OPEN-SHELL SCF CI CALCULATIONS FOR NAPHTHALENE IONS

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The open-shell SCF method with configuration interaction including all singly excited configurations is used, in a semiempirical scheme, for studying optical absorption and electron spin resonance spectra of conjugated naphthalene ions as well as the ionization potential and electron affinity of the naphthalene molecule. The results are compared with those of other authors. Some terms, appearing in open-shell Fock operator, are discussed.

Introduction

Many different semiempirical methods have been used in theoretical investigations on electronic properties of conjugated ions of aromatic hydrocarbons. The optical absorption spectra of these systems have been studied by the well-known methods of the analysis of aromatic molecules spectra [1–6]. Open-shell type treatment, including more directly the presence of an unpaired electron has also been used [7, 8]. The electron spin resonance (ESR) spectra of the ions have been investigated by the Hückel method, *e.g.* [9, 10]; though rather more advanced, *restricted* or *unrestricted* SCF methods have been applied [11, 12]. The ionization potentials (IP) and electron affinities (EA) of aromatic molecules were the subjects of separate papers, [13–15]. In the cases of Hückel or restricted SCF methods, the configuration interaction (CI) procedure has also been applied; however the lengths of CI basis were very different.

It should be noted that generally, different properties of the above mentioned systems have been studied by means of different methods. Sometimes values of certain empirical parameters have been chosen so, as to reproduce selected experimental results, *e.g.* [1, 15]. However, no systematic attempts have been made to fix values of the empirical parameters especially to describe the ionized states of aromatic hydrocarbons. It seems to be useful to interpret a possibly wide set of the experimental results available for the ions by means of a properly chosen method and using fixed values of the parameters. This is one of the aims of the present work. Here, the open-shell SCF method of Roothaan [16] is used for the interpretation of optical absorption and ESR spectra of the monovalent anion and cation

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of naphthalene, as well as of ionization potential and electron affinity of the naphthalene molecule. The well known semiempirical scheme of Pariser and Parr [3] has been adopted. In the CI procedure all singly excited configurations have been included. The influence of terms connected with the spin density in the open-shell Fock operator, on the solutions of the SCF equations, was studied. Some results obtained by applying the open- and closed--shell [17] SCF methods have been compared, as well.

Method of calculations

A doublet state of a system of $2N+1$ electrons can be described by the one-determinantal wave function

$$^2\Psi = |\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2 \cdots \varphi_N\bar{\varphi}_N\varphi_{N+1}|,$$

constructed from the one-electron functions, molecular orbitals (MO), φ_i. Minimization of the expectation value, $\langle {}^2\Psi|\hat{H}|{}^2\Psi\rangle$, of two-electron hamiltonian

$$\hat{H} = \sum_{p=1}^{2N+1} \hat{h}(p) + \sum_{p>q=1}^{2N+1}\sum \frac{1}{r_{pq}}$$

in this state, leads to the particular case of the SCF equations for MO's, [16]:

$$\hat{F}^{\text{open}}\varphi_i = \varepsilon_i\varphi_i, \tag{1}$$

where the open-shell Fock operator $\hat{F}^{\text{open}}$ has the form

$$\hat{F}^{\text{open}} = \hat{h} + \sum_a (2\hat{J}_a - \hat{K}_a) + \hat{J}_n - \frac{3}{2}\hat{K}_n + 2\sum_a \hat{M}_a + \hat{M}_n.$$

Here, $\hat{h}$ is the one-electron kinetic energy and nuclear Coulomb potential operator, $\hat{J}$ and $\hat{K}$ are the Coulomb and exchange operators, respectively; $\hat{M}$ are the exchange-coupling operators, introduced by Roothaan [16] and defined by their action on the one-electron functions in the following way:

$$2\hat{M}_i\varphi_j = \langle\varphi_i|\hat{K}_n|\varphi_j\rangle\varphi_i + \langle\varphi_i|\varphi_j\rangle\hat{K}_n\varphi_i.$$

The following convention is accepted for the subscripts: i, j are used for arbitrary MO's; a (and also b) denote the MO's, which are doubly occupied in the state under considerations; n denotes the singly occupied MO. The subscripts x, y for unoccupied MO's, are also introduced.

The molecular orbitals can be expressed as linear combinations of atomic orbitals χ_r:

$$\varphi_i = \sum_r \chi_r c_{ri} = \boldsymbol{\chi}\mathbf{c}_i$$

(LCAO approximation); then the integro-differential equations (1) are transformed into the matrix form

$$\mathbf{F}^{\text{open}}\mathbf{c}_i = \varepsilon_i\mathbf{S}\mathbf{c}_i, \tag{2}$$

where $\mathbf{F}^{\text{open}}$ is the matrix representation of the $\hat{F}^{\text{open}}$ operator and column vector $\mathbf{c}_i$ represents the i-th MO, φ_i, in the $\boldsymbol{\chi}$ basis; $\mathbf{S}$ is the matrix of overlap integrals, $\langle\boldsymbol{\chi}|\boldsymbol{\chi}\rangle$. If we adopt the ZDO approximation [3], $\mathbf{S}$ becomes the unit matrix and the elements of $\mathbf{F}^{\text{open}}$ matrix take the form

$$F_{rs}^{\text{open}} = h_{rs} - \gamma_{rs}\left(\frac{1}{2}P_{rs} + Q_{rs}\right) + \delta_{rs}\sum_t \gamma_{rt}P_{tt} + \\ + \frac{1}{2}\sum_t (\gamma_{rt}P_{st}Q_{rt} + Q_{st}P_{rt}\gamma_{st}), \tag{3}$$

where: h_{rs} are matrix elements of the $\hat{h}$ operator; in the *pi*-electronic approximation, adopted in this work, the one-electron *core* operator $\hat{h}^c$ and its matrix elements h_{rs}^c will be used here, instead; γ_{rs} are the atomic Coulomb integrals, $\delta_{rs} = 1$ for $r = s$, 0 for $r \neq s$.

The P_{rs} and Q_{rs} are the elements of matrices which represent the spinless, $P_1({}^2\Psi, {}^2\Psi|1;1')$ and spin, $Q_1({}^2\Psi, {}^2\Psi|1;1')$ density matrieces, respectively, in the $\boldsymbol{\chi}$ basis (for the notation used, see *e.g.* [18]). The elements of these $\mathbf{P}$ and $\mathbf{Q}$ matrices are defined by an electronic configuration of the system in the following way:

$$P_{rs} = 2\sum_a c_{ra}c_{sa} + c_{rn}c_{sn}, \tag{4}$$

$$Q_{rs} = c_{rn}c_{sn}.$$

A choice of an electronic configuration of the system is equivalent to the determination, what sets of values can be reached by the MO's subscripts: a or b, n, x or y. The wave function ${}^2\Psi$ for a given electronic configuration has the form

$${}^2\Psi_n = |\varphi_{a_1}\bar{\varphi}_{a_1} \cdots \varphi_{a_N}\bar{\varphi}_{a_N}\varphi_n|. \tag{5}$$

The presence of terms depending on the spin density in the $\hat{F}^{\text{open}}$ causes the differences between this operator and the similar one, appearing in the standard, closed-shell Hartree–-Fock method and makes possible an additional optimitazion of the MO's describing the open-shell state of the electronic system. The one-determinantal wave function of this state is not, in general, totally symmetrical. In the case of doublet configuration with one unpaired electron, the symmetry properties of the function ${}^2\Psi_n$ are determined by this irreducible (and nondegenerate) representation of the point symmetry group of the system, according to which the singly occupied orbital φ_n transforms. On the other hand, the $\hat{F}^{\text{open}}$ operator (always totally symmetrical) is not uniquely determined by the multiplicity of the state, because it depends upon the postulated electronic configuration by the $\mathbf{P}$ and $\mathbf{Q}$ matrices (see Eqs (3, 4)). According to the general properties of the variational method, the SCF equations (1) or (2) make sense only if the electronic configuration is energetically the lowest of all possible configurations of the same symmetries. However, for the system having nontrivial symmetry (like *e.g.* the naphthalene molecule, the D_{2h} point symmetry group), there exist some irreducible representations according to which the orbitals can be classified. For such systems another kind of optimization of MO's is then possible, which

consists in obtaining the solutions of equations (2) separately for each of the lowest electronic configurations of different symmetries. It should be noted, that the orbitals belonging to the same irreducible representations, but obtained from the different (in this meanning) SCF processes will be different and, generally, nonorthogonal. This manner of solving the SCF equations (2) will be refered to as the *symmetry-adapted optimization* (SADOP) of the MO's.

The algorithm of the iterative solution of the SCF equations for an arbitrary electronic configuration (5), *i.e.* with a possiblility of SADOP, has been written as an ALGOL — procedure.

Starting from the open-shell SCF method, the configuration interaction (CI) procedure can be included in two ways:

1°: we can accept the energetically lowest electronic configuration among the solutions of different symmetries of (2), as the ground (open-shell) state of the system and construct wave functions of all excited configurations with the orbitals, optimal for this ground state. The SADOP plays no part in this case (the lowest configuration is always automatically "symmetry-adapted"), but this procedure corresponds strictly to the standard, closed-shell SCF CI method: all the MO's are orthogonal and the concept of singly- (or multi-) excited configurations is well defined with respect to the ground state;

2°: we can construct wave functions of excited configurations of some definite symmetry from the orbitals, optimal for the lowest electronic configuration of this symmetry, taking full advantage of the SADOP. Then, the excited configurations of different symmetries are built up from the non-orthogonal orbitals and this leads to some trouble when the transition moments have to be calculated. We have also to leave out the rather formal, but convenient classification of the configurations into the singly- or multi-excited ones, because it becomes nonadequate. Namely, configurations of the same symmetries, being "singly-excited" with respect to the lowest configuration of this symmetry, are often "multi-excited" with respect to the lowest configurations of other symmetries, particularly to the ground state of the system.

In the present work, the first way of approach has essentially been applied, because the author is convinced that it is more appriopriate for semiempirical calculations. It is also possible to compare the results obtained in this way with the results of the closed-shell SCF CI method. On the other hand, some of the calculations shown below provide an insight into the approach 2°.

Now, we shall understand ${}^2\Psi_n = |\ldots \varphi_a\bar{\varphi}_a \ldots \varphi_n|$ as the wave function of the ground state of system, in the sense, as explained in 1°. In the CI procedure all four types of the singly excited, doublet configurations have been included

$$
\begin{aligned}
{}^2\Psi_{a\to n} &= |..\varphi_a\bar{\varphi}_n..\varphi_n|,\\
{}^2\Psi_{n\to x} &= |..\varphi_a\bar{\varphi}_a..\varphi_x|,\\
{}^2\Psi_{a\to x} &= \frac{1}{\sqrt{6}}[|..\varphi_x\bar{\varphi}_a..\varphi_n| - |..\varphi_a\bar{\varphi}_x..\varphi_n| - 2|..\varphi_a\bar{\varphi}_n..\varphi_x|],\\
{}^2\Psi'_{a\to x} &= \frac{1}{\sqrt{2}}[|..\varphi_x\bar{\varphi}_a..\varphi_n| + |..\varphi_a\bar{\varphi}_x..\varphi_n|].
\end{aligned}
\tag{6}
$$

Elements of the CI matrix between these functions, $\langle {}^2\Psi_K|\hat{H}|{}^2\Psi_L\rangle$, can be easily expressed by elements of the matrix

$$\mathbf{E} = \mathbf{C}^T\mathbf{F}^{\text{open}}\mathbf{C}, \tag{7}$$

where $\mathbf{C}$ is the square matrix constructed from arbitrary orthogonal column vectors $\mathbf{c}_i$, and the following molecular integrals:

$$(i|\hat{h}|j) = \int \varphi_i^*(p)\hat{h}(p)\varphi_j(p)dv_p,$$

$$(ij|kl) = \int\int \varphi_i^*(p)\varphi_j(p)\frac{1}{r_{pq}}\varphi_k^*(q)\varphi_l(q)\, dv_p dv_q,$$

$$I_{ij} = (i|\hat{h}|j) + \sum_a [2(ij|aa) - (ia|ja)].$$

Different types of elements of the $\mathbf{E}$ matrix (7) can be written as:

$$E_{ab} = I_{ab} + (ab|nn) + \frac{1}{2}(an|bn),$$

$$E_{an} = I_{an} + (an|nn),$$

$$E_{ax} = I_{ax} + (ax|nn) - \frac{1}{2}(an|nx),$$

$$E_{nn} = I_{nn} + \frac{1}{2}(nn|nn),$$

$$E_{nx} = I_{nx},$$

$$E_{xy} = I_{xy} + (nn|xy) - \frac{3}{2}(nx|ny). \tag{8}$$

In particular, the $\mathbf{C}$ matrix can be built from the open-shell SCF MO's — eigenvectors of the $\mathbf{F}^{\text{open}}$; then the diagonal elements $\mathbf{E}_{ii}$ are simply the eigenvalues ε_i, and the off-diagonal elements E_{ij} vanish. If we take an orbital basis different than the SCF MO's (*e.g.* the closed-shell SCF or Hückel orbitals), the application of (7, 8) essentially simplifies the CI procedure as well.

30 types of formulae for the CI matrix elements for all possible combinations of the ground state ${}^2\Psi_n$ and (6) functions, as well as the spinless $P_1(KL|1;1)$ and spin $Q_1(KL|1;1')$ transition density matrices between these configurations, are collected in Table I.

It can be noted that if we take the open-shell SCF orbital basis, only configurations of the type ${}^2\Psi_{a\to x}$ interact directly with the ground state configuration, *i.e.* the element $\langle {}^2\Psi_n|\hat{H}|{}^2\Psi_{a\to x}\rangle$ does not vanish identically; this is a certain generalization of the Brillouin theorem, well known in the closed-shell SCF CI method. For this reason in some papers only these configurations have been included in the CI procedure. On the other hand, in some papers only energetically lower configurations with single unpaired electrons, of the types ${}^2\Psi_{a\to n}$ or ${}^2\Psi_{n\to x}$ have been taken into account.

The algorithms of construction of the CI matrix (based on (7, 8)) and the spinless and spin density matrices, have also been written as ALGOL-procedures.

TABLE I

Elements of the configuration interaction (CI) matrix and the spinless and spin transition density matrices for doublet states. All possible combinations of the ground state and singly excited configurations are included. The symbol (ij) means the product $\varphi_i(1)\,\varphi_j^*(1')$

Configurations		Elements of CI matrix $\langle {}^2\Psi_K \vert \hat{H} \vert {}^2\Psi_L \rangle$	Spinless transition density matrices: $P_1(K, L\vert 1;1')$	Spin transition density matrices: $Q_1(K,L\vert 1;1')$
${}^2\Psi_K$	${}^2\Psi_L$			
1	2	3	4	5
${}^2\Psi_n$	${}^2\Psi_n$	E^{pi} (total pi — electronic energy of the ground state)	$2\sum_a (aa)+(nn)$ ($\equiv \mathbf{P}$)	(nn) ($\equiv \mathbf{Q}$)
—	${}^2\Psi_{a\to n}$	E_{an}	(an)	$-(an)$
—	${}^2\Psi_{n\to x}$	E_{nx}	(nx)	(nx)
—	${}^2\Psi_{a\to x}$	$-\sqrt{\frac{3}{2}}\,(an\vert nx)$	0	$\sqrt{\frac{2}{3}}\,(ax)$
—	${}^2\Psi'_{a\to x}$	$\sqrt{2}E_{ax}$	$\sqrt{2}\,(ax)$	0
${}^2\Psi_{a\to n}$	${}^2\Psi_{a\to n}$	$-E_{aa}+E_{nn}+\frac{1}{2}(nn\vert nn)-(aa\vert nn)+\frac{3}{2}(an\vert an)+E^{pi}$	$\mathbf{P}-(aa)+(nn)$	(aa)
—	${}^2\Psi_{b\to n}$	$-E_{ab}-(ab\vert nn)+\frac{3}{2}(an\vert bn)$	$-(ab)$	(ab)
—	${}^2\Psi_{n\to x}$	$(an\vert nx)$	0	0
—	${}^2\Psi_{a\to x}$	$\sqrt{\frac{3}{2}}\,[-E_{nx}+(aa\vert nx)-(nn\vert nx)]$	$-\sqrt{\frac{3}{2}}\,(nx)$	$-\sqrt{\frac{1}{6}}\,(nx)$
—	${}^2\Psi_{b\to x}$	$\sqrt{\frac{3}{2}}\,(ab\vert nx)$	0	0
—	${}^2\Psi'_{a\to x}$	$\sqrt{\frac{1}{2}}\,[E_{nx}-(aa\vert nx)+(nn\vert nx)+2(an\vert ax)]$	$\sqrt{\frac{1}{2}}\,(nx)$	$-\sqrt{\frac{1}{2}}\,(nx)$
—	${}^2\Psi'_{a\to x}$	$\sqrt{\frac{1}{2}}\,[-(ab\vert nx)+2(an\vert bx)]$	0	0
${}^2\Psi_{n\to x}$	${}^2\Psi_{n\to x}$	$-E_{nn}+E_{xx}+\frac{1}{2}(nn\vert nn)-(nn\vert xx)+\frac{3}{2}(nx\vert nx)+E^{pi}$	$\mathbf{P}-(nn)+(xx)$	(xx)
—	${}^2\Psi_{n\to x}$	$E_{xy}-(nn\vert xy)+\frac{3}{2}(nx\vert ny)$	(xy)	(xy)
—	${}^2\Psi_{a\to x}$	$\sqrt{\frac{3}{2}}\,[-E_{an}-(an\vert xx)+(an\vert nn)]$	$-\sqrt{\frac{3}{2}}\,(an)$	$\sqrt{\frac{1}{6}}\,(an)$
—	${}^2\Psi_{a\to y}$	$-\sqrt{\frac{3}{2}}\,(an\vert xy)$	0	0
—	${}^2\Psi'_{a\to x}$	$\sqrt{\frac{1}{2}}\,[-E_{an}+(an\vert xx)+(an\vert nn)+2(ax\vert nx)]$	$-\sqrt{\frac{1}{2}}\,(an)$	$-\sqrt{\frac{1}{2}}\,(an)$
—	${}^2\Psi'_{a\to y}$	$\sqrt{\frac{1}{2}}\,[-(an\vert xy)+2(ax\vert ny)]$	0	0

Table I, continued

1	2	3	4	5
$^2\Psi_{a\to x}$	$^2\Psi_{a\to x}$	$-E_{aa}+E_{xx}-(aa\|xx)+2(an\|an)+2(nx\|nx)+E^{pi}$	$\mathbf{P}-(aa)+(xx)$	$\frac{2}{3}(aa)-\frac{1}{3}(nn)+\frac{2}{3}(xx)$
—	$^2\Psi_{b\to x}$	$-E_{ab}-(ab\|xx)+2(an\|bn)$	$-(ab)$	$\frac{2}{3}(ab)$
—	$^2\Psi_{a\to y}$	$E_{xy}-(aa\|xy)+2(nx\|ny)$	(xy)	$\frac{2}{3}(xy)$
—	$^2\Psi_{b\to y}$	$-(ab\|xy)$	0	0
—	$^2\Psi'_{a\to x}$	$\frac{\sqrt{3}}{2}[(an\|an)-(nx\|nx)]$	0	$-\sqrt{\frac{1}{3}}(aa)+\sqrt{\frac{1}{3}}(xx)$
—	$^2\Psi'_{b\to y}$	$\frac{\sqrt{3}}{2}(an\|bn)$	0	$-\sqrt{\frac{1}{3}}(ab)$
—	$^2\Psi'_{a\to y}$	$-\frac{\sqrt{3}}{2}(nx\|ny)$	0	$\sqrt{\frac{1}{3}}(xy)$
—	$^2\Psi'_{b\to y}$	0	0	0
$^2\Psi'_{a\to x}$	$^2\Psi'_{a\to x}$	$-E_{aa}+E_{xx}-(aa\|xx)+2(ax\|ax)+(an\|an)+(nx\|nx)+E^{pi}$	$\mathbf{P}-(aa)+(xx)$	(nn)
—	$^2\Psi'_{b\to x}$	$-E_{at}-(ab\|xx)+(an\|bn)+2(ax\|bx)$	$-(ab)$	0
—	$^2\Psi'_{a\to y}$	$E_{xy}-(aa\|xy)+(nx\|ny)+2(ax\|ay)$	(xy)	0
—	$^2\Psi'_{b\to y}$	$-(ab\|xy)+2(ax\|by)$	0	0

Calculations: SCF *and* CI *procedures*

The well known semiempirical scheme of Pariser and Parr (PP) [3] has been used to determine the values of elements of the core hamiltonian matrix h^c_{rs} and the basic Coulomb integrals γ_{rs}, which are needed for the calculations. The values of ionization potential and electron affinity for carbon atoms in the sp^2 valence state have been accepted according to [19] as: $I_C = 11.22$ eV and $A_C = 0.62$ eV. This gives the value 10.6 eV for the one-center Coulomb integral $\gamma_{CC}(0)$. For the evaluation of two-center integrals $\gamma_{CC}(R_{rs})$ the PP approximation has been assumed. The core resonance integral β_{CC} value for the carbon atoms — neighbours in the aromatic ring has also been accepted according to [3], as —2.39 eV. Furthermore, it was assumed that the systems studied — naphthalene molecule and its ions — have hexagonal geometries with bond lengths 1.4 Å and the standard numeration of ring positions was used.

The closed-shell SCF equations have been solved for the ground state of naphthalene and then the open-shell SCF procedure has been applied to the lowest electronic configurations

of different symmetries of naphthalene anion and cation. Results of the SCF procedures: molecular orbitals φ_i, orbital energies ε_i and total *pi*-electronic energies of the configurations, E^{pi}, are presented in Table II. The *i*-th MO is represented in Table II by three coefficients: c_{1i}, c_{2i} and c_{9i}, the other ones being determined by the symmetry. Because of the well known pairing properties of the ions of alternant hydrocarbons in the approximation assumed (see *e.g.* [2,20]), full results are only shown for the anion configurations. The results (MO's and differences of ε's) for cation configurations of symmetries different from A_{1u} (this is

TABLE II

Results of the SCF procedures for naphthalene molecule (N), naphthalene cation (N^+), and the lowest electronic configurations of different symmetries of naphthalene anion (N^-): molecular orbitals φ_i, orbital energies ε (eV), and total *pi*-electronic energies E^{pi}. The MO's designated (=) are doubly occupied (*a*, *b* set), these designated (–) are the singly occupied MO, φ_n

i	N ($^1A_{1g}$) $E^{pi} = -369.640$ eV					$N^+(^2A_{1u})$ $E^{pi} = -359.432$ eV					$N^-(^2B_{2g})$ $E^{pi} = -371.272$ eV				
	sym-metry	ε_i	c_{1i}	φ_i c_{2i}	c_{9i}	*sym-metry*	ε_i	c_{1i}	φ_i c_{2i}	c_{9i}	*sym-metry*	ε_i	c_{1i}	φ_i c_{2i}	c_{9i}
1	=, b_{3u}	−15.53	.302	.243	.447	=, b_{3u}	−20.58	.295	.199	.497	=, b_{3u}	−9.80	.304	.265	.417
2	–, b_{2g}	−13.60	.264	.425	.000	=, b_{2g}	−17.84	.257	.429	.000	=, b_{2g}	−8.05	.247	.435	.000
3	=, b_{1g}	−12.56	.398	.189	.333	=, b_{3u}	−16.58	.043	.417	.385	=, b_{1g}	−6.70	.402	.190	.324
4	=, b_{3u}	−11.36	.005	.394	.434	=, b_{1g}	−16.55	.394	.161	.371	=, b_{3u}	−5.64	.044	.392	.434
5	=, a_{1u}	−10.31	.425	.264	.000	–, a_{1u}	−12.95	.435	.247	.000	=, a_{1u}	−4.26	.429	.257	.000
6	b_{2g}	−1.53	.425	.264	.000	b_{2g}	−7.58	.429	.257	.000	–, b_{2g}	1.11	.435	.247	.000
7	b_{1g}	−0.48	.005	.394	.434	b_{1g}	−6.20	.044	.392	.434	b_{3u}	4.71	.394	.161	.371
8	b_{3u}	0.72	.398	.189	.333	b_{3u}	−5.14	.402	.190	.324	b_{1g}	4.74	.043	.417	.385
9	a_{1u}	1.76	.264	.425	.000	a_{1u}	−3.79	.247	.435	.000	a_{1u}	6.00	.257	.429	.000
10	b_{1g}	3.69	.302	.243	.447	b_{1g}	−2.04	.304	.265	.417	b_{1g}	8.74	.295	.199	.497

i	$N^-(^2B_{1g})$ $E^{pi} = -370.190$ eV					$N^-(^2B_{3u})$ $E^{pi} = -369.060$ eV					$N^-(^2A_{1u})$ $E^{pi} = -367.894$ eV				
	sym-metry	ε_i	c_{1i}	φ_i c_{2i}	c_{9i}	*sym-metry*	ε_i	c_{1i}	φ_i c_{2i}	c_{9i}	*sym-metry*	ε_i	c_{1i}	φ_i c_{2i}	c_{9i}
1	=, b_{3u}	−9.56	.310	.270	.402	=, b_{3u}	−9.55	.300	.296	.382	=, b_{3u}	−10.02	.307	.228	.456
2	=, b_{2g}	−7.86	.263	.425	.000	=, b_{2g}	−8.15	.247	.435	.000	=, b_{2g}	−7.88	.268	.422	.000
3	=, b_{1g}	−6.72	.400	.202	.314	=, b_{1g}	−6.41	.406	.203	.297	=, b_{1g}	−7.07	.401	.191	.326
4	=, b_{3u}	−5.03	.032	.379	.460	=, b_{3u}	−5.48	.059	.366	.474	=, b_{3u}	−5.58	.009	.404	.417
5	=, a_{1u}	−4.59	.412	.283	.000	=, a_{1u}	−4.49	.418	.274	.000	=, a_{1u}	−4.75	.430	.254	.000
6	–, b_{1g}	2.40	.012	.380	.460	b_{2g}	2.39	.435	.247	.000	b_{1g}	2.45	.102	.449	.275
7	b_{2g}	3.75	.425	.263	.000	–, b_{3u}	3.51	.396	.169	.360	b_{2g}	2.71	.422	.268	.000
8	a_{1u}	5.48	.283	.412	.000	b_{1g}	4.92	.052	.404	.409	–, a_{1u}	4.51	.254	.430	.000
9	b_{3u}	6.14	.391	.183	.357	a_{1u}	6.63	.274	.418	.000	b_{3u}	5.60	.395	.187	.344
10	b_{1g}	8.48	.300	.255	.436	b_{1g}	8.13	.287	.213	.494	b_{1g}	8.12	.281	.109	.564

the lowest configuration of the cation), can be easily reproduced; this is evident from the comparison of the 2-nd and 3-rd groups of columns of Table II. The MO's written in these columns are optimal for the ground states of the ions. The orbitals presented in the next groups of columns are optimal for the higher electronic configurations, in the meanning of SADOP. As it can be seen from Table II, the singly occupied orbital φ_n is not always the lowest possible one (*i.e.* lower than all unoccupied MO's). It seems to be a reason for a rather slow convergence of the iteration process, often of an oscillating character.

In the CI procedure, the ground state of the ions and all possible 49 singly excited configurations have been included. The algorithm used made it possible to builtup the sub-sections of given symmetries of the CI matrix, from an arbitrary orbital basis. Using all the MO's obtained in the SCF procedures, three series of calculations have been carried out. Namely, the CI matrix have been constructed from:

1°: the closed-shell MO's of the ground state of naphthalene,

2°: the open-shell MO's, being optimal for the ground states of the ions,

3°: sub-sections of the CI matrix for naphthalene anion, of symmetries which are different than that of the ground state (B_{2g}), were constructed using MO's optimal for the lowest configurations of these symmetries (the 4-, 5- and 6-th groups of columns of Table II). This corresponds to the 2° CI approach from the preceding section, but here the same configuration as those in 1° and 2° were taken into account.

Moreover, the CI procedures including all singly excited, singlet and triplet configurations, have been carried out for naphthalene molecule, starting from the closed-shell MO's, the same as in 1°. In the series 1° and 2° the spinless and spin density matrices have been calculated.

All the calculations needed for the work have been done on GIER computer at the Department of Numerical Calculations, Warsaw University.

Discussion of the results

Absorption spectra

Table III presents experimental and calculated transition energies ΔE, for the absorption spectra of the naphthalene ions and naphthalene molecule. Some values, calculated by other authors, are also shown. Because of the pairing properties of the ions, the calculated spectra of alternant anions and cations are identical when the CI basis used are of the same types (*e. g.* singly excited). Therefore the results are only shown for the anion. The experimental results for alternant hydrocarbon cations indicate, *e. g.* [27, 28], that their spectra are practically identical with these of the anions. The symmetry designations used in the 1-st column of Table III are the direct products of the representations of ground states (A_{1g} for **N**, A_{1u} for $\mathbf{N}^+$ and B_{2g} for $\mathbf{N}^-$) and the final excited states, according to the multiplication table of the D_{2h} point symmetry group. The transitions designated B_{1u} are x-polarized (long symmetry axis of the molecule); those designated B_{2u} are y-polarized. The first three sets of calculated transition energies, presented for the anion, correspond to the three CI processes mentioned

in the preceding section. The energies in the 3° set have been calculated as differences of total *pi*-energies of respective states, each energy being evaluated using the MO's optimal for the lowest electronic configuration having the symmetry of this state:

$$\Delta E_i(B_{1u}) = E_i^{pi}(^2B_{3u}) - E^{pi}(^2B_{2g}),$$

$$\Delta E_i(B_{2u}) = E_i^{pi}(^2A_{1u}) - E^{pi}(^2B_{2g}). \qquad (9)$$

The similar method of calculations of transition energies has been used by Berthier [29] in his investigations on the benzyl radical spectrum. The next groups of columns of Table III contain some results of other authors: the results of Hinchliffe *et al.* [6] were obtained using the simplified semiempirical scheme [5] (the results of other methods, presented in [6] are significantly worse); those in [8] were received by means of approximate open-shell method [7]. In both the cases limited CI basis were used.

Although the theoretical interpretation of the anion spectrum presented below seems to be satisfactory, it is worse than that for the naphthalene molecule. The use of open-shell

TABLE III

Experimental and calculated transition energies, ΔE (in eV) for the absorption spectra of naphthalene molecule (N) and naphthalene (N^-)

symmetry of transition	polarization	N^- transitions from the $^2B_{2g}$ state						N transitions from the $^1A_{1g}$ state				
		calculated:					experimental	singlets			triplets	
		in the present work, CI process No.			by other authors			calculated	experimental		calculated	experimental
		1°	2°	3°	[6]	[8]			[24]	[23]		
B_{3g}	(forbidden)	1.05	1.13		1.05		0.97, 1.18, [21]					
B_{1u}	x	2.10 4.80 5.35	2.13 4.90 5.39	2.11 4.91 5.43	1.82 4.17 5.35	1.97 4.29 5.03	1.52,[21];1.57,[22] 3.83, [21] 4.25, [22]	4.19 6.16 7.97	4.02 5.89	3.97 5.63 7.41	3.87	3.62 [26]
B_{2u}	y	2.66 3.52	2.70 3.50	2.74 3.58	2.59 3.26	2.66 3.71	hidden?, see [8] 3.38, [21]	4.24 6.37	4.45	4.29 6.51	2.52	2.64 [25]

or SADOP MO's has no practical influence on the calculated transition energies. The energies of transitions of *y* polarization are in all the cases closer to the experimental values and the values obtained by means of the other methods, than these of *x* polarization. The first *x* transition in the anion spectra differs significantly from the experimental value and is distinctly higher than in the other calculations; the next ones are still too high, but closer to the

values obtained by other authors. It is evident from Table III, that the results obtained for the anion spectrum by means of the open-shell SCF CI method are not of the same quality as the ones, obtained for the naphthalene molecule by means of the standard SCF CI approach. This indicates, that the values of empirical parameters for ionized states should rather be changed.

TABLE IV

Charge and spin densities and bond orders — elements of the spinless **P** and spin **Q** density matrices, and proton hyperfine coupling constants a_r, for naphtalene ions. Where double signs occur, the higher one refers to the cation, N^+, the lower one to the anion, N^-. M — relation (10), [30]; CB — relation (11), [31]; GNP — relation (12), [32]

	positions	The closed — shell MO's of **N** used				The open — shell MO's of N^+ or N^- used			
		P	**Q**	$\mathbf{P}^{CI}$	$\mathbf{Q}^{CI}$	**P**	**Q**	$\mathbf{P}^{CI}$	$\mathbf{Q}^{CI}$
N^+	1,1	0.820	0.180	0.822	0.227	0.809	0.189	0.811	0.229
	2,2	0.930	0.070	0.923	0.042	0.909	0.061	0.905	0.042
	9,9	1.000	0	1.009	−.038	1.065	0	1.068	−.042
N^-	1,1	1.180	0.180	1.176	0.227	1.191	0.189	1.190	0.229
	2,2	1.070	0.070	1.079	0.042	1.091	0.061	1.094	0.042
	9,9	1.000	0	0.991	−.038	0.935	0	0.931	−.042
N^+ or N^-	1,2	0.637	±.112	0.626	±.127	0.607	±.107	0.603	±.127
	1,9	0.532	0	0.530	∓.015	0.553	0	0.549	∓.013
	2,3	0.649	∓.070	0.660	∓.088	0.683	∓.061	0.682	∓.088
	9,10	0.555	0	0.550	±.024	0.515	0	0.512	±.027

	coupling constants	relation	SCF	SCF+CI	SCF	SCF+CI	experiment
N^+	$-a_1$	M	4.86	6.13	5.00	6.18	5.54; [34]
		CB	5.27	6.64	5.56	6.74	4.90?; [33]
		GNP	5.53	6.85	5.71	6.89	
	$-a_2$	M	1.89	1.16	1.65	1.16	2.06; [34]
		CB	1.95	1.20	1.72	1.21	1.83?; [33]
		GNP	2.18	1.41	1.91	1.40	
N^-	$-a_1$	M	4.86	6.13	5.00	6.18	4.90; [33]
		CB	4.44	5.61	4.64	5.63	5.01; [9]
		GNP	4.19	5.41	4.29	5.57	
	$-a_2$	M	1.89	1.16	1.65	1.16	1.83; [33]
		CB	1.83	1.12	1.58	1.11	1.79; [9]
		GNP	1.60	0.91	1.39	0.92	

Density matrices and ESR spectra

Table IV presents charge and spin distribution, bond orders and proton coupling constants of the naphthalene ions, necessary for the interpretation of hyperfine structure of the ESR spectra. All these quantities have been calculated using the closed-shell orbitals of **N** (1-st group of columns, correspondind to the 1° CI process), as well as the MO's being optimal for the ground states of the ions (nest group of colums, corresponding to the 2° CI process; because only the properties of ground states of the ions are interesting, this corresponds also to the CI process 3°). The matrices **P** and **Q** are evaluated after the SCF procedures (see definitions (4) and the 1-st row of Table I); the ones designated $\mathbf{P}^{CI}$ and $\mathbf{Q}^{CI}$ are matrix representations, in the χ basis, of the spinless and spin density matrices after the CI procedure, P_1^{CI} and Q_1^{CI}, respectively. If we represent the wave function of the CI method as

$$\Psi = \sum_K A_K \Psi_K,$$

then

$$P_1^{CI} = P_1(\Psi, \Psi|1;1') = \sum_{K,L}\sum A_K A_L P_1(K, L|1;1'),$$

$$Q_1^{CI} = Q_1(\Psi, \Psi|1;1') = \sum_{K,L}\sum A_K A_L Q_1(K, L|1;1'),$$

the transition density matrices on the right sides are shown in Table I.

A comparison of the presented elements of the density matrices, interpreted as the charge and spin densities and bond orders, indicates that the use of open-shell orbitals has an evident influence on the calculated values, whereas the CI procedure changes distinctly only the spin distribution, but not the elements of spinless density matrix.

A simple relation between the spin density on the r-th conjugated atom in *pi*-electronic ion or radical Q_{rr}, and the hyperfine coupling constant for interaction of the unpaired electron spin with the spin of proton adjacent to this atom, a_r, was given by McConnell and Chesnut (M) [30]:

$$a_r \text{ (in gauss)} = -27\, Q_{rr}. \tag{10}$$

According to the above mentioned pairing properties of the ions, this relation implies identical splittings in the ESR patterns of the anion and cation of the same alternant aromatic system. On the other hand, it is the well known experimental fact, that for these systems the largest coupling constants in the cations are still larger than the corresponding ones in the anions. To explain this, two ways of improvement of the relation (10) were proposed. Colpa and Bolton (CB) [31] justified a linear dependence of the splittings on the excess electronic charge on r-th conjugated atom, $(1-P_{rr})$:

$$a_r = -[27+12.8\,(1-P_{rr})]\, Q_{rr}. \tag{11}$$

On the other hand, Giacometti, Nordio and Pavan (GNP) [32] included effects derived from the nearest conjugated atoms and used the following formula:

$$a_r = -27\, Q_{rr} - 6.3 \sum_{(nn)} Q_{r,(nn)}, \tag{12}$$

the summation runs over the nearest neighbours of r-th position. The constants appearing in the formuae (10–12) are now generally used according to [12], but those applied in the original papers [31, 32] had other values. The physical intuition expressed by the CB relation (11) is rather obvious, but the GNP relation (12) has evidently simpler theoretical basis. It should be emphasized that the elements of density matrices appearing in (10–12) refer only to the matrices of one-determinantal approximations (*e. g.* the Hückel or SCF methods without the CI, the UHF method without projections). Some authors have been surprised, that these relations, providing a very good interpretation of the ESR spectra in the one-determinantal approximations, do not interpret the experiments if the electron correlation is included in any way; it is also evident from the results of the CI method, which are presented in Table IV only in order to complete the results. More exact analysis of the inclusion of the *pi*-electronic CI procedure into the calculations of the coupling constants indicates, that none of the relations (10–12) is directly valid in this case [35].

The constants a_r presented in Table IV have been evaluated using all the three relations. The best results for the anion have been obtained with the M formula (10), when using the closed-shell MO's. The GPN relation (12) is often quoted as more effective than (11) (especially for the higher polyacene ions); here it changes the values rather considerably. Some doubts arise about the ESR spectrum of naphthalene cation, though the experimental results [33] are generally quoted for the anion as well as for the cation. The values of coupling constants offered by Lewis and Singer [34] are derived from the spectrum of naphthalene dimer cation, obtained in $SbCl_5$ (the spectrum in H_2SO_4, well known for the higher polyacene cations, has not been obtained for naphthalene).

Ionization potentials (IP) and electron affinity (EA)

These quantities for naphthalene molecule have been evaluated directly from their definitions in the *pi*-electronic approximation, *i. e*, as the differences of the total *pi*-electronic energies of the molecule and the ions:

$$\begin{aligned} \mathrm{IP}(\mathbf{N}) &= \mathrm{E}^{pi}(\mathbf{N}^+, {}^2\mathrm{A}_{1u}) - \mathrm{E}^{pi}(\mathbf{N}, {}^1\mathrm{A}_{1g}). \\ \mathrm{EA}(\mathbf{N}) &= \mathrm{E}^{pi}(\mathbf{N}, {}^1\mathrm{A}_{1g}) - \mathrm{E}^{pi}(\mathbf{N}^-, {}^2\mathrm{B}_{2g}). \end{aligned} \tag{13}$$

When using the closed-shell MO's of **N** for the evaluation of all the energies, the results are obviously the same, as the ones calculated from the Koopmans' theorem in the standard SCF method; in this case it gives the values 10.31 and 1.52 eV, respectively. But using the optimal MO's for a particular state for the evaluation of the energy of this state, we have a chance to include into the calculations some effects of deformation of the orbitals under (positive or negative) ionization. Such calculations give the values 10.21 and 1.63 eV, respectively (for the E^{pi} values — see Table II). Both these results are rather far from the experimental ones: 8.3 eV [36] for the IP and 0.15 eV [37] for the EA. The use of open-shell MO's, as well as the CI procedure, does not change, in practice, the results of Koopmans' theorem and it can be seen, that the sum of IP and EA is constant, which is a further aspect of the pairing properties (the energies of ground states are depressed identically for the anion and cation after the CI procedure). The evaluation of all the energies in (13), using the same values of empirical parameters, seems to be the main reason of the evident discrepancy

between the results of calculations and experiments. Some suggestions, concerning the changes of the parameters for ionized states, are enclosed in the works of Hoyland and Goodman [15]. These authors used the parameters, which were dependent on the excess electronic charge; they have also shown, that the values obtained from Koopmans' theorem or relations of the type (13) should be decreased by *ca* 0.8 eV bacause of changes of *sigma*--energies upon the *pi*-ionization. The agreement of calculated and experimental IP values, obtained in [15], is excellent; however it is not obvious that these parameters will also be more appropriate for the interpretation of absorption spectra of the ions.

Conclusions

The use of open-shell MO's in calculations for ionized systems practically does not change the results; the only advantage of this is a more simple construction of the CI matrix. The use of SADOP orbitals for excited states has negligible effects, though this conclusion is rather in opposition to the results of Berthier [29], where the calculations similar to these given by (9) gave strong effects on the values of transition energies in the benzyl radical spectrum; however, only a primitive CI basis was used there.

On the other hand, some changes of values of the empirical parameters for ionized states, the core integrals as well as the Coulomb ones, seem to be nacessary for obtaining reasonable values of ionization potentials and electron affinties, and for the interpretation of absorption spectra of the ions which would be comparable with the interpretation reached for singlet and triplet states of the molecules. However, when the new set of parameters values is chosen, all possible electronic properties of the ions should be calculated with it.

Some reasons for the necessity of changes of the parameters values for the open-shell states seem, generally speaking, to be related with unequivalent treatments of the electron correlation in the closed- and open-shell SCF CI methods. It should be noted, that the values of parameters in the standard PPP method are "influenced" by the correlation, connected with the inclusion of determined CI basis, which in the case of singly excited configurations consists of approximately $\frac{N^2}{4}$ configurational functions (N — number of conjugated atoms in the system). On the other hand, the basis of (formally) singly excited configurations for the system with one unpaired electron contains $N+N\left(\frac{N}{2}-1\right)$ functions and is evidently more wide. In addition, $\frac{N}{2}\left(\frac{N}{2}-1\right)$ configurations, of the type ${}^2\Psi_{a\to x}$, interact directly with the ground state; this does not take place in formally the same approximation for the closed-shell ground states. Moreover, the open-shell procedure itself includes some electron correlation, in the meanning of the definition based on the standard Hartree-Fock method. Therefore, the parameters for open-shell states, equivalent to the ones generally used in the closed-shell calculations, have to be "influenced" by the correlation to a rather different degree.

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REFERENCES

[1] P. Balk, S. deBruijn, G. J. Hoijtink, *Rec. Trav. Chim.*, **76**, 860, 907 (1957).
[2] G. J. Hoijtink, N. H. Velthorst, P. J. Zandstra, *Molecular Phys.*, **3**, 533 (1960).
[3] R. Pariser, R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).
[4] J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).
[5] H. C. Longuet-Higgins L. Salem, *Proc. Roy. Soc.*, **A257**, 445 (1960).
[6] A. Hinchliffe, J. N. Murrell, N. Trinajstić, *Trans. Faraday Soc.*, **62**, 1362 (1966).
[7] H. C. Longuet-Higgins, J. A. Pople, *Proc. Phys. Soc.*, **A68**, 591 (1955).
[8] A. Ishitani, S. Nagakura, *Theoret. Chim. Acta* (Berl.) **4**, 236 (1966).
[9] E. deBoer, S. I. Weissman, *J. Amer. Chem. Soc.*, **80**, 4549 (1958).
[10] G. J. Hoijtink, *Molecular Phys.*, **1**, 157 (1958).
[11] A. Hinchliffe, *Theoret. Chim. Acta* (Berl.), **5**, 208 (1966).
[12] L. C. Snyder, T. Amos, *J. Chem. Phys.*, **42**, 3670 (1965).
[13] N. S. Hush, J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).
[14] R. M. Hedges, F. A. Matsen, *J. Chem. Phys.*, **28**, 950 (1958).
[15] J. R. Hoyland, L. Goodman, *J. Chem. Phys.*, **36**, 12, 21 (1962).
[16] C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).
[17] C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
[18] R. McWeeny, Y. Mizuno, *Proc. Roy. Soc.*, **A295**, 554 (1960).
[19] G. Pilcher, H. A. Skinner, *J. Inorg. Nuclear Chem.*, **24**, 937 (1962).
[20] A. D. McLachlan, *Molecular Phys.*, **2**, 271 (1959).
[21] P. Balk, G. J. Hoijtink, J. W. H. Schreurs, *Rec. Trav. Chim.*, **76**, 813 (1957).
[22] K. H. J. Buschow, G. J. Hoijtink, *J. Chem. Phys.*, **40**, 2501 (1964).
[23] H. B. Klevens, J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949).
[24] O. E. Weigang Jr., *J. Chem. Phys.*, **33**, 892 (1960).
[25] D. F. Evans, *J. Chem. Soc.*, **1957**, 1351.
[26] R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).
[27] W. I. Aalbersberg, G. J. Hoijtink, E. L. Mackor, W. P. Weiland, *J. Chem. Soc.*, **1959**, 3049.
[28] T. Shida, W. H. Hamill, *J. Chem. Phys.*, **44**, 2375 (1966).
[29] G. Berthier, in *Molecular Orbitals in Chemistry, Physics and Biology*, Academic Press, New York–London 1964, p. 57.
[30] H. M. McConnell, D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958).
[31] J. P. Colpa, J. R. Bolton, *Molecular Phys*, **6**, 273 (1963).
[32] G. Giacometti, P. L. Nordio, M. V. Pavan, *Theor. Chim. Acta* (Berl.), **1**, 404 (1963).
[33] A. Carrington, F. Darvnieks, M. C. R. Symons, *J. Chem. Soc.*, **1959**, 947.
[34] I. C. Lewis, L. S. Singer, *J. Chem. Phys.*, **43**, 2712 (1965).
[35] J. Wasilewski, to be published.
[36] M. E. Wacks, V. H. Dibeler, *J. Chem. Phys.*, **31**, 1557 (1959).
[37] R. S. Becker, E. Chen, *J. Chem. Phys.*, **45**, 2403 (1966).