CROATICA CHEMICA ACTA CCACAA **59** (3) 711—717 (1986)

YU ISSN 0011 1643
CCA-1681 UDC 541
Original Scientific Paper

The Alternant Hydrocarbon Pairing Theorem and All-Valence Electrons Theory. An Approximate LCOAO Theory for the Electronic Absorption and MCD Spectra of Conjugated Organic Compounds. 1.

*Jens Spanget-Larsen**

Royal Danish School of Educational Studies, Department of Chemistry,
Emdrupvej 115 B, DK-2400 Copenhagen NV, Denmark

Received October 15, 1985

The significance of the pairing theorem for alternant hydrocarbons is demonstrated by a variety of experimental data, but standard all-valence electrons methods based on the »Neglect of Differential Overlap« (NDO) approximation fail to predict the observed pairing properties for this class of compounds. In this communication, a new all-valence electrons method is presented, using a basis of Löwdin orthogonalized atomic orbitals. This »Linear Combination of Orthogonalized Atomic Orbitals« (LCOAO) method is designed to predict the electronic absorption and magnetic circular dichroism data for organic π systems with particular emphasis on the pairing properties of alternants. Results for phenanthrene and hiphenylene are discussed.

It is well known that the classical π-electron theories by Hückel[1] and by Pariser, Parr, and Pople[2] (PPP) contain the pairing symmetry for alternant hydrocarbons.[3] This pairing symmetry has fundamental consequences for the predicted electronic transitions; e. g., only dipole transitions between so-called plus and minus states are allowed by the pairing symmetry,[4] and a mirror image relationship is predicted for the spectra of paired anions and cations.[5]

The perfect pairing symmetry of electronic states is predicted only by idealized model Hamiltonians; it is an abstract, purely mathematical concept. However, the physical and chemical significance of this concept is demonstrated by a wealth of experimental evidence, particularly for benzenoid hydrocarbons. For example, recent Magnetic Circular Dichroism (MCD) spectroscopic investigations of paired cations and anions have most convincingly confirmed the mirror image relationships required by the pairing symmetry.[6] There can be no doubt that the pairing theorem provides a unique insight into the electronic structure of alternants.

It is, therefore, disturbing that the widely adopted all-valence electrons methods, based on the Neglect of Differential Overlap (NDO) assumption[7], do not predict the pairing properties of alternant hydrocarbons. In particular, predictions based on the popular CNDO/S procedure[8] do not even approximate

---

* From August 1, 1986: Division of organic chemistry, DIA-K, Building 375, DK-2800 Lyngby, Denmark.

the degeneracies required by the pairing theorem.[9] The main reason for the strong breakdown of the pairing symmetry is the inclusion of next-neighbour interactions which are too large, essentially as a result of the inadequate treatment of orbital overlap effects within the NDO assumption.[10] This assumption simplifies the treatment of electron interaction, but it introduces serious errors in the one-electron terms.[11] The development of simple procedures which at the same time deal effectively with overlap effects and electron interaction terms is not straightforward.

An approach towards such a procedure is briefly outlined here. A new »Linear Combination of Orthogonalized Atomic Orbitals« (LCOAO) method is presented, using a basis of Löwdin OAOs.[12] The method is designed to predict the electronic absorption and MCD data for organic π systems,[13] with particular emphasis on the pairing properties of alternants.

Consider the elements $f_{\mu\nu}$ of the Fock matrix $\mathbf{f}$ for a closed shell molecule in a basis of AOs[7]

$$f_{\mu\nu} = t_{\mu\nu} + v_{\mu\nu} + \sum_{\lambda\sigma} p_{\lambda\sigma} [(\mu\nu, \lambda\sigma) - {}^1/_2\, (\mu\lambda, \nu\sigma)] \tag{1}$$

Here $t_{\mu\nu}$ and $v_{\mu\nu}$ are matrix elements of the kinetic energy operator and of the potential energy operator in the field of all atomic cores, respectively, and $p_{\lambda\sigma}$ is an element of the molecular density matrix. We now reformulate the Fock matrix in the following way:

$$\mathbf{f} = \mathbf{f}^{o} + \mathbf{f}^{q} \tag{2}$$

where $\mathbf{f}^{o}$ is the Fock matrix for a hypothetical superposition of neutral atoms in their valence states, and $\mathbf{f}^{q}$ is a molecular term depending on the electron displacements. The elements of $\mathbf{f}^{o}$ and $\mathbf{f}^{q}$ can be written

$$f_{\mu\nu}{}^{o} = t_{\mu\nu} + u_{\mu\nu} \tag{3}$$

$$f_{\mu\nu}{}^{q} = \sum_{\lambda\sigma} (p_{\lambda\sigma} - \delta_{\lambda\sigma}\, n_{\lambda}) [(\mu\nu, \lambda\sigma) - {}^1\!/_2\, (\mu\lambda, \nu\sigma)] \tag{4}$$

where n_{λ} is an averaged valence state AO occupation number and $u_{\mu\nu}$ is a penetration term

$$u_{\mu\nu} = v_{\mu\nu} + \sum_{\lambda} n_{\lambda} [(\mu\nu, \lambda\lambda) - {}^1\!/_2\, (\mu\lambda, \nu\lambda)] \tag{5}$$

As previously discussed in detail,[10] this formalism is particularly relevant in the present connection. $\mathbf{f}^{o}$ contains just those terms which have complicated transformation properties under orthogonalization, namely kinetic energy and penetration terms.[14] In contrast, the electron interaction terms tend to vanish in the OAO basis except for one- and two-center Coulomb repulsion integrals.[14,15] This is considered a justification of the NDO treatment of these integrals, and we may approximate the elements of $\mathbf{f}^{q}$ according to this treatment. We thus adopt the following operational scheme for an approximate evaluation of the Fock matrix in the Löwdin OAO basis (the λ-basis):

$${}^{\lambda}\mathbf{f} = \mathbf{S}^{-1/2}\, \mathbf{f}^{o}\, \mathbf{S}^{-1/2} + \mathbf{f}^{q}\ (\mathrm{NDO}) \tag{6}$$

The elements of $\mathbf{f}^{o}$ are evaluated explicitly in the OAO basis (from parametric integrals valid for AOs) via a full Löwdin transformation[12] involving the inverse square root of the AO overlap matrix **S**. The elements of $\mathbf{f}^{q}$ may be treated according to any of the invariant levels of NDO approximation, such as CNDO, INDO, and NDDO.[7] This scheme is conceptually related to those of Roby[16] and de Bruijn,[11] but it is based on a different partitioning of the Hamiltonian in order to avoid the difficulties with those schemes, as previously discussed.[10]

The details of the method will be given in a forthcoming paper.[17] Here we consider only one essential point concerning the parametrization of the off-diagonal elements of $\mathbf{f}^{\circ}$. We adopt the functional relationship[10]

$$f^{\circ}_{\mu\nu} = \tfrac{1}{2}\, S_{\mu\nu}\,(f_{\mu\mu}{}^{\circ} + f_{\nu\nu}{}^{\circ})\,[1 + k_{\mu\nu}\,(R_{AB})] \tag{7}$$

where $k_{\mu\nu}\,(R_{AB})$ is an analytical function of the internuclear distance. It is convenient to have a rough quide to the relation between ${}^{\lambda}f_{\mu\nu}{}^{\circ}$ and $f_{\mu\nu}{}^{\circ}$. Under the assumption that $f_{\mu\mu}{}^{\circ} = f_{\nu\nu}{}^{\circ}$ for all μ and ν (e. g., the π system of benzene) we get to the second order in $\Delta_{\mu\nu} = S_{\mu\nu} - \delta_{\mu\nu}$

$${}^{\lambda}f_{\mu\nu}{}^{\circ} = \{\mathbf{S}^{-1/2}\,\mathbf{f}^{\circ}\,\mathbf{S}^{-1/2}\}_{\mu\nu} \approx f_{\mu\mu}{}^{\circ}\,[\delta_{\mu\nu} + \Delta_{\mu\nu}\,k_{\mu\nu} - 1/2\,\sum_{\lambda} \Delta_{\mu\lambda}\,\Delta_{\lambda\nu}\,(k_{\mu\lambda} + k_{\lambda\nu})] \tag{8}$$

where the distance dependence of $k_{\mu\nu}$ is implicit. Keeping only the most significant terms leads to the expressions

$${}^{\lambda}f_{12}{}^{\circ} \approx f_{11}{}^{\circ}\,S_{12}\,k_{12} \tag{9}$$

$${}^{\lambda}f_{13}{}^{\circ} \approx f_{11}{}^{\circ}\,[S_{13}\,k_{13} - 1/2\,S_{12}\,S_{23}\,(k_{12} + k_{23})] \tag{10}$$

It is important to realize that the next-neighbour term ${}^{\lambda}f_{13}{}^{\circ}$ is essentially a three-centre term, and it may be positive, zero, or negative.[10,11] For next-neighbour terms to vanish in alternant π systems, which is one of the conditions for the presence of pairing symmetry, we have from Eq. (10) the relation[10]

$$k_{13}/k_{12} \approx S_{12}{}^{2}/S_{13} \tag{11}$$

constituting a bound on the distance dependence of $k_{\mu\nu}$. Considering benzene as a model compound, the pertinent overlap integrals between Slater-type $p\pi$ AOs are $S_{12} = 0.2455$ and $S_{13} = 0.0305$, leading to

$$k_{13}/k_{12} \approx 2.0 \tag{12}$$

In the implementation of the model, Eq. (12) is fulfilled by adopting the exponential relationship

$$k_{\mu\nu}\,(R_{AB}) \propto \exp\,(0.37\,R_{AB}) \tag{13}$$

for carbon-carbon interactions.[17] As a result, next-neighbour ${}^{\lambda}f_{\mu\nu}{}^{\circ}$ terms in the π system of benzene and benzenoid hydrocarbons tend to vanish, and near-perfect pairing symmetry is predicted for these compounds, in agreement with the experimental evidence. On the other hand, for those π systems with bond angles deviating significantly from 120° non-vanishing next-neighbour terms are predicted. The value of ${}^{\lambda}f_{13}{}^{\circ}$ tend to be negative or positive according to whether the angle C_1—C_2—C_3 is less than or larger than 120°, respectively (cf. Eq. (10)), leading in both cases to a perturbation of the alternant pairing symmetry.

As mentioned above, the main objective of the present all-valence electrons LCOAO method is the prediction of MCD spectra for organic π systems. The so-called MCD B-terms[13] for alternant hydrocarbons are extremely sensitive to the pairing properties of these systems,[18] but so far no computational method has been published which would be generally applicable to this class of compounds.[19] We conclude this paper by a very brief consideration of the calculated MCD B-terms for two alternants, namely phenanthrene and biphenylene. The B-terms were computed on the basis of the LCOAO-CI wavefunctions,[17] using a perturbation procedure similar to that of Warnick and Michl.[20,21]

The observed[22] and calculated MCD spectra of phenanthrene are shown in Figure 1. For comparison, the previously published results using a modified PPP method[19] are also given. In the PPP model the transitions labelled A, C, and F are forbidden by the pairing symmetry, leading to the prediction of zero MCD B-terms for these transitions. In the LCOAO model the pairing symmetry is closely approximated but it is not perfect; the transitions A, C, and F are allowed and B-terms are predicted which are in agreement with the observed MCD signs.[23] On the whole, the calculated

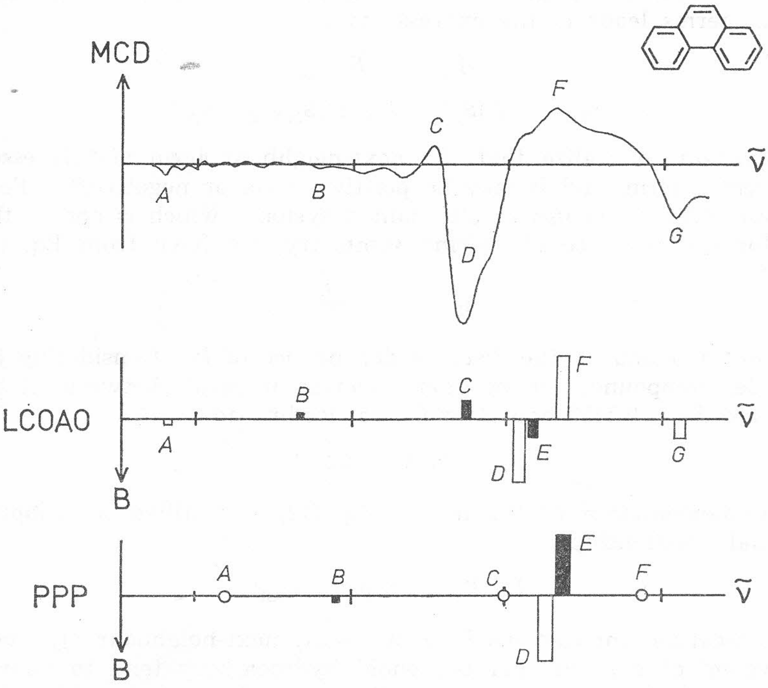

Figure 1. General outline of the observed[22] and calculated MCD spectra for phenanthrene in the 30000—45000 cm^{-1} region. The MCD B-terms for π—π^* transitions were calculated by the LCOAO method (this work) and by an PPP-type method,[13,19] with inclusion of next-neighbour terms in the approximation for matrix elements of the magnetic dipole moment operator. The sign and relative magnitude of the calculated B-terms are indicated by the direction and area of the bars. Black and white bars indicate long and short axis polarized electronic transitions, respectively; forbidden transitions are indicated by circles.

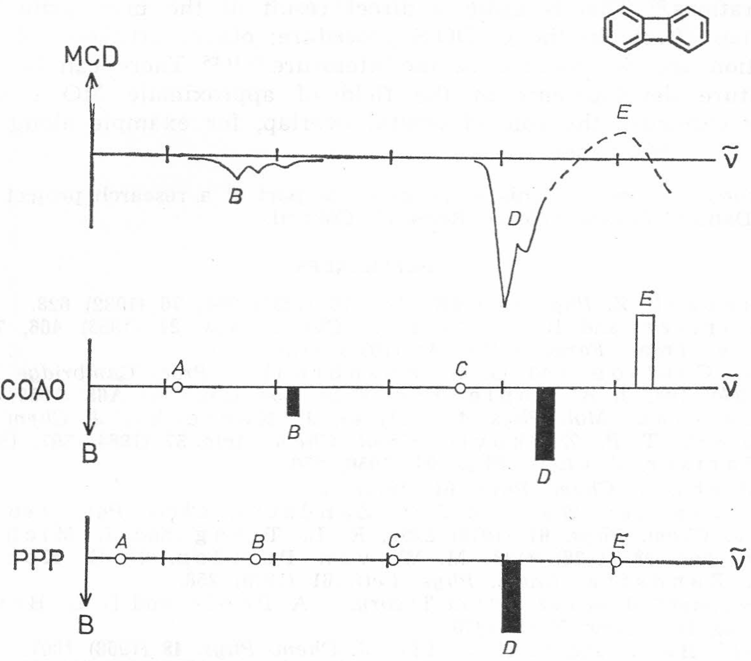

Figure 2. General outline of the observed[19] and calculated MCD spectra for biphenylene in the 25000—45000 cm^{-1} region. The transitions labelled A and C are electronically forbidden in the D_{2h} point group; see Figure 1 caption.

MCD spectrum reproduces fairly well the structure of the experimental curve. Seven excited singlet states are predicted below 47000 cm^{-1}, in consistency with the results of extensive CNDO-SDCI calculations.[24]

The MCD spectrum of biphenylene is shown in Figure 2.[19] The transitions labelled B an E are forbidden by the pairing symmetry in the PPP model, but are predicted to be fairly intense by the LCOAO method, with positive and negative B-terms, respectively. This is due to a significant breakdown of the pairing symmetry in the LCOAO model as a result of non-vanishing next-neighbour terms in the region of the four-membered ring in biphenylene. The calculated B-terms are in excellent agreement with the experimental spectrum. This result is a significant achievement of the present approach, considering the failure of previous attempts to predict the MCD spectrum of biphenylene.[19]

The results for phenanthrene and biphenylene, as well as those for numerous other hydrocarbons including alternant and non-alternant systems,[25] indicate that the present LCOAO procedure is generally successful in describing the MCD B-terms of π—π^* transitions. An application of the method to the electronic structure of radical ions has been previously published.[26] It is significant that the ordering of so-called Koopmans' and non-Koopmans' configurations is correctly described by the model.[26] In contrast, to be useful for the radical ions, the CNDO/S method requires an unphysical empirical scaling of the Koopmans' relative to the non-Koopmans' configurations.[27] This is again a direct result of the inadequate treatment of overlap effects in the CNDO/S procedure; other »artifacts« of the NDO assumption are documented in the literature.[10,11,28] There can be no doubt that future developments in the field of approximate MO theory must consider explicitly the role of orbital overlap, for example along the lines indicated in this paper.

Acknowledgment. — This investigation is part of a research project supported by the Danish Natural Science Research Council.

REFERENCES

1. E. Hückel, *Z. Phys.* **60** (1930) 423; **70** (1931) 204; **76** (1932) 628.
2. R. Pariser and R. G. Parr, *J. Chem. Phys.* **21** (1953) 466, 767; J. A. Pople, *Trans. Faraday Soc.* **49** (1953) 1375.
3. C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil. Soc.* **36** (1940) 193; J. A. Pople, *Proc. Phys. Soc. (London)* **A68** (1955) 81; A. D. McLachlan, *Mol. Phys.* **4** (1961) 49; J. Koutecký, *J. Chem. Phys.* **44** (1966) 3702; T. P. Živković, *Croat. Chem. Acta* **57** (1984) 367, 1553.
4. R. Pariser, *J. Chem. Phys.* **24** (1956) 250.
5. J. Michl, *J. Chem. Phys.* **61** (1974) 4270.
6. R. J. van der Wal and P. J. Zandstra, *Chem. Phys. Lett.* **36** (1975) 500; *J. Chem. Phys.* **64** (1976) 2261; K. L. Tseng and J. Michl, *J. Am. Chem. Soc.* **98** (1976) 6138; M. W. van Paridon, R. E. Koning, and P. J. Zandstra, *Chem. Phys. Lett.* **61** (1979) 258.
7. *Approximate Molecular Orbital Theory,* J. A. Pople and D. L. Beveridge, McGraw-Hill, New York 1970.
8. J. Del Bene and H. H. Jaffé, *J. Chem. Phys.* **48** (1968) 1807.
9. R. L. Ellis and H. H. Jaffé, *J. Mol. Spectr.* **50** (1974) 474; P. Jørgensen and J. Chr. Poulsen, *J. Phys. Chem.* **78** (1974) 1420; J. H. Obbink and A. M. F. Hezemans, *Chem. Phys. Lett.* **50** (1977) 133.
10. J. Spanget-Larsen, *Theor. Chim. Acta* **55** (1980) 165.
11. S. de Bruijn, *Chem. Phys. Lett.* **54** (1978) 399; erratum, *ibid.* **61** (1979) 420; *Int. J. Quantum Chem.* **25** (1984) 367.
12. P.-O. Löwdin, *J. Chem. Phys.* **18** (1950) 365; **21** (1953) 496; *Advan. Quantum Chem.* **5** (1970) 185.
13. *Linear and Magnetic Circular Dichroism of Planar Organic Molecules,* E. W. Thulstrup, Springer Verlag, Heidelberg 1980.
14. I. Fischer-Hjalmars, *J. Chem. Phys.* **42** (1965) 1962.
15. G. S. Chandler and F. E. Grader, *Theor. Chim. Acta* **54** (1980) 131, and references given therein.
16. K. R. Roby, *Chem. Phys. Lett.* **11** (1971) 6; **12** (1972) 579.
17. J. Spanget-Larsen, in preparation.
18. J. Michl, *J. Am. Chem. Soc.* **100** (1978) 6801, and subsequent papers.
19. N. H. Jørgensen, P. B. Pedersen, E. W. Thulstrup, and J. Michl, *Int. J. Quantum Chem.* **S12** (1978) 419.
20. S. M. Warnick and J. Michl, *J. Am. Chem. Soc.* **96** (1974) 6280.
21. J. Spanget-Larsen, *QCPE Bull.* **1** (1981) 37.
22. M. Vasek, M. R. Whipple, and J. Michl, *J. Am. Chem. Soc.* **100** (1978) 6867.
23. Positive B-term corresponds to negative MCD, and vice versa.
24. B. Dick and G. Hohlneicher, *Theor. Chim. Acta* **53** (1979) 221.
25. J. Spanget-Larsen, unpublished results.
26. J. Spanget-Larsen, *Croat. Chem. Acta* **57** (1984) 991.
27. G. Kluge and M. Scholz, *Int. J. Quantum Chem.* **20** (1981) 669; R. W. Bigelow, *Chem. Phys.* **80** (1983) 45.
28. N. C. Baird, *J. Chem. Soc. D. Chem. Commun.* 1970, 199; *Mol. Phys.* **18** (1970) 39; A. R. Gregory and M. N. Paddon-Row, *J. Am. Chem. Soc.* **98** (1976) 7521; J. Spanget-Larsen, C. de Korswagen, M. Eckert-Maksić, and R. Gleiter, *Helv. Chim. Acta* **65** (1982) 968; J. Spanget-Larsen and R. Gleiter, *Tetrahedron* **39** (1983) 3345.

SAŽETAK

Teorem sparivanja i teorija svih valentnih elektrona. Aproksimativna LCOAO teorija za analiziranje UV i MCD spektara konjugiranih organskih spojeva. 1.

J. Spanget-Larsen

Predložena je nova MO teorija svih valentnih elektrona, koja upotrebljava Löwdinove ortogonalizirane AO. Ta LCOAO metoda izvedena je s ciljem da služi za proučavanje UV i MCD spektara organskih π-elektronskih sustava, posebno svojstava alternantnih konjugiranih ugljikovodika.