Theoret. chim. Acta (Berl.) 8, 244—248 (1967)

Aproximate Pairing Properties of SCF Solutions in Highly Symmetric Heteroatomic Systems*

JAROSLAV KOUTECKÝ**

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland

Received May 29, 1967

Approximate pairing properties are proved for the Hartree-Fock solutions for highly symmetric heteroatomic molecules. These molecules have an alternant topology and are built from two kinds of atoms in such a way that by an operation the atoms of one kind go over into the atoms of the second kind and vice versa.

Es werden genäherte alternierende Eigenschaften für Hartree-Fock-Lösungen hochsymmetrischer heterocyclischer Moleküle abgeleitet. Diese Moleküle haben eine alternierende Topologie, sie sind aus zwei Sorten von Atomen in solcher Weise aufgebaut, daß die Atome der ersten Sorte in die Atome der zweiten Sorte — und umgekehrt — transformiert werden können.

Des propriétés d'accouplement orbital approché sont prouvées pour les solutions de type Hartree-Fock des molécules hétéroatomiques hautement symétriques. Ces molécules ont une topologie alternante et sont formées de deux classes d'atomes de telle sorte qu'il existe une opération interchangeant les atomes des deux classes.

Consider a conjugated molecule with two kinds of atoms A and B, in which atoms B are the nearest neighbors of atoms A and vice versa, and for which there exists an operation R which interchanges the positions of atoms A and atoms B. The molecule has an alternant topology. The numbers of π-electrons Z_{A} and Z_{B} contributed by an atom of the kind A and B, respectively, are related by the relationship:

$$Z_{\mathrm{A}} + Z_{\mathrm{B}} = 2\,. \tag{1}$$

Triazine is an example of such a molecule. A reflection in the plane, perpendicular to and bisecting any C–N bond can be taken as R. The π-electron approximation is assumed.

If the Hamiltonian of such a molecule is $\hat{H}_1$, the Hamiltonian for a molecule obtained by application of R is $\hat{R}\hat{H}_1\hat{R}^{-1} = \hat{H}_2$. In particular, the Hamiltonian $\hat{H}_h$ corresponding to the Hückel approximation, together with the operator $\hat{R}\hat{H}_h\hat{R}^{-1}$, fulfill the equation defining the pairing properties (cf. [*1*]):

$$\hat{B}_1\hat{R}\hat{H}_h\hat{R}^{-1} + \hat{H}_h\hat{B}_1 = 2k\hat{B}_1 \tag{2}$$

where

$$\alpha_{\mathrm{A}} + \alpha_{\mathrm{B}} = 2k \tag{3}$$

---

* Supported in part by a grant to The Johns Hopkins University from the Petroleum Research Fund of the American Chemical Society.

** Permanent address: Institute of Physical Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia.

and

$$\hat{B}_1 = \hat{L}_A - \hat{L}_B . \tag{4}$$

α_A and α_B are Coulomb integrals for atomic orbitals on A and B, respectively. $\hat{L}_K$ is the projection operator into the subspace of the atomic orbitals localized on the atoms of the kind K(K = A, B).

Thus the following exchange relation holds:

$$\hat{R}\hat{L}_A + \hat{L}_B\hat{R} = \hat{0} . \tag{5}$$

Thus, to any Hückel molecular orbital $| \varepsilon >$ with an orbital energy ε there corresponds a molecular orbital $\hat{R}\hat{B}_1 \,|\varepsilon\rangle = - \hat{B}_1\hat{R}\,|\varepsilon\rangle$ with the orbital energy $(2k - \varepsilon)$.

The atomic orbital B is labeled $\bar{j}$, if it goes over into the atomic orbital A labeled by j, when the operation R is applied. It follows from the pairing properties of an even molecule that

$$p^0_{jk} + p^0_{\bar{j}\bar{k}} = 2\,\delta_{jk} \tag{6}$$

where p^0_{jk} and $p^0_{\bar{j}\bar{k}}$ are the bond orders obtained by the Hückel method.

The Theorem 1 of paper [2] (cf. [3]) formulates the exact conditions which garantee that heteroatomic systems with alternant topology have pairing properties in the Pariser-Parr-Pople approximation. Here I will show that the solution of the Hartree-Fock problem in the Pariser-Parr-Pople approximation for the kind of even conjugated molecules described earlier can have approximate pairing properties even if the conditions of the Theorem mentioned are not fulfilled. The approximate validity of the following equation for the Hartree-Fock effective Hamiltonian $\hat{F}$ must be proved:

$$\hat{R}\hat{F}\hat{R}^{-1} + \hat{B}_1^{-1}\hat{F}\hat{B}_1 = 2\,\varkappa\,\hat{I} , \tag{7}$$

where $\varkappa$ is a constant.

$$\hat{L}_A(\hat{R}\hat{F}\hat{R}^{-1} - \hat{F})\,\hat{L}_B = \hat{L}_B\,(\hat{R}\hat{F}\hat{R}^{-1} - \hat{F})\,\hat{L}_A = \hat{0} . \tag{8}$$

Eq. (8) is exact because

$$\begin{aligned} p_{j\bar{k}} &= p_{\bar{j}k} , \\ \gamma_{j\bar{k}} &= \gamma_{\bar{j}k} ; \end{aligned} \tag{9}$$

p_{jk} are the Hartree-Fock bond orders; γ_{jk} are the one- and two-center electron repulsion integrals. We are therefore obliged to study only the sum of diagonal elements F_{jj} and $F_{\bar{j}\bar{j}}$ and the sum of the off-diagonal elements F_{jk} and $F_{\bar{j}\bar{k}}$ of the operator $\hat{F}$ in the representation of the atomic orbitals:

$$\begin{aligned} F_{jj} + F_{\bar{j}\bar{j}} = 2k &+ \tfrac{1}{2}(p_{jj}\,\gamma_{jj} + p_{\bar{j}\bar{j}}\,\gamma_{\bar{j}\bar{j}}) + \\ &+ \sum_{t} (p_{tt} + p_{\bar{t}\bar{t}} - Z_A - Z_B)\,\gamma_{t\bar{j}} + \\ &+ \sum_{t \neq j} [(p_{tt} - Z_A)\,\gamma_{tj} + (p_{\bar{t}\bar{t}} - Z_B)\,\gamma_{\bar{t}\bar{j}}] , \\ F_{jk} + F_{\bar{j}\bar{k}} = &- \tfrac{1}{2}(p_{jk}\,\gamma_{jk} + p_{\bar{j}\bar{k}}\,\gamma_{\bar{j}\bar{k}}) , \qquad (j \neq k) . \end{aligned} \tag{10}$$

The bond orders calculated by the SCF procedure no longer fulfill relationship (6) exactly but the deviation from this relationship can be considered as small:

$$p_{jk} + p_{\bar{j}\bar{k}} = 2(\delta_{jk} + \lambda_{jk}) \tag{11}$$

where λ_{jk} is supposed to be a small number.

If the following symbols are introduced:

$$\begin{gathered} \bar{\gamma}_{jk} = \tfrac{1}{2}\,(\gamma_{jk} + \gamma_{\bar{j}\bar{k}})\,, \qquad \Delta_{jk} = \tfrac{1}{2}\,(\gamma_{jk} - \gamma_{\bar{j}\bar{k}})\,, \\ 2\mu = 2k + \bar{\gamma}\,, \qquad \bar{\gamma}_{jj} = \bar{\gamma}\,, \qquad \Delta_{jj} = \Delta\,, \end{gathered} \tag{12}$$

the expressions (10) can be rewritten as follows:

$$\begin{aligned} F_{jj} + F_{\bar{j}\bar{j}} &= 2\mu - \bar{\gamma}\,\lambda_{jj} + \tfrac{1}{2}\,(p_{jj} - p_{\bar{j}\bar{j}})\,\Delta + 2\sum_{t}\lambda_{tt}(\gamma_{t\bar{j}} + \bar{\gamma}_{tj}) + \\ &\quad + 2\sum_{t \neq j}[p_{tt} - p_{\bar{t}\bar{t}} - Z_{\mathrm{A}} + Z_{\mathrm{B}}]\,\Delta_{tj}\,, \\ F_{jk} + F_{\bar{j}\bar{k}} &= -\,p_{jk}\,\Delta_{jk} - \lambda_{jk}\,\gamma_{\bar{j}\bar{k}}\,, \qquad (j \neq k)\,. \end{aligned} \tag{13}$$

If we start the iteration procedure using the Hückel orbitals we get for the zero approximation $\hat{F}^0$ of the Hartree-Fock Hamiltonian:

$$\begin{aligned} F^0_{jj} + F^0_{\bar{j}\bar{j}} &= 2\mu + \tfrac{1}{2}\,(p^0_{jj} - p^0_{\bar{j}\bar{j}})\,\Delta + 2\sum_{t=j}[p^0_{tt} - p^0_{\bar{t}\bar{t}} - Z_{\mathrm{A}} + Z_{\mathrm{B}}]\,\Delta_{tj} \\ F^0_{jk} + F^0_{\bar{j}\bar{k}} &= -\,p^0_{jk}\,\Delta_{jk} \qquad (j \neq k)\,. \end{aligned} \tag{13a}$$

[The relation (6) is exact for the Hückel bond orders]. Eq. (13a) demonstrate that the primary reason for the deviations from pairing properties are the differences Δ_{jk} in the electron repulsion integrals. The diagonal elements of the density matrix of the first order are primarily determined by the electronegativities so that we can assume that the expressions $(p^0_{jj} - p^0_{\bar{j}\bar{j}})$ and even $(p_{jj} - p_{\bar{j}\bar{j}})$ are nearly constant. The quantities Δ_{jk} for larger distances are quite small. On the right hand side of the second Eq. (13a) these latter quantities are multiplied by the bond orders between nonadjacent atoms belonging to the same class. We can expect that these bond orders will also not be too large. From these considerations it can be concluded that the right hand side of the first Eq. (13a) is not too different from a constant for the molecules studied, and that the right hand side of the second Eq. (13a) not far from zero. The deviations from alternancy being not too important in the first step, the quantities λ_{jk} expressing these deviations should be small. Therefore, the right-hand side of the first Eq. (13) should also not be too far from a constant-independent of the index j — and the right hand side of the second Eq. (13) should be approximately zero.

Thus, one can expect for these systems the approximate fulfillement of the same kind of pairing properties as stated in an earlier paper for the corresponding Hückel solutions of the same molecules.

The approximate pairing properties can be demonstrated by calculations on the *s*-triazine molecule and on the (nonexistent) molecule 1,3,5,7,9-azanaphthalene in which the parameters of all "nitrogen" atoms were assumed to be the same (see the table). The parameters used in the Pariser-Parr-Pople approximation are $\beta_{\mathrm{CC}} = -2.318$ eV, $\beta_{\mathrm{CN}} = 2.700$ eV, $I_{\mathrm{C}} = 11.42$ eV, $A_{\mathrm{C}} = 0.58$ eV, $I_{\mathrm{N}} = 16.55$ eV, $A_{\mathrm{N}} = 1.78$ eV. The I are the semiempirical "ionization potentials", the A the semiempirical "electron affinities". The interatomic distances between nearest neighbors were assumed equal to 1.39 Å and the electron repulsion integrals were calculated by the Mataga procedure.

Table. *The* SCF *molecular orbitals of s-triazine and 1,3,5,7,0-azanaphthalene*[a]

s-Triazine

i	ε	−8.628938	−5.407137	−5.406911	+5.406911	+5.407143	+8.662653
1		0.442883	0.413414	0.527016	0.364795	−0.291442	−0.370384
2		0.370351	0.462270	−0.065953	−0.623731	−0.244236	0.442837
3		0.442840	0.249763	−0.621537	0.070057	0.461667	−0.370349
4		0.370384	−0.288194	−0.367366	0.523323	−0.418079	0.442883
5		0.442943	−0.663087	0.094466	−0.434787	−0.170138	−0.370413
6		0.370411	−0.173993	0.433260	0.100348	0.662221	0.442946

1,3,5,7,9-azanaphthalene

i	ε	−9.486323	−7.416913	−6.311783	−5.339635	−4.154548	+9.154548	5.336012	+6.361824	7.431416	+9.557799
1		0.305148	0.248571	0.316397	0.033953	0.301593	0.524392	−0.037872	−0.471445	−0.268753	−0.286299
2		0.267533	0.483062	0.142145	0.486533	0.296801	−0.212439	−0.296739	0.202286	0.365391	0.206039
3		0.208009	0.365835	−0.203781	0.296009	−0.214777	−0.296747	0.487446	0.140816	−0.481724	−0.264708
4		0.286101	0.266618	−0.471289	−0.040320	−0.524217	0.302997	−0.037662	−0.316217	0.249529	0.305015
5		0.286094	−0.266669	−0.471229	−0.040234	0.524256	−0.303032	−0.037594	−0.316226	−0.249507	0.304998
6		0.207964	−0.365810	−0.203705	0.296222	0.214662	0.296787	0.487588	0.140788	0.481600	−0.264623
7		0.267450	−0.482946	0.142115	0.486670	−0.296840	0.212319	−0.296958	0.202210	−0.365361	0.205993
8		0.305131	−0.248548	0.316406	0.033881	−0.301628	−0.524429	−0.037776	−0.471387	0.268806	−0.286292
9		0.525543	−0.000104	0.378119	−0.476140	−0.000036	0.000097	0.343699	0.300149	−0.000099	0.381973
10		0.379816	−0.000095	−0.298683	−0.344693	0.000097	0.000034	−0.473913	0.379463	0.000108	−0.528326

---

[a] The coefficient before the atomic orbital localized on the atom i in the molecular orbital with orbital energy $\varepsilon - \varkappa'$ is in the row i and in the column headed by ε.

One can find for any SCF molecular orbital $|\varepsilon_j\rangle$ of *s*-triazine or 1,3,5,7,9-azanaphthalene an SCF molecular orbital $|\varepsilon_j'\rangle$ such that the corresponding MO energies fulfill the relationship

$$\varepsilon_j' + \varepsilon_j = \varkappa' + \varepsilon_j \Delta_j \qquad (14)$$

where $\varkappa' = -7.188082$ eV, $|\Delta_j| < 4 \cdot 10^{-3}$ for *s*-triazine and $\varkappa' = -7.108407$ eV, $|\Delta_j| < 8 \cdot 10^{-3}$ for 1,3,5,7,9-azanaphthalene. The differences between the coefficients in $|\varepsilon_j'\rangle$ and $\hat{R}\hat{B}_1\,|\varepsilon_j\rangle$ are smaller than $6 \cdot 10^{-3}$ in the case of *s*-triazine and smaller than $4 \cdot 10^{-3}$ in the case of 1,3,5,7,9-azanaphthalene.

The properties described can be of importance not only for the *s*-triazine but also for the aromatic compounds of boron and nitrogen.

References

1. Koutecký, J.: J. chem. Physics **44**, 3702 (1966).
2. — J. chem. Physics. In press 1967.
3. Greenwood, H. H., and T. H. J. Hayward: Molecular Physics **3**, 495 (1960).

Prof. Dr. Jaroslav Koutecký
Institut für Physikalische Chemie
der Akademie der Wissenschaften
Prag 2 (Vinohrady), Machova 7
Tschechoslowakei