic orbitals $\chi$ (in the meaning of the last squares method) [28]:

$$\mathrm{Tr}\,\langle\chi-\lambda|\chi-\lambda\rangle = \textit{minimum}.$$

Now, the expansion (3) can be written as

$$\varphi_i = \sum_m \lambda_m \mathrm{D}_{mi}, \quad |\varphi_i\rangle = |\lambda\rangle\,\mathbf{D}_i,$$

and the eigenvalue problem (4) takes the form

$$\mathbf{F}^{(\lambda)\mathrm{open}}\mathbf{D}_i = \varepsilon_i\mathbf{D}_i, \tag{8}$$

where

$$\mathbf{F}^{(\lambda)\mathrm{open}} = \langle\boldsymbol{\lambda}|\hat{F}^{\mathrm{open}}|\boldsymbol{\lambda}\rangle = \mathbf{S}^{-1/2}\mathbf{F}^{\mathrm{open}}\mathbf{S}^{-1/2}$$

and the same relation holds for the matrix representations of any one-electron operator. On the other hand, regarding the fact that $\mathbf{D}_i = \mathbf{S}^{1/2}\mathbf{C}_i$, we obtain for the density matrices (6):

$$\mathbf{P}^{(\lambda)} = 2\,[\sum_a \mathbf{D}_a\mathbf{D}_a^T + f\sum_k \mathbf{D}_k\mathbf{D}_k^T] = \mathbf{S}^{1/2}\,\mathbf{P}\mathbf{S}^{1/2},$$

$$\mathbf{Q}^{(\lambda)} = 2f\sum_k \mathbf{D}_k\mathbf{D}_k^T = \mathbf{S}^{1/2}\,\mathbf{Q}\mathbf{S}^{1/2}. \tag{9}$$

The super-matrix $\boldsymbol{\Lambda}$ of two-electron integrals in the LOAO basis

$$\Lambda_{mn,rt} = (\lambda_m\lambda_r|\lambda_n\lambda_t),$$

can easily be related to the super-matrix **X**:

$$\boldsymbol{\Lambda} = (\mathbf{S}^{-1/2}\times\mathbf{S}^{-1/2})\mathbf{X}(\mathbf{S}^{-1/2}\times\mathbf{S}^{-1/2}), \tag{10}$$

where $(\mathbf{S}^{-1/2}\times\mathbf{S}^{-1/2})$ means the direct product of the $\mathbf{S}^{-1/2}$ matrix by itself.

*Modified semiempirical method*

If the conjugated molecules are being investigated and we accept the pi-electronic approximation, *e.g.* [29], the $\mathbf{F}^{(\lambda)\text{open}}$ matrix can be considerably simplified. Instead of the operator $h$ we have an effective core Hamiltonian $\hat{h}^{\text{core}}$, and only the orbitals for pi-electrons are explicitly taken into account. On the other hand, the application of LOAO basis in the investigations based on the pi-electronic approximation has been extensively studied, *cf. e. g.* [29–32], and the most important conclusion is, that in the super-matrix $\mathbf{\Lambda}$ only the diagonal elements have significant values, while the off-diagonal elements can be neglected:

$$\Lambda_{mn,rt} \cong \Lambda_{mn,mn}\delta_{mr}\delta_{nt} \equiv \Gamma_{mn}\delta_{mr}\delta_{nt}, \tag{11}$$

"Coulomb integrals" $(\lambda_m\lambda_m|\lambda_n\lambda_n) = \Gamma_{mn}$ have been collected in the matrix $\mathbf{\Gamma}$; however, they are still of multicentral character, because the $\lambda$ basis is essentially of multicentre type. When the approximation (11) is included, $\mathbf{F}^{(\lambda)\text{open}}$ has the form, identical with the one used in the open-shell analogue of the PPP method, but with all the matrices defined in the LOAO basis. For the above mentioned half-closed shell configurations it reduces to, *cf.* [16]:

$$F_{mn}^{(\lambda)\text{open}} = h_{mn}^{(\lambda)\text{core}} - \Gamma_{mn}(\tfrac{1}{2}\,P_{mn}^{(\lambda)} + Q_{mn}^{(\lambda)}) + \delta_{mn}\sum_t \Gamma_{mt}P_{tt}^{(\lambda)} +$$

$$+ \tfrac{1}{2}\sum_t (\Gamma_{mt}P_{nt}^{(\lambda)}Q_{mt}^{(\lambda)} + Q_{nt}^{(\lambda)}P_{mt}^{(\lambda)}\Gamma_{nt}).$$

In fact, it is generally accepted at present, *e. g.* [22], that the equations of the PPP method should be understood as written in the $\lambda$ basis, and therefore the relation (11) represents the well-known ZDO approximation [13, 29]. However, quantities defined in terms of $\lambda$'s cannot be referred to the atoms or atom pairs, and consequently — they cannot be treated as empirical parameters in any semiempirical method. Only the integrals determined in the basis of "true" atomic orbitals $\chi_\mu$ can be used as the parameters, transferable from one system to the another; an extensive discussion of this point has been done in [21]. Thus, if we have the atomic Coulomb integrals $\gamma_{\mu\nu}$ (7), a relation between the matrices $\boldsymbol{\gamma}$ and $\mathbf{\Gamma}$ (11) is needed. It can be reached when the Mulliken approximation [33] is applied to (10); we obtain, *cf. e. g.* [18]:

$$\Gamma = \mathbf{T}\,\boldsymbol{\gamma}\,\mathbf{T}, \quad T_{m\mu} = (\mathbf{S}^{-1/2})_{m\mu}\,(\mathbf{S}^{1/2})_{m\mu}.$$

The atomic Coulomb integrals $\gamma_{\mu\nu}$, for selected internuclear distances $R_{\mu\nu}$, are further treated as the empirical parameters.

To evaluate the elements $\mathbf{h}_{mn}^{(\lambda)\text{core}}$, the matrix $\mathbf{h}^{\text{core}}$ (in $\boldsymbol{\chi}$ basis) can be devided into the diagonal part, $\mathbf{h}_0^{\text{core}}$, and the off-diagonal one, $\mathbf{h}_1^{\text{core}}$. Defining the new matrix

$$\mathbf{B} = \mathbf{h}_1^{\text{core}} - \tfrac{1}{2}\,[\mathbf{h}_0^{\text{core}}\,(\mathbf{S}-\mathbf{1}) + (\mathbf{S}-\mathbf{1})\,\mathbf{h}_0^{\text{core}}], \tag{12}$$

we can easily show the following:

$$\mathbf{h}^{(\lambda)\text{core}} = \tfrac{1}{2}\,(\mathbf{S}^{-1/2}\,\mathbf{h}_0^{\text{core}}\mathbf{S}^{1/2} + \mathbf{S}^{1/2}\,\mathbf{h}_0^{\text{core}}\,\mathbf{S}^{-1/2}) + \mathbf{S}^{-1/2}\,\mathbf{B}\,\mathbf{S}^{-1/2}.$$

We assume [21], that the atomic orbital $\chi_\mu$ is formally the solution of the eigenvalue problem:

$$\hat{h}_\mu^{\text{eff}} \chi_\mu = -I_\mu^{\text{eff}} \chi_\mu,$$

where $\hat{h}_\mu^{\text{eff}}$ is the kinetic energy operator plus some effective potential, derived from the conjugated atom $\mu$ *and its nearest environment* in the molecule; this atom gives $n_\mu^{(\pi)}$ pi-electrons to the conjugated system of the neutral molecule. The eigenvalue $I_\mu^{\text{eff}}$ should be interpreted as the ionization potential of the atom $\mu$ in its molecular surrounding; the value of $I_\mu^{\text{eff}}$ is treated as the empirical parameter and it should *not* be identified with the valence-state ionization potential. In view of the Goeppert-Mayer and Sklar approximation [34] we obtain

$$(\mathbf{h}_0^{\text{core}})_{\mu\mu} = -I_\mu^{\text{eff}} + \gamma_{\mu\mu} - \sum_\nu n_\nu^{(\pi)} \gamma_{\mu\nu}.$$

For the elements of matrix **B** (12), Woźnicki [21] justified the relation

$$B_{\mu\nu} = \tfrac{1}{2} (I_\mu^{\text{eff}} + I_\nu^{\text{eff}}) S_{\mu\nu}(S_{\mu\nu} - 1).$$

To complete this modified semiempirical method, a formula for the evaluation of the overlap integrals $S_{\mu\nu}$ is necessary. Here, the theoretical values for the Slater-type $2p_z$ orbitals have been used, and then the effective nuclear charge $\zeta_\mu$ for the atom $\mu$, appearing in the Slater orbitals, is also treated as the empirical parameter.

### *Calculations and discussion*

According to the semiempirical method presented above the calculations have been carried out for the anions and cations of naphthalene and anthracene. Hexagonal geometries with the standard bond length 1.4 Å have been asumed and the set of parameters, originally found in [21] has been used:

$$\zeta_C = 1.405, \qquad I_C^{\text{eff}} = 10.02 \text{ eV},$$

$$\gamma_{CC}(R = 0) = 9.3051 \text{ eV}, \qquad \gamma_{CC}(R = 1) = 6.1925 \text{ eV},$$

$$\gamma_{CC}(R = \sqrt{3}) = 4.7137 \text{ eV}, \qquad \gamma_{CC}(R = 2) = 3.8118 \text{ eV},$$

$$\gamma_{CC}(R = \sqrt{7}) = 3.5520 \text{ eV}, \qquad \gamma_{CC}(R = \sqrt{13}) = 3.2020 \text{ eV},$$

$$\gamma_{CC}(R \geqslant 5) = \frac{e^2}{R}$$

($R$ — the internuclear distance, in the standard bond length units; for the intermediate distances the values have been linearly interpolated). All the carbon atoms have been treated equally, although the parameter $I_C^{\text{eff}}$ for the joint positions (carbon atoms 9,10 in naphthalene, 11–14 in anthracene) can essentially be different than those for the other ones.

The SCF equations (8) have been solved for the ground states of the ions and starting from the orbitals obtained, the configuration interaction (CI) procedure including all the singly excited, doublet configurations has been applied, as described in [16]. All the calcula-

tions needed have been done on the GIER computer, at the Department of Numerical Calculations, Warsaw University.

It should be noted, that when the SCF equations (8) are solved, we have the $\mathbf{D}_i$ vectors and the density matrices $\mathbf{P}^{(\lambda)}$, $\mathbf{Q}^{(\lambda)}$ (9). Although they are well normalized (Tr $\mathbf{P}^{(\lambda)}$ = the number of pi-electrons, Tr $\mathbf{Q}^{(\lambda)}$ = the number of unpaired spins), the elements of $\mathbf{P}^{(\lambda)}$ cannot be used for evaluations of the dipole moments or interpreted as the bond orders, because this matrix is defined in the multicentre LOAO basis; the subscripts $m$, $n$ are not, in fact, connected with any conjugated atom. For the same reasons the quantity $Q^{(\lambda)}_{mm}$ cannot be interpreted as the spin density on any atom. On the other hand, transformations of the type $\mathbf{S}^{-\frac{1}{2}}\mathbf{P}^{(\lambda)}\mathbf{S}^{-\frac{1}{2}} = \mathbf{P}$ do not preserve the normalization of density matrices and do not enable one to interpret their diagonal elements as the charge (for $\mathbf{P}$), or spin (for $\mathbf{Q}$) densities on the conjugated atoms, despite of the fact that the matrices $\mathbf{P}$ and $\mathbf{Q}$ are defined in the basis of "true" atomic orbitals $\chi$. It was shown [21], using the Mulliken approximation [33], that if the pi-electronic part of dipole moment is expressed as a sum of contributions connected only with the conjugated atoms, the diagonal elements of the matrix

$$\mathbf{p} = \tfrac{1}{2}(\mathbf{S}^{-\frac{1}{2}}\mathbf{P}^{(\lambda)}\mathbf{S}^{\frac{1}{2}} + \mathbf{S}^{\frac{1}{2}}\mathbf{P}^{(\lambda)}\mathbf{S}^{-\frac{1}{2}}) \tag{13}$$

represent the charge densities on these atoms. This matrix is also well normalized and will be treated as the charge and bond-order matrix. In view of such a definition of the charge densities, the diagonal elements of the matrix

$$\mathbf{q} = \tfrac{1}{2}(\mathbf{S}^{-\frac{1}{2}}\mathbf{Q}^{(\lambda)}\mathbf{S}^{\frac{1}{2}} + \mathbf{S}^{\frac{1}{2}}\mathbf{Q}^{(\lambda}(\mathbf{S}^{-\frac{1}{2}}) \tag{14}$$

should be interpreted as the spin densities on the conjugated atoms. Numerical results indicate, that the definition (13) is especially effective in predicting the bond distances from the bond orders; also, the corresponding elements of $\mathbf{p}$ and $\mathbf{P}^{(\lambda)}$, and respectively $\mathbf{q}$ and $\mathbf{Q}^{(\lambda)}$

TABLE 1

Calculated spin densities $q_{\mu\mu}$ and experimental nyperfine splittins $a_{H_\mu}$ (in gaus), for the anions and cations of naphthalene (N) and anthracene (A)

| | position $\mu$ | anion | | | cation | | |
|---|---|---|---|---|---|---|---|
| | | $q_{\mu\mu}$ | $a_{H_\mu}$ (gaus) | ratio $a_{H_\mu}/q_{\mu\mu}$ (gaus) | $q_{\mu\mu}$ | $a_{H_\mu}$ (gaus) | ratio $a_{H_\mu}/q_{\mu\mu}$ (gaus) |
| | | | [8] | | | [10] | |
| N | 1 | 0.178 | −4.90 | −27.53 | 0.182 | −5.53 | −30.38 |
| | 2 | 0.072 | −1.83 | −25.42 | 0.068 | −2.06 | −30.29 |
| | | | [9] | | | [9] | |
| | 1 | 0.098 | −2.74 | −27.96 | 0.090 | −3.06 | −34.00 |
| A | 2 | 0.051 | −1.51 | −29.61 | 0.043 | −1.38 | −32.09 |
| | 9 | 0.182 | −5.34 | −29.34 | 0.216 | −6.53 | −30.23 |
| | average ratio | | | −27.82 | | | −31.53 |

are very similar, whereas they differ significantly from the elements of **P** and **Q**, respectively.

The results of the calculations for naphthalene and anthracene ions, together with the corresponding experimental data, are presented in the Tables I and II. In the standard PPP method, the spin densities and transition energies calculated for both the ions of the same alternant system are identical; here these pairing properties are explicitly broken. As it can be seen from Table I, the direction of this breakdown is especially favourable for the ESR spectra, what is evident from an inspection of the values of the ratio $a_{H_\mu}/q_{\mu\mu}$. This ratio is simply the constant, appearing in the well known relation on McConnell [17], between the experimental hyperfine splitting produced by the proton adjacent to the conjugated atom $\mu$, $a_{H_\mu}$, and the spin density calculated for this atom, $q_{\mu\mu}$:

$$a_{H_\mu} = \text{constant} \times q_{\mu\mu}.$$

As a matter of fact, the average values of these ratios (the last row of Table I) are still different for the anions and cations, but for the largest splittings: positions 1 for naphthalene and 9 for anthracene, these two values are considerably closer to each other. It is worth to note, that just for these splittings the differences between the anion and cation ESR spectra are clearly observed experimentally. The numerical results obtained for the spin densities indicate, that these experimental differences of the ESR spectra can be explained on the basis of topological properties of alternant systems, because the one-electron density matrices

TABLE II

Calculated and experimental transition energies (eV) in the absorption spectra of anions and cations of naphthalene (N) and anthracene (A) ($x$ is the longer symmetry axis of the molecules, polarization of the transitions are experimentally known only for the anions, [3])

| | polarization | anion | | | cation | | |
|---|---|---|---|---|---|---|---|
| | | calculated (eV) | experimental (eV) | | calculated (eV) | experimental (eV) | |
| | | | [1] | [4] | | [5] | [7] |
| | $x$ | 2.43 | 1.52–1.69 | 1.57 | 1.73 | ~1.7 | 1.75 |
| | $y$ | 3.16 | 2.66? | | 2.66 | ~2.5 | |
| N | $y$ | 3.86 | 3.38 | | 3.42 | >3.0? | 3.14 |
| | $x$ | 4.11 | 3.83 | 3.84 | 4.24 | | |
| | $x$ | 5.17 | | 4.25 | 4.82 | | |
| | $x$ | 6.37 | 5.45, [3] | | 5.92 | | |
| | | | [1] | [4] | | [2] | [6] |
| | $x$ | 2.16 | 1.73 | 1.73 | 1.56 | 1.73 | 1.74 |
| | $y$ | 2.18 | ? | | 1.98 | | |
| | $y$ | 3.67 | 3.09 | 3.10 | 2.82 | 2.85 | 3.04 |
| A | $x$ | 3.47 | 3.36 | 3.35 | 3.39 | 3.47 | 3.29 |
| | $x$ | 4.74 | 3.80 | 3.80 | 4.05 | 3.80 | 3.63 |
| | $x$ | 5.66 | | 4.83 | 5.02 | 4.60 | |
| | $x$ | 6.20 | ~5.2, [3] | | 5.77 | 5.20 | |

depend strongly on these properties and rather weakly on the empirical parametrization. It should be noted, that the differences of calculated $q_{\mu\mu}$ values for anions and cations are *not* the result of the definition (14), accepted here; the same effect is observed for corresponding elements of $\mathbf{Q}^{(\lambda)}$ matrix.

The breaking of pairing symmetry for the transition energies is evident from Table II. The energies for the cations are lower than those for the anions. The strongest effect can be observed for the first $x$ transition, the weakest (or even a reversed one) for the second $x$ band. Consequently, optical spectra of the cations are considerably better interpreted here, than in the standard semiempirical methods, whereas the interpretation of absorption spectra of the anions is comparable with the one, obtained previously, *cf.* [16]. The observed behaviour of the calculated transition energies indicate, that if we accept a possibility of some modifications of the parameters values, the direction of these modifications can depend on the sign of excess electronic charge of the ion.

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