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, part 2*

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Abstract. An approximate linear combination of orthogonalized atomic orbitals (LCOAO) all-valence electrons theory is described, based on a previously suggested partitioning of the Fock operator. Kinetic energy and penetration terms are evaluated explicitly in a Löwdin OAO basis, while two-electron repulsion terms are treated according to the conventional neglect of differential overlap (NDO) approximation. One-electron and penetration integrals are parameterized explicitly to predict approximate alternant pairing symmetry for the π-systems of benzene and napthalene. Application of the resulting LCOAO theory to a variety of alternant and non-alternant hydrocarbons demonstrates significant improvements in the prediction of MCD B-terms and transition moment directions, particularly for alternant $(4N+2)$- or $4N$-perimeter π-systems for which traditional NDO procedures fail.

Key words: All-valence electrons MO theory – AO orthogonalization effects – Alternant hydrocarbon pairing symmetry – Electronic transitions – Magnetic circular dichroism

1 Introduction

Progress in computational and theoretical chemistry [2] has made it possible to predict a variety of chemical phenomena by quantum chemical calculations from first principles to a high degree of accuracy. However, one of the most difficult problems in molecular theory, the description of excited electronic states, still poses difficulties. For a medium-sized molecule (e.g., the important carcinogen benzo[a]pyrene) accurate prediction of electronic transitions and excited state properties by ab initio procedures is extremely demanding in terms of computational effort and theoretical know-how. For most compounds of chemical and biochemical interest, the modelling of excited states is a field where the chemist for years to come must rely on the application of simplified theoretical procedures.

Approximate, semiempirical LCAO-MO procedures for the prediction of a variety of molecular properties have been developed to a considerable degree of perfection [3]. These procedures generally rely on the neglect of differential overlap (NDO) approximation [4], or more precisely, it is assumed that errors due to the inaccurate treatment of orbital overlap within the NDO approximation can be compensated for by a suitable adjustment of empirical parameters in the model. The NDO formalism greatly simplifies the treatment of two-electron interaction so that calculations on large molecules become feasible. However, it has become increasingly clear that this simplification is achieved at the expense of serious errors in the one-electron terms. For example, the repulsion between closed shells is a second-order overlap effect and is not reproduced by NDO methods [5]. This error is partially compensated for by neglect of penetration integrals [4] and by empirical parametrization of core-core repulsion terms [3], but NDO methods frequently have difficulties in modelling conformational, steric, and other properties that depend on specific closed-shell repulsion effects [5–9]. Moreover, as a result of the inadequate treatment of orbital overlap, NDO methods systematically overestimate the magnitude of non-bonded next-neighbour core integrals (resonance integrals) [1, 5, 9–11]. This is a serious error that cannot easily be repaired by empirical parametrization procedures; de Bruijn holds this error responsible for most of the failures of NDO theories [5]. In the present study we shall be particularly concerned with the circumstance that these errors are largely responsible for the failure of standard all-valence electrons NDO theories to predict the observed pairing properties for the electronic states of alternant conjugated hydrocarbons [1, 9].

It is well known that the classical π-electron models of Hückel (HMO) [12] and of Pariser, Parr, and Pople (PPP) [13] contain the perfect orbital pairing symmetry for alternant hydrocarbons [14]. This pairing symmetry

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* For part 1, see Ref. [1]

has important consequences for the predicted electronic transitions for this class of compounds; for example, only dipole transitions between so-called plus and minus states are allowed by the pairing symmetry [15] and a mirror image relationship is predicted for the spectra of paired anions and cations [16]. Perfect pairing symmetry is an abstract, purely mathematical concept and is predicted only by idealized model Hamiltonians [14], but the physical and chemical significance of this concept is demonstrated by a wealth of experimental evidence, particularly for benzenoid hydrocarbons [1, 9]. For example, the magnetic circular dichroism (MCD) spectra of paired cations and anions most convincingly confirm the mirror image relationships implied by the pairing symmetry [17, 18].

An important measure of the degree of orbital pairing symmetry for an alternant hydrocarbon is given by the quantity $\Delta HL = \Delta H - \Delta L$ [19], where ΔH is the energy difference between the two highest doubly occupied π MOs and ΔL that between the two lowest unoccupied π^* MOs. In the case of perfect pairing, $\Delta HL = 0$, as obtained in the HMO and PPP models, but the ΔHL values predicted with other calculational procedures are sensitive to details of the methods. The results of ab initio Hartree-Fock calculations [2] thus depend significantly on the basis set, as illustrated by ΔHL values predicted for naphthalene (**1**): -0.214 (STO-3G), -0.054 (6-31G*), and -0.013 eV (6-311G**) (HF calculations [20] at the experimental geometry [21]). Evidently, with a large basis set HF theory leads to close approximation of orbital pairing symmetry in the frontier region. The CIS/6-311G** [20] wave function for the lowest excited singlet state of **1** (L_b in Platt's perimeter model [19]) has leading contributions 48.0% $|1 \rightarrow -2\rangle - 48.8\%$ $|2 \rightarrow -1\rangle$, in close agreement with perfect minus-state symmetry (CIS = configuration interaction between singly excited configurations; $|i \rightarrow -j\rangle$ indicates an excited singlet configuration derived from the ground configuration by promotion of an electron from the i'th highest occupied to the j'th lowest unoccupied MO). Transition to this state is electronically allowed by the spatial symmetry but near-forbidden by approximate pairing symmetry, resulting in computed oscillator strength $f < 10^{-4}$. Recently, an advanced ab initio multi-configurational investigation of **1** by Roos and coworkers [22a] resulted in state wave functions with obvious pairing properties, e.g., predicted L_b and B_b states are dominated by minus and plus combinations of $|1 \rightarrow -2\rangle$ and $|2 \rightarrow -1\rangle$, etc.

There is thus strong experimental and theoretical evidence for the presence of approximate orbital and state pairing in benzenoid hydrocarbons and there can be no doubt that the pairing theorem provides a unique insight into their electronic structure. It is therefore disturbing that the widely adopted all-valence electrons methods based on the NDO formalism fail to predict the observed pairing properties for this important class of compounds. In fact, predictions based on the popular CNDO/S method of Del Bene and Jaffé [23] do not even approximate the degeneracies required by the pairing theorem [24–28]: CNDO/S yields large *positive* ΔHL values (naphthalene: $\Delta HL = +0.22$ eV; see Sect. 3.1.1 in this paper). The main reason for the strong breakdown

of the pairing symmetry is the inclusion of next-neighbour one-electron interactions that are too large, as indicated above. A number of attempts have been made to correct for this deficiency. For example, Obbink and Hezemans [24e] applied a PPP-like tight-binding approximation within the framework of the CNDO/S model (see also [29]). However, it is preferable to eliminate the inconsistencies of the underlying theory.

The development of convenient, approximate methods that deal effectively with overlap effects as well as electron interaction terms is a subject of current interest (see [3b, 30] and references cited therein). In this paper, an approximate linear combination of orthogonalized atomic orbitals (LCOAO) method is described that is conceptually related to a procedure suggested 25 years ago by Roby [31]. He introduced a simple scheme within the framework of ab initio Hartree-Fock theory where the one-electron part of the Hamiltonian is evaluated rigorously in a basis of symmetrically orthogonalized atomic orbitals (OAOs) [32], but the two-electron part is simplified according to the NDO formalism. Thereby the important one-electron overlap effects are accounted for, while at the same time the numerous multicentre integrals are avoided. At the semiempirical INDO level [4], de Bruijn [5] has suggested a scheme similar to that of Roby. However, both schemes are problematic, particularly because of the unbalanced representation of attractive and repulsive Coulomb interactions [1, 9]. As previously discussed in detail [1, 9], the present LCOAO strategy is based on a different partitioning of the Hamiltonian, thereby avoiding the difficulties with the schemes of Roby and de Bruijn. This paper describes the implementation of the LCOAO model and reports predicted electronic absorption and MCD data for a variety of conjugated hydrocarbons, considering alternants as well as non-alternants, and $4N$- as well as ($4N+2$)-perimeter π-electron systems.

2 Theory

2.1 An approximate LCOAO Fock matrix

Consider the elements $f_{\mu v}$ of the Fock matrix f for a closed-shell molecule in a basis of AOs [4]:

$$f_{\mu v} = t_{\mu v} + v_{\mu v} + \sum_{\rho\sigma} p_{\rho\sigma}[(\mu v|\rho\sigma) - \tfrac{1}{2}(\mu\sigma|\rho v)] \ . \tag{1}$$

Here $t_{\mu v}$ is a matrix element of the kinetic energy operator, $v_{\mu v}$ is an element of the potential energy operator in the field of all atomic cores, $p_{\rho\sigma}$ are elements of the molecular density matrix, and $(\mu v|\rho\sigma)$ are two-electron interaction integrals in Mulliken's notation. Using the grand canonical (GC) ensemble averaging procedure [33a] this expression is applicable also to simple open-shell systems; the density matrix is then defined as

$$p_{\mu v} = 2 \sum_i N_i c_{\mu i} c_{v i} \ , \tag{2}$$

where $c_{\mu i}$ and $c_{v i}$ are LCAO coefficients and the N_i are the MO half-occupation numbers in the GC ground

state: 1 for doubly occupied, 1/2 for singly occupied, and zero for virtual MOs. The Fock matrix f can be formulated as

$$f = f^\circ + f^q \quad , \tag{3}$$

where f° is the Fock matrix for a hypothetical superposition of neutral atoms in their valence states, and f^q is a molecular term depending on the electronic displacements. The elements of f° and f^q can be written

$$f_{\mu\nu}^\circ = t_{\mu\nu} + u_{\mu\nu} \tag{4}$$

$$f_{\mu\nu}^q = \sum_{\rho\sigma} (p_{\rho\sigma} - \delta_{\rho\sigma} n_\rho)[(\mu\nu|\rho\sigma) - \tfrac{1}{2}(\mu\sigma|\rho\nu)] \quad , \tag{5}$$

where n_ρ is an averaged valence state AO occupation number for the neutral atom and $u_{\mu\nu}$ is a penetration term

$$u_{\mu\nu} = v_{\mu\nu} + \sum_\rho n_\rho[(\mu\nu|\rho\rho) - \tfrac{1}{2}(\mu\rho|\rho\nu)] \quad . \tag{6}$$

Consider the transformation of f° and f^q into a basis of symmetrically orthonormalized AOs, the Löwdin OAO basis [32]. As discussed in detail in the literature [32, 34], all two-electron integrals tend to vanish in this basis except for one- and two-centre terms. This is considered as a justification of the NDO treatment of these integrals in semiempirical theories, and the elements of f^q may be treated according to any of the invariant levels of NDO approximation, such as CNDO, INDO and NDDO [4]. The elements of f° are more problematic. The results of Fischer-Hjalmars [34a] for π-systems indicate that f° contains just those terms that have complicated transformation properties under orthogonalization, i.e., kinetic energy and penetration terms. These terms should be evaluated explicitly in the Löwdin OAO basis, and we thus adopt the following operational scheme for an approximate evaluation of the Fock matrix in the Löwdin basis (the λ basis) [1, 9]:

$$^\lambda f = \mathbf{S}^{-1/2} f^\circ \mathbf{S}^{-1/2} + f^q(\text{NDO}) \quad . \tag{7}$$

The f° matrix is transformed into the OAO basis by an explicit Löwdin transformation [32] involving the inverse square root of the AO overlap integral matrix $\mathbf{S}$. The elements of f^q are treated according to conventional NDO theory.

As previously discussed in detail [9], the LCOAO procedure outlined in Eq. (7) accounts correctly for the important overlap effects on kinetic energy and penetration terms in f°, while maintaining the computational simplicity of the NDO treatment of the two-electron terms in f^q. It avoids the unbalanced representation of attractive and repulsive Coulomb effects which is a consequence of Roby's and de Bruijn's approach [5, 31]. The Coulomb contributions to f° and f^q involve only differences between equivalent terms; in a theory based on Eq. (7) attractive and repulsive Coulomb interactions are thus treated at the same level of approximation. In the following a semiempirical implementation of this scheme is described, using a basis of s and p valence AOs and parameterized with particular attention to a proper description of the pairing properties of alternant hydrocarbons.

2.2 Implementation of f°

2.2.1 One-centre terms

As defined above, f° is the Fock matrix for a hypothetical superposition of neutral atoms in their valence states. Consider the diagonal element in the AO basis

$$\begin{aligned} f_{\mu\mu}^\circ &= t_{\mu\mu} + u_{\mu\mu} \\ &= t_{\mu\mu} + \sum_B u_{\mu\mu}^B, \end{aligned} \tag{8}$$

where the summation is over all atoms and $u_{\mu\mu}^B$ represents the potential from the neutral atom B:

$$u_{\mu\mu}^B = v_{\mu\mu}^B + \sum_\rho^B n_\rho[(\mu\mu|\rho\rho) - \tfrac{1}{2}(\mu\rho|\rho\mu)] \quad . \tag{9}$$

The one-centre contribution $t_{\mu\mu} + u_{\mu\mu}^A$ (μ on atom A) can be interpreted as an AO electronegativity closely related to Mulliken's scale [35]. This is readily seen by consideration of the energy functional for an atom A in the averaged, spin-paired valence state [36]

$$E_A = \sum_\mu^A n_\mu(t_{\mu\mu} + v_{\mu\mu}^A) + \tfrac{1}{2}\sum_{\mu\nu}^A n_\mu n_\nu g_{\mu\nu} \quad , \tag{10}$$

where $g_{\mu\nu}$ is an effective electron interaction term corresponding to $[(\mu\mu|\nu\nu) - \tfrac{1}{2}(\mu\nu|\nu\mu)]$. With $I_\mu = E_A(n_\mu - 1) - E_A(n_\mu)$ and $A_\mu = E_A(n_\mu) - E_A(n_\mu + 1)$ we obtain

$$\begin{aligned} -\tfrac{1}{2}(I_\mu + A_\mu) &= (t_{\mu\mu} + v_{\mu\mu}^A) + \sum_\nu^A n_\nu g_{\mu\nu} \\ &= t_{\mu\mu} + u_{\mu\mu}^A \quad . \end{aligned} \tag{11}$$

Introducing this result in Eq. (8) we have (μ on A)

$$f_{\mu\mu}^\circ = -\tfrac{1}{2}(I_\mu + A_\mu) + \sum_{B(\neq A)} u_{\mu\mu}^B \quad . \tag{12}$$

The AO ionization energies I_μ and electron affinities A_μ can be evaluated empirically from appropriate atomic spectral data; in this work, the AO parameters derived by Sichel and Whitehead are adopted [37].

The two-centre penetration terms $u_{\mu\mu}^B$ in Eq. (12) represent the attraction of an electron in the AO μ by a distant, neutral atom B. $u_{\mu\mu}^B$ is a rapidly decreasing function of the internuclear distance R_{AB} because the electrostatic potentials due to the core and the electrons of atom B tend to cancel outside the atom. These terms are usually neglected in NDO theories [3, 4], but they should be included in theories that include a proper treatment of overlap effects [5c, 9, 30, 38]. An adequate representation of two-centre penetration terms in semiempirical all-valence electrons theories is problematic [4, 38–40], but it has been shown by Jørgensen et al. [38] that these contributions have great influence on the pairing properties of calculated wave functions for alternant hydrocarbons. Here we shall tentatively apply an anisotropic pseudo-potential of the form (μ, ν on A)

$$u_{\mu\nu}^B = -\tfrac{1}{2}\sum_\rho^B S'_{\mu\rho}(I_\rho + A_\rho)S'_{\rho\nu} \quad , \tag{13}$$

consistent with the assumption that penetration behaves asymptotically as the square of the orbital overlap. The choice of this functional form was inspired by the energy weighted maximum overlap (EWMO) formalism [41]. Note that penetration terms $u_{\mu v}^B$ are included in one-centre off-diagonal as well as diagonal elements of f°, thereby preserving rotational invariance. The overlap integrals $S'_{\mu v}$ in Eq. (13) are computed in the usual basis of Slater-type s and p valence AOs ($\zeta_H = 1.2$) [4], but the prime (') indicates that the off-diagonal overlaps are empirically scaled

$$S'_{\mu v} = d_{\mu v} S_{\mu v} \ , \tag{14}$$

where the scaling factors $d_{\mu v}$ are chosen as $d_p = 1.5$ (μ and v both p AOs) and $d_s = 0.5$ (otherwise). The numerical values, in particular the value for 1.5 for p AOs, were adjusted to obtain near-perfect pairing for naphthalene (see below). The resulting two-centre penetration contributions to $f_{\mu\mu}^\circ$ (Eq. 12) for $p\pi$-AOs in naphthalene (**1**) are

$$\sum_{B(\neq A)} u_{\pi\pi}^B \simeq -1.65 \text{ eV} \tag{15}$$

for positions A linked to two carbon atoms (i.e., α and β positions), and

$$\sum_{B(\neq A)} u_{\pi\pi}^B \simeq -2.25 \text{ eV} \tag{16}$$

for positions linked to three carbon atoms (i.e., positions 9 and 10 in **1**). The empirical values applied by Jørgensen et al. [38] are larger by approximately 50%.

The pseudo-potential in Eq. (13) is physically unrealistic in that it assumes that penetration effects are transmitted solely through orbital overlap. For a planar molecule, the potential does not describe the penetration of π-electrons into the σ core. Most importantly, the term $u_{\pi\pi}^H$ describing the penetration of a $p\pi$- electron into a (neighbouring) hydrogen atom is equal to zero. This approximation seems quite acceptable, however, judging from the results of Jørgensen et al. [38], who found that the observed pairing properties of benzenoid hydrocarbons could only be reproduced under the assumption that the magnitude of $u_{\pi\pi}^H$ is much less than that of $u_{\pi\pi}^C$: Jørgensen et al. thus adopted the empirically determined values $u_{\pi\pi}^H = -0.2$ eV and $u_{\pi\pi}^C = -1.1$ eV.

To summarize, the one-centre elements of f° are given by Eqs. (12)–(14) and can be written (μ, v on A)

$$f_{\mu v}^\circ = -\tfrac{1}{2} \sum_\rho S'_{\mu\rho}(I_\rho + A_\rho)S'_{\rho v} \ , \tag{17}$$

where the summation is over all valence AOs in the molecule. This expression involves the atomic parameters I_μ and A_μ that are taken from the tables of Sichel and Whitehead [37], and the two molecular penetration parameters d_s and d_p used in Eq. (14).

2.2.2 Two-centre terms

The two centre elements of f° can be written (μ on A, v on B)

$$f_{\mu v}^\circ = t_{\mu v} + u_{\mu v}^A + u_{\mu v}^B + \sum_{C(\neq A,B)} u_{\mu v}^C \ . \tag{18}$$

The three-centre penetration integrals in the summation term can be assumed to be negligible; $f_{\mu v}^\circ$ is essentially a local, di-atomic term. We consider the functional relationship [1, 9]

$$f_{\mu v}^\circ = \tfrac{1}{2} S_{\mu v}(f_{\mu\mu}^\circ + f_{vv}^\circ)[1 + k_{\mu v}(R_{AB})] \ , \tag{19}$$

where $k_{\mu v}(R_{AB})$ is an analytical function of the internuclear distance, to be determined according to a semiempirical strategy. It is useful to have some guidelines on the relation between $f_{\mu v}^\circ$ and $^\lambda f_{\mu v}^\circ$, the elements of f° in the AO and OAO bases. Under the assumption that $f_{\mu\mu}^\circ \simeq f_{vv}^\circ$ for all μ and v, we obtain to second order in $\Delta_{\mu v} \equiv S_{\mu v} - \delta_{\mu v}$:

$$^\lambda f_{\mu v}^\circ = \{S^{-1/2} f^\circ S^{-1/2}\}_{\mu v}$$
$$\simeq f_{\mu v}^\circ \left[\delta_{\mu v} + \Delta_{\mu v}k_{\mu v} - \tfrac{1}{2}\sum_p \Delta_{\mu\rho}(k_{\mu\rho} + k_{\rho v})\Delta_{\rho v} \right] \ , \tag{20}$$

where the distance dependence of the k's is implicit. Keeping only the most significant terms leads to the expressions [9]

$$^\lambda f_{11}^\circ \simeq f_{11}^\circ \left[1 - \sum_\rho S_{1\rho}^2 k_{1\rho} \right] \tag{21}$$

$$^\lambda f_{12}^\circ \simeq f_{11}^\circ S_{12}k_{12} \tag{22}$$

$$^\lambda f_{13}^\circ \simeq f_{11}^\circ [S_{13}k_{13} - \tfrac{1}{2}S_{12}(k_{12} + k_{23})S_{23}] \ . \tag{23}$$

These expressions are valid for small overlaps, e.g., for π-systems. Comparison of Eqs. (12)–(13) and (21) indicates that penetration and orthogonalization effects on a diagonal element $^\lambda f_{11}^\circ$ are of opposite sign and thus tend to cancel, a prerequisite for an adequate representation of alternant pairing symmetry in the model. $^\lambda f_{12}^\circ$ is essentially a local term, but the next-neighbour element $^\lambda f_{13}^\circ$ is effectively the sum of a two-centre "through-space" and a three-centre "through-bond" contribution. $^\lambda f_{13}^\circ$ may be positive, zero, and negative, depending on the relative magnitude of the two contributions. In NDO theories only the first term in Eq. (23) is included, with the result that next-neighbour interactions in π-systems are too large, leading to different errors in energy for different MOs according to their nodal structure. Next-neighbour terms must essentially vanish for alternant π-systems if the pairing symmetry is to be contained in the model and Eq. (23) thus constitutes a bound on the distance dependence of $k_{\mu v}$ [1, 9]. Considering the π-system of benzene as a model case, we have

$$k_{13}/k_{12} \simeq S_{12}^2/S_{13} \ . \tag{24}$$

The pertinent overlap integrals between Slater-type $p\pi$ AOs in benzene are $S_{12} = 0.2455$ and $S_{13} = 0.0305$, leading to

$$k_{13}/k_{12} \simeq 1.98 \tag{25}$$

Equation (25) requires that $|k_{\mu v}|$ is an increasing function of R_{AB}. We shall adopt the exponential relationship

$$k_{\mu v} = a\, e^{bR_{AB}(\zeta_A + \zeta_B)/2} \quad , \tag{26}$$

where a and b are positive constants and ζ_A and ζ_B are the Slater AO exponents: 1.625 for C, 1.2 for H, etc. [4]. Equations (25) and (26) yield $b \simeq 0.22\, a_0^{-1}$ (inverse Bohr radii). In a full calculation on benzene $^\lambda f_{13}^\circ$ vanishes for $b = 0.23\, a_0^{-1}$, and we shall adopt this value. $k_{\mu v}$ increases with R_{AB}, but with $b < a_0^{-1}$ the functional form in Eq. (26) ensures that the product $S_{\mu v} k_{\mu v}$, and thereby $f_{\mu v}^\circ$ in Eq. (19), goes to zero for large R_{AB}, as it should, also for Slater functions diffuser than those of carbon.

As a result, values close to zero will be predicted for next-neighbour $^\lambda f_{\mu v}^\circ$ terms in the π-systems of benzenoid hydrocarbons. On the other hand, for those π-systems with bond angles deviating significantly from $120°$ non-vanishing next-neighbour terms are obtained. The value for $^\lambda f_{13}^\circ$ tends to be negative or positive according to whether the angle C_1-C_2-C_3 is less than or larger than $120°$. In the first case, C_1 is relatively close to C_3 and $^\lambda f_{13}^\circ$ is dominated by the direct "through-space" contribution. In the second case, C_1 and C_3 are more distant and the "through-bond" term in Eq. (23) dominates. In both cases the result is a perturbation of the pairing symmetry [1].

The multiplicative constant a in Eq. (26) is determined by a consideration of $^\lambda f_{12}^\circ$ in Eq. (22). It is well known from standard PPP-CIS theory [13] that the resonance integral β^c must be around -2.5 eV in order to predict electronic transition energies for hydrocarbon π-systems. In the present theory $^\lambda f_{12}^\circ$ plays a similar role to the classical β^c parameter and must be of similar magnitude, which is achieved by taking $a = 0.75$. This value applies to π-type interactions; for σ-type interactions we adopt a value of unity.

The final expression for two-centre $f_{\mu v}^\circ$ elements can be written (μ on A, v on B)

$$f_{\mu v}^\circ = \tfrac{1}{2}(f_{\mu\mu}^\circ + f_{vv}^\circ)[S_{\mu v} + (S_{\mu v}^\sigma + aS_{\mu v}^\pi)e^{bR_{AB}(\zeta_A + \zeta_B)/2}] \quad , \tag{27}$$

with $a = 0.75$ and $b = 0.23\, a_0^{-1}$. $S_{\mu v}^\sigma$ and $S_{\mu v}^\pi$ are the σ and π components of the diatomic overlap integral. The constant a thus corresponds to the κ parameter in CNDO/S theory [23].

This concludes the definition of $\boldsymbol{f}^\circ$ which is given in Eqs. (17) and (27). It involves four molecular parameters, namely $d_S = 0.5$ and $d_p = 1.5$ in Eq. (14) and $a = 0.75$ and $b = 0.23\, a_0^{-1}$ in Eq. (27). $\boldsymbol{f}^\circ$ and $^\lambda \boldsymbol{f}^\circ \equiv \boldsymbol{S}^{-1/2}\boldsymbol{f}^\circ \boldsymbol{S}^{-1/2}$ need only be computed once for a given nuclear configuration. A standard secular problem on the basis of $^\lambda \boldsymbol{f}^\circ$ initiates the SCF procedure and yields in effect the "random state" or "tempered" MOs discussed by Mehrotra and Hoffmann [42]. In the subsequent SCF cycles, the secular problem involves the full Fock matrix $^\lambda \boldsymbol{f}$ in Eq. (7) which depends on the molecular ground state density matrix $\boldsymbol{p}$ through the elements of $\boldsymbol{f}^q$.

2.3 Implementation of $\boldsymbol{f}^q$

The elements of $\boldsymbol{f}^q$ are easily expressed and evaluated within the NDO framework. We are primarily concerned with the prediction of π–π^* transitions, which means that a CNDO approximation to the elements of $\boldsymbol{f}^q$ should be adequate (μ on A, v on B) [9]:

$$f_{\mu\mu}^q(\text{CNDO}) = -\tfrac{1}{2}q_\mu \gamma_{AA} + \sum_B Q_B \gamma_{AB} \tag{28}$$

$$f_{\mu v}^q(\text{CNDO}) = -\tfrac{1}{2}p_{\mu v}\gamma_{AB} \tag{29}$$

with the notation

$$q_\mu = p_{\mu\mu} - n_\mu \tag{30}$$

$$Q_B = \sum_v^B q_v \quad . \tag{31}$$

The average AO occupation numbers n_μ are defined according to the prescription by Mehrotra and Hoffmann [42]:

$$n_\mu = N_{\text{el}}/N_{\text{orb}} \tag{32}$$

for all AOs on atom A, where N_{orb} is the number of valence orbitals and N_{el} the number of valence electrons in the neutral atom. For hydrocarbons, all n_μ are thus equal to unity. The atomic electron repulsion parameters γ_{AA} are taken from the tables of Sichel and Whitehead [37], and the diatomic parameters γ_{AB} are evaluated as discussed in the following section (Eq. 41).

2.4 Electronic states

2.4.1 Grand canonical and canonical ensemble theory

In Hartree-Fock and grand canonical (GC) Hartree-Fock theory [33a] the electronic energy of the ground state is obtained as

$$^{GC}E_0 = 2\sum_i N_i \varepsilon_i - 2\sum_i \sum_{j \neq o} N_i N_j \left[(ii|jj) - \tfrac{1}{2}(ij|ij)\right] \tag{33}$$

where i and j indicate MOs, the ε_i are the MO energies, and N_i are the half-occupation numbers (Eq. 2). For open-shell systems, the sum over j does not involve singly occupied MOs, labeled o. For these systems Eq. (33) refers to a spin-averaged "pseudo-singlet" state [33a]. In the important case of an open-shell system with one electron in a single, non-degenerate MO, a canonical (C) Hartree-Fock doublet ground state energy can be projected as [33a]

$$^{C}E_0 = {}^{GC}E_0 - \tfrac{1}{4}(oo|oo) \quad , \tag{34}$$

corresponding to Dewar's "half-electron" model [33b]. Excited electronic states may be predicted by the usual configuration interaction (CI) procedure. In the GC CIS approximation, excited singlet states and excitation energies are obtained by solution of a CI secular problem with matrix elements [33a]

$$^{GC}\langle i \to k|\hat{\mathscr{H}}|j \to l\rangle = \delta_{ij}\delta_{kl}(\varepsilon_k - \varepsilon_i)$$

$$- [(N_i - N_k)(N_j - N_l)]^{1/2}[(ij|kl) - 2(ik|jl)] \tag{35}$$

In the closed-shell case, all $N_i = N_j = 1$ and all $N_k = N_l = 0$; the factors involving the half-occupation numbers can thus be omitted. For open-shell systems, Eq. (35) refers to spin-averaged pseudo-singlet configurations. For a radical with one unpaired electron in a single, non-degenerate MO, the doublet state canonical CI matrix elements are given by [33a]

$$^C\langle i \rightarrow k|\hat{\mathscr{H}}|j \rightarrow l\rangle = {}^{GC}\langle i \rightarrow k|\hat{\mathscr{H}}|j \rightarrow 1\rangle$$

$$+ [(N_i - N_k)(N_j - N_l)]^{-1/2}\tfrac{1}{4}\left(\delta_{lo}\delta_{io}(ko|jo) + \delta_{jo}\,\delta_{ko}\,(io|lo)\right.$$

$$\left. - \delta_{ko}\delta_{lo}(jo|io) - \delta_{io}\delta_{jo}(lo|ko)\right) ,$$

$$(36)$$

where the label o refers to the singly occupied MO. Predictions based on Eq. (36) are valid in the low-energy region dominated by transitions involving this MO. Electric dipole transition moments for transitions from ground to excited configurations are obtained as

$$\langle 0|\vec{\hat{M}}|i \rightarrow k\rangle = (N_i - N_k)^{1/2}\sqrt{2}\langle i|\vec{\hat{M}}|k\rangle ,$$

$$(37)$$

where $\vec{\hat{M}}$ is the electronic dipole moment operator, and oscillator strengths f are calculated as usual by the dipole length formalism [23, 49].

2.4.2 Implementation

The integrals $(ij|kl)$ and $\langle i|\vec{\hat{M}}|k\rangle$ are treated according to the principles of conventional CNDO theory [4, 23]. It is of particular importance to consider the parameters γ_{AB} appearing in the CNDO expansion of the two-electron integrals. The CIS results discussed in this paper were obtained with consideration of mono-excited π-π^* configurations only (excluding the in-plane π-orbitals associated with the acetylenic linkages in compounds **9** and **10**, Sect. 3.1.2). Within this approximation the difference in energy of the two lowest excited states of D_{6h} benzene is given by a simple expression determined by symmetry [13a]:

$$E\left(^1\mathrm{B}_{1u}^-\right) - E\left(^1\mathrm{B}_{2u}^+\right) = \tfrac{1}{6}[2\gamma_{11} - 6\gamma_{12} + 10\gamma_{13} - 6\gamma_{14}] \quad (38)$$

The energy difference predicted by Eq. (38) is very sensitive to the numerical values of the γ_{AB} parameters and in particular to the steepness of the function used to evaluate the diatomic terms. The most widely adopted functions can be written as

$$\gamma_{AB} = \left[R_{AB}^t + 2^t(\gamma_{AA} + \gamma_{BB})^{-t}\right]^{-1/t} .$$

$$(39)$$

For $t = 1$ we have the Mataga-Nishimoto (MN) formula [43], and for $t = 2$ the Dewar-Sabelli-Ohno-Klopman (DSOK) formula [44]. Taking $\gamma_{AA} = 10.93\,\mathrm{eV}$ for carbon [37] the parameters included in Eq. (38) obtain the following values (eV):

	MN	DSOK	
γ_{11}	10.93	10.93	
γ_{12}	5.30	7.50	
γ_{13}	3.85	5.23	
γ_{14}	3.50	4.66	(40)

On the basis of MN parameters, Eq. (38) yields an energy difference equal to 1.26 eV, whereas the DSOK parameters lead to a value close to 0.2 eV. The experimental value is 1.25 eV, indicating that MN parameters are adequate. It is a general result that in CI calculations including only singly excited configurations (CIS), γ functions with a steep R-dependence must be applied, corresponding to a strongly screened Coulomb potential. If the CI expansion is extended to include doubly or multiply excited configurations, thereby explicitly introducing terms in electron correlation, less strongly screened γ potentials are appropriate [45]. The relation adopted in the present LCOAO procedure is [46]

$$\gamma_{AB} = [R_{AB}^t + 2^{-t}(\gamma_{AA}^{-1} + \gamma_{BB}^{-1})^t]^{-1/t} ,$$

$$(41)$$

with $t = 1$ and with application of the atomic γ_{AA} parameters derived by Sichel and Whitehead for two-centre repulsion terms in CNDO theories [37]. In the homo-nuclear case, Eqs. (39) and (41) are equivalent, but Eq. (41) predicts slightly larger γ_{AB} values in the hetero-nuclear case. The CI expansion generally included a maximum of 100 singly excited configurations with an excitation energy below 15 eV.

2.5 MCD B-terms

MCD spectroscopy [47–49] provides unique information on fundamental aspects of the electronic structure of organic π- systems, as discussed in particular by Michl [19]. In the present investigation MCD B-terms for π-π^* transitions are predicted by a perturbation procedure similar to that of Warnick and Michl [48, 50]. The B-term for a transition from the ground state $|0\rangle$ to the excited state $|F\rangle$ is obtained by the sum-over-states expansion

$$B(0 \rightarrow F) = B_0 + B_F$$

$$= \sum_{I(\neq 0)} B_{0,I} + \sum_{I(\neq F)} B_{F,I} ,$$

$$(42)$$

where

$$B_{0,I} = [\langle I| - i\vec{\hat{\mathscr{M}}}|0\rangle \cdot \langle 0|\vec{\hat{M}}|F\rangle \times \langle F|\vec{\hat{M}}|I\rangle]/(E_I - E_0) \quad (43)$$

$$B_{F,I} = [\langle F| - i\vec{\hat{\mathscr{M}}}|I\rangle \cdot \langle 0|\vec{\hat{M}}|F\rangle \times \langle I|\vec{\hat{M}}|0\rangle]/(E_I - E_F) .$$

$$(44)$$

The sums are over the electronic states $|I\rangle$ with energies E_I, and $\vec{\hat{\mathscr{M}}}$ is the magnetic and $\vec{\hat{M}}$ the electric dipole moment operator. B_0 expresses the contribution to the B-term due to magnetic coupling between the ground state $|0\rangle$ and the excited state $|F\rangle$, and B_F is the contribution due to coupling of state $|F\rangle$ with other excited states $|I\rangle$. The latter contribution to $B(0 \rightarrow F)$ is generally the more important, because of the smaller denominators $E_I - E_F$ in Eq. (44). For two excited states with a small energy difference, the B-terms are often dominated by the magnetic coupling between the two states, leading to B-terms with opposite signs (since

$B_{I,J} = -B_{J,I}$). MCD spectroscopy thus frequently leads to resolution of otherwise overlapping transitions.

Elements of $\hat{\vec{M}}$ and $\hat{\vec{\mathcal{M}}}$ over π-type OAOs are estimated by the expressions [19, 38, 48, 49] (μ on A, v on B)

$$\langle \mu | \hat{\vec{M}} | v \rangle = -e\vec{R}_A \, \delta_{\mu v} \tag{45}$$

$$\langle \mu | -i\hat{\vec{\mathcal{M}}} | v \rangle = \frac{m_e}{\hbar^2} \beta'_{\mu v}(\vec{R}_A \times \vec{R}_B) \quad , \tag{46}$$

where $\vec{R}_A$ is the position vector of centre A and $\beta'_{\mu v}$ is an effective β parameter related to the core integral β^c in PPP theory. Equation (46) is based on Linderberg's relation [51] and expresses an element of $-i\hat{\vec{\mathcal{M}}} = \vec{r} \times \vec{\nabla}$ in units of Bohr magneton ($\beta_e = e\hbar/2m_e$); for a detailed account see, for example, Ref. [48].

If $\beta'_{\mu v}$ in Eq. (46) is set equal to the PPP β^c parameter with inclusion of neighbour terms only, a PPP calculation using Eqs. (45) and (46) predicts vanishing MCD B-terms for alternant hydrocarbons [19, 49]. This disagrees with the experimental evidence. More realistic results are obtained if β' is adjusted empirically. The relations

$$\begin{align} \beta'_{12} &= \beta^c \\ \beta'_{13} &= -0.15\,\beta^c \end{align} \tag{47}$$

have been applied with success in PPP calculations on benzenoid hydrocarbons [19, 38, 48, 49]. Here β^c is the standard PPP parameter appropriate for the calculation of wave functions (with perfect alternant pairing symmetry), and β'_{12} and β'_{13} are the parameters used in Eq. (46) for neighbour and next-neighbour terms. In the present LCOAO theory, $\beta'_{\mu v}$ in the OAO basis is estimated by the relation

$$\beta'_{\mu v} = \{ \mathbf{S}^{-1/2} \mathbf{f}' \mathbf{S}^{-1/2} \}_{\mu v} \quad , \tag{48}$$

where S is the AO overlap integral matrix and $\mathbf{f}'$ is defined in the AO basis by

$$\begin{align} f'_{\mu\mu} &= f^\circ_{\mu\mu} \\ f'_{\mu v} &= \tfrac{1}{2} S_{\mu v}(f^\circ_{\mu\mu} + f^\circ_{v v})[1 + k] \end{align} \tag{49}$$

with $k = 1.5$. $f^\circ_{\mu\mu}$ is given by Eq. (17) and is of the order of -7.5 to -8 eV for π AOs in planar hydrocarbons. The $\beta'_{\mu v}$ values predicted on the basis of Eqs. (48) and (49) for benzenoid compounds are in agreement with the empirical rules in Eq. (47).

For π-systems with less than D_{2h} symmetry, MCD B-terms calculated by the theory outlined above depend on the origin of the molecular coordinate system. However, the results of a series of trial calculations, as well as previous results using π-electron models [19, 38, 48, 49], indicate that the origin dependence is insignificant as long as the origin is kept inside the molecule. In the present calculations the origin is chosen as the centre of gravity of the ground state π-electron density, and the resulting MCD B-terms are given in units of 10^{-3} $\beta_e \mathrm{D}^2/\mathrm{cm}^{-1}$ ($\beta_e = $ Bohr magneton, D = Debye).

3 Results and discussion

In the following, the LCOAO theory described above is applied to several hydrocarbons, considering alternant as well as non-alternant systems. The compounds investigated are indicated in Scheme 1. Experimental
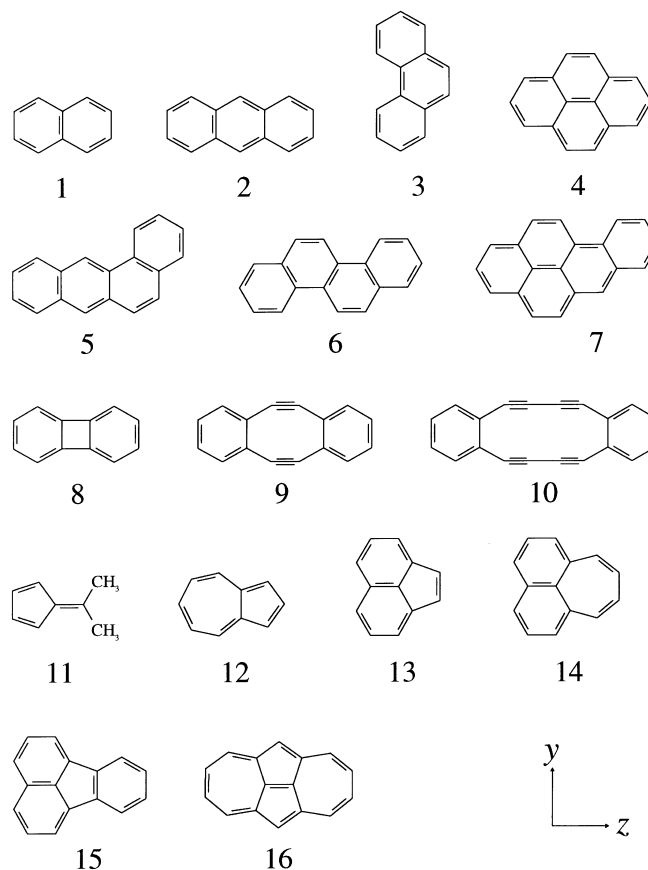
geometries were adopted for naphthalene (**1**) [21], anthracene (**2**) [52], phenanthrene (**3**) [53], pyrene (**4**) [54], chrysene (**6**) [55], benzo[*a*]pyrene (**7**) [56], biphenylene (**8**) [57], *sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne (**9**) [58], 6,6-dimethylfulvene (**11**) [59], azulene (**12**) [60], and acenaphthylene (**13**) [61]. The geometries of the remaining compounds were taken as predicted by the MNDO method [62], except for the naphthalene radical ions ($\mathbf{1}^{\cdot-}$ and $\mathbf{1}^{\cdot+}$) where geometries predicted with PM3-UHF [63] were applied.

The results are given in Tables 1–17. In most cases, the experimental wave numbers given in the tables refer to band onsets, $\tilde{v}_{00}$ (in *italics*), but the calculated wave numbers correspond to vertical transitions and should thus be compared with observed $\tilde{v}_{max}$ values (or "centres of gravity" of the bands); the calculated wave numbers actually tend to be slightly larger than the observed $\tilde{v}_{00}$ values. Poor agreement is expected for those excited states that depend significantly on doubly or higher excited configurations in the CI description, since these contributions are absent in the present CIS calculations. This frequently affects states of g-parity, e.g., the $1\,^1B_{3g}^+$ and $2\,^1A_g^-$ states of **1** (Table 2). The oscillator strengths computed within the dipole length formulation are systematically too large, as is generally the case in CIS

calculations. For similar reasons, the computed MCD B-terms are also frequently too large. On the other hand, B-terms derived from experimental MCD curves are often underestimated because of cancellation of overlapping MCD bands with opposite sign (positive MCD corresponds to negative B-term, and vice versa). The perturbation theory used to compute the B-terms tends to be less reliable in spectral regions with a high density of states, and in the case of accidental near-degeneracy the predicted B-terms "blow-up"; this occurs, for example, for acenaphthylene (**13**) and fluoranthene (**15**) (Tables 14, 16). A different and more fundamental problem concerns contributions of vibronic nature, which are not included in the theoretical model. The experimental spectra indicate that these contributions are frequently significant, particularly for weak electronic transitions, and it is often difficult to elucidate the purely electronic contribution; consider for example the case of pyrene (**5**) where different assignments of the MCD spectrum have been suggested [79, 80].

3.1 Alternants

3.1.1 Benzenoid compounds

The LCOAO theory is explicitly parameterized to reproduce the alternant pairing properties for naphthalene (**1**). We shall therefore consider the results for **1** in some detail and compare them with those obtained with NDO theories, primarily CNDO/S [23]. The π and π^* MO energies predicted for naphthalene (**1**) are shown in Fig. 1. The LCOAO energy diagram reveals the presence of approximate orbital pairing symmetry in this model; the energy patterns of the π and π^* MOs are essentially mirror images of each other. In contrast, a strong breakdown of this symmetry is obtained with CNDO/S: The spacing in energy of the bonding π MOs is larger than that of the antibonding π^* MOs. This is an artefact of the NDO procedure which systematically overestimates the bonding character of the former and underestimates the antibonding character of the latter. The NDO artefact is directly reflected in the CNDO/S prediction [24b, 24d] of electronic transition energies for the radical cation **1**$\cdot^+$ that are much larger than those predicted for the corresponding radical anion **1**$\cdot^-$, in strong disagreement with the experimental data of Shida and Iwata [64] (Table 1; transition to the optically forbidden 1 $^2B_{3u}$ cation state was not observed, but a wave number around 6000 cm^{-1} can be estimated from photoelectron data [98]). The failure of CNDO/S was noticed by Jaffé and coworkers [24b], who remarked that the results for radical cations in general "seriously overestimate all transition energies". For related reasons, CNDO/S fails to predict the relative energies of Koopmans' and non-Koopmans' configurations; for a discussion, see Ref. [99]. LCOAO predicts very similar excitation energies and absorption data for paired radical ions like **1**$\cdot^-$ and **1**$\cdot^+$, consistent with the experimental spectra (Table 1). The relative shifts seem well reproduced. The long-axis (z) polarized absorption of the cation is blue-shifted by 2000 cm^{-1} relative to the
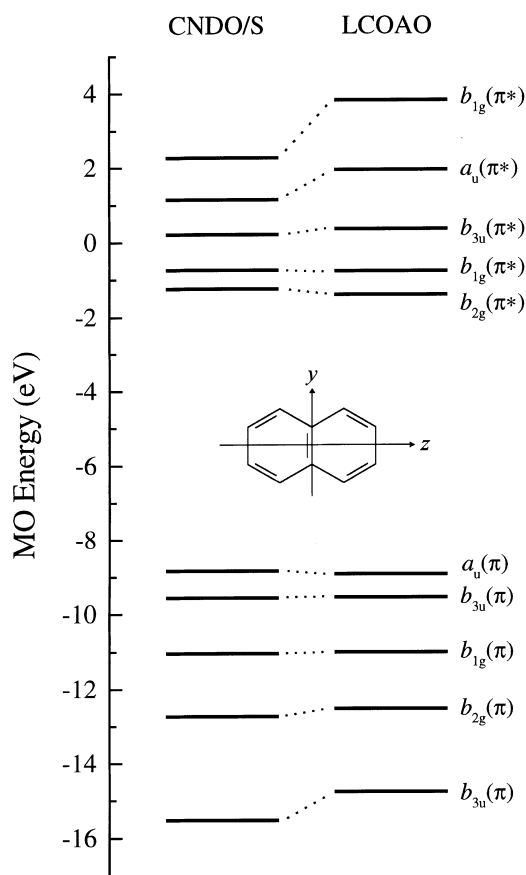

Fig. 1. π and π^* molecular orbital energies for naphthalene (**1**) computed with CNDO/S [23c] and LCOAO

anion, while the short-axis (y) polarized absorption is almost unchanged [64].

As a consequence of the NDO artefact, NDO theories generally predict too large and positive ΔHL values for alternant hydrocarbons [28]. For **1**, the CNDO/S version of Baumann [23c, 45e] and the INDO/S procedure of Ridley and Zerner [100] yield ΔHL values equal to $+0.22$ eV and $+0.11$ eV, respectively. As a result, the corresponding L_b state wave functions are dominated by the $|1 \rightarrow -2\rangle$ configuration; the leading contributions to the CNDO/S CIS wave function for **1** are 57% $|1 \rightarrow -2\rangle - 41\%|2 \rightarrow -1\rangle$, indicating a severe perturbation of the minus state symmetry. NDO theories thus tend to overestimate the intensity of the L_b transition; in the case of **1** they predict oscillator strengths f in the range 0.002–0.03 depending on the details of the calculation [24c, 24e, 100, 101]; the electronic part of the observed oscillator strength has been estimated to be of the order of 0.0005 [70]. The NDO failure has even more drastic consequences for the computed MCD B-terms. With $\Delta HL > 0$, π-electron systems derived from a $(4N+2)$-electron perimeter are predicted to be positive-hard MCD chromophores (in the terminology of Michl [18, 19]) with positive and negative B-terms for the L_b and L_a transitions, respectively. The CNDO/S calculations on **1** of Obbink and Hezemans [24e] thus obtained the values $+1.11$ and -1.63 ($10^{-3}\beta_e\mathrm{D}^2/\mathrm{cm}^{-1}$); see also

Table 1. Calculated and observed transitions for the radical ions of naphthalene, $\mathbf{1}\cdot^-\,(^2B_{2g})$ and $\mathbf{1}\cdot^+\,(^2A_u)$: Wave numbers $\tilde{v}$ ($10^3\,\mathrm{cm}^{-1}$), polarization directions, and oscillator strengths f. Wave numbers in *italics* indicate band onset

Term		CNDO/S[a]			LCOAO			Observed[b]		
		$\tilde{v}$	pol.	f	$\tilde{v}$	pol.	f	$\tilde{v}$	pol.	f^{c}
$\mathbf{1}\cdot^-$	$1\;^2B_{3g}$	6.0	–	0	6.3	–	0	*7.7*	–	*w*
	$1\;^2B_{1u}$	16.2	z	0.16	14.5	z	0.10	*12.3*	z	*s*
	$1\;^2B_{2u}$	22.1	y	0.10	23.3	y	0.001	*21.3*	y	*m*
$\mathbf{1}\cdot^+$	$1\;^2B_{3u}$	7.3	–	0	6.8	–	0	–	–	–
	$1\;^2B_{1g}$	21.5	z	0.20	16.8	z	0.11	*14.3*	z	*s*
	$1\;^2B_{2g}$	32.6	y	0.006	24.0	y	0.001	*20.7*	y	*m*

[a] Ref. [24d]
[b] Ref. [64]
[c] w = weak, m = medium, s = strong

Ref. [24f]. But this disagrees with the observed B-terms, -0.08 and $+2.2$ [38, 65].

Of course, LCOAO correctly models **1** as a soft MCD chromophore [19] with a ΔHL value close to zero (as it was designed to do): LCOAO obtains $\Delta HL = -0.004\,\mathrm{eV}$ and an L_b state wave function close to minus-state symmetry, $50\%|1 \rightarrow -2\rangle - 48\%|2 \rightarrow -1\rangle$. The predicted absorption and MCD data for **1** are consistent with the observed spectra (see Table 2). However, as anticipated, the energies of the optically forbidden $1\;^1B_{3g}^+$ and $2\;^1A_g^-$ states are overestimated; these states depend significantly on doubly excited configurations in the CI description [22, 45, 71]. Relative to the experimental assignment based on two-photon polarization data [71], LCOAO reverses the energy ordering of the two states. However, the reversed ordering, corresponding to $1\;^1B_{3g}^+$ above $2\;^1A_g^-$, is also predicted by advanced ab initio theory [22].

The LCOAO results for benzenoid hydrocarbons are generally in good agreement with the experimental spectra, as shown in Tables 2–8. In the case of anthracene (**2**) the L_b and L_a transitions are near-degenerate [38, 72, 73]. LCOAO predicts the L_b state $300\,\mathrm{cm}^{-1}$ below the L_a state, in disagreement with the assignment of the observed transitions (Table 3). The computed ordering is sensitive to details of the calculation; assumption of a regular hexagon geometry with CC and CH bond lengths equal to 140 and 110 pm leads to the prediction of L_a and L_b transitions at 26 500 and $27 100\,\mathrm{cm}^{-1}$ with positive and negative MCD B-terms, consistent with the observed spectrum.

As briefly discussed previously [1], the computed transitions for phenanthrene (**3**) agree with the experimental data except for the sign of the B-term for the $1\;^1B_2^+\;(L_a)$ transition (Table 4). The three leading terms in the perturbation expansion of this B-term represent contributions due to magnetic coupling with the states $4\;^1A_1^-$, $3\;^1A_1^+\;(B_b)$, and $2\;^1A_1^-\;(L_b)$; the individual contributions are equal to $+1.08$, -0.83, and -0.24 ($10^{-3}\,\beta_e\,\mathrm{D}^2/\mathrm{cm}^{-1}$). The predicted sign of the B-term thus depends on the exact cancellation of large contributions with an opposite sign. The strong coupling with the nominal minus state $4\;^1A_1^-$ is noteworthy, and apparently at variance with the assumptions underlying Michl's perimeter model [18, 19, 73]. Within standard PPP theory, magnetic coupling between plus and minus states is forbidden by pairing symmetry. The LCOAO model closely approximates orbital pairing for **3**, but the minus symmetry of the $4\;^1A_1^-$ state computed at $41\,800\,\mathrm{cm}^{-1}$ is strongly perturbed because of interaction with the nearby $3\;^1A_1^+\;(B_b)$ state; the leading contributions to the CI wave function are $47\%\,|1 \rightarrow -3\rangle$, $27\%\,|3 \rightarrow -1\rangle$, and $14\%\,|2 \rightarrow -1\rangle$. Transition to this state is not easily observed in absorption because of overlap with the intense B bands, but the strong positive MCD maximum around $42\,000\,\mathrm{cm}^{-1}$ can probably be assigned to this state (Table 4).

Benz[a]anthracene (**5**), chrysene (**6**), and benzo[a]pyrene (**7**) belong to the point groups C_s or C_{2h} which means that moment directions of allowed π-π^* transitions are not uniquely determined by molecular symmetry but can take any angle in the molecular plane

Table 2. Calculated and observed transitions for naphthalene (**1**): wave numbers $\tilde{v}$ ($10^3\,\mathrm{cm}^{-1}$), polarization directions, intensities (oscillator strengths f or log ε values), and MCD B-terms ($10^{-3}\,\beta_e\,\mathrm{Debye}^2/\mathrm{cm}^{-1}$). Wave numbers in *italics* indicate band onset

Term	LCOAO				Observed			
	$\tilde{v}$	pol.	f	B	$\tilde{v}^{a}$	pol.[b]	f^{c}	B^{a}
$1\;^1B_{1u}^-\;(L_b)$	33.0	z	10^{-7}	-0.004	*31.4*	z	0.002^{d}	-0.08
$1\;^1B_{2u}^+\;(L_a)$	37.5	y	0.16	$+0.19$	*35.0*	y	0.10	$+2.2$
$1\;^1B_{3g}^+$	48.5	–	0	0	42.1^{e}			
$2\;^1A_g^-$	46.8	–	0	0	44.5^{e}			
$2\;^1B_{1u}^+\;(B_b)$	46.5	z	2.11	$+4.8$	*45.2*	z		$+4$
$2\;^1B_{2u}^+\;(B_a)$	48.8	y	0.70	-4.9	~46	y	1.3	<0

[a] Refs. [38, 65]
[b] Refs. [66, 67]
[c] Refs. [68, 69]
[d] The purely electronic part of the observed oscillator strength is estimated to be of the order of 10^{-4} [70]
[e] Two-photon absorption [71]

Table 3. Calculated and observed transitions for anthracene (**2**) (see legend to Table 2)

Term	LCOAO				Observed[a]			
	$\tilde{v}$	pol.	f	B	$\tilde{v}$	pol.	f	B
$1\ {}^1B_{2u}^+(L_a)$	28.4[b]	y	0.24	−1.1[b]	26.9	y	0.1	+0.9
$1\ {}^1B_{1u}^-(L_b)$	28.1[b]	z	10^{-5}	+1.3[b]	27.8	z		−0.05
$1\ {}^1B_{3g}^+$	39.4	−	0	0	35.8[c]			+0.4[d]
$2\ {}^1A_g^-$	41.5	−	0	0	38.0[c]			
$2\ {}^1B_{3g}^-$	40.4	−	0	0	39.0[c]			
$2\ {}^1B_{1u}^+(B_b)$	40.2	z	3.1	+2.0	39.5	z	2.3	+3
$2\ {}^1B_{2u}$	45.5	y	0.03	−0.44	43[e]			<0[e]
$3\ {}^1B_{2u}^+(B_a)$	45.9	y	0.44	−1.7	45.5	y	0.2	−0.8

[a] Refs. [38, 72, 73]
[b] The predicted ordering and MCD signs for the near-degenerate L_b and L_a transitions are sensitive to calculational details (see text)
[c] Two-photon absorption [74]
[d] MCD feature observed at 37 000 cm^{-1} [73]
[e] Maximum in the negative MCD curve [73]

Table 4. Calculated and observed transitions for phenanthrene (**3**) (see legend to Table 2)

Term	LCOAO				Observed[a]			
	$\tilde{v}$	pol.	f	B	$\tilde{v}^{a}$	pol.[a]	f^{b}	B^{b}
$2\ {}^1A_1^-(L_b)$	29.7	z	10^{-4}	+0.17	29.4	z	0.004	+0.05
$1\ {}^1B_2^+(L_a)$	33.3	y	0.41	−0.11[c]	33.9	y	0.1	+0.2
$2\ {}^1B_2^-$	38.7	y	0.03	−2.7	37.4[d]	y		−0.08
$3\ {}^1A_1^+(B_b)$	40.4	z	0.39	+13	38.1	z	0.1	+4
$3\ {}^1B_2^+(B_a)$	40.7	y	1.49	+2.7	39.2	y	1	
$4\ {}^1A_1^-$	41.8	z	0.19	−14	40–42[e]			−2[f]
$5\ {}^1A_1^+$	45.5	z	0.29	+1.5	45.0	z	0.1	+(1)
$4\ {}^1B_2$	47.9	y	0.08	−1.3				
$5\ {}^1B_2$	50.0	y	0.45	+12	47.0	y	>0.2	

[a] Refs. [38, 75, 76]
[b] Ref. [77]
[c] The predicted negative B-term is the result of several large contributions with opposite signs (see text)
[d] MCD feature [77]
[e] Strong two-photon absorption [78]
[f] The maximum of the MCD curve is observed close to 42 000 cm^{-1} [77]

Table 5. Calculated and observed transitions for pyrene (**4**) (see legend to Table 2)

Term	LCOAO				Observed[a]			
	$\tilde{v}$	pol.	f	B	$\tilde{v}$	pol.	f	B^{b}
$1\ {}^1B_{2u}^-\ (L_b)$	27.5	y	10^{-4}	+1.0	26.8	y	0.005	+1[c]
$1\ {}^1B_{1u}^+\ (L_a)$	30.1	z	0.59	−1.2	29.5	z	0.6	−0.5[c]
$1\ {}^1B_{3g}$	34.7	−	0	0	34			
$2\ {}^1B_{3g}$	36.7	−	0	0				
$2\ {}^1B_{2u}^+\ (B_b)$	38.2	y	0.94	+4.1	36.2	y	0.6	+3
$2\ {}^1A_g$	39.2	−	0	0	38	z	0.1	+1
$2\ {}^1B_{1u}^+\ (B_a)$	42.2	z	1.85	−4.0	41.0	z	1.0	−0.8[d]
$3\ {}^1B_{3g}$	42.7	−	0	0	44	y	0.1	−0.3[d]
$3\ {}^1A_g$	42.8	−	0	0				

[a] Refs. [38, 79, 80]
[b] Ref. [79]
[c] A different assignment is preferred in [80], resulting in positive B-terms for both L bands
[d] Ref. [80]

(Fig. 2). The determination of transition moment directions in compounds with low symmetry is non-trivial. In his classical book, Murrell considered possible polarizations of the L_a band of **5** as a demonstration [102]. More recently, moment angles for several transitions in this hydrocarbon were determined by Waluk et al. [26] by a combination of linear dichroism and polarized fluorescence spectroscopy; the results are listed in Table 6 and illustrated graphically in Fig. 3 together with angles predicted by a variety of theoretical procedures. The moment directions predicted by LCOAO are in pleasing agreement with the observed angles, even for
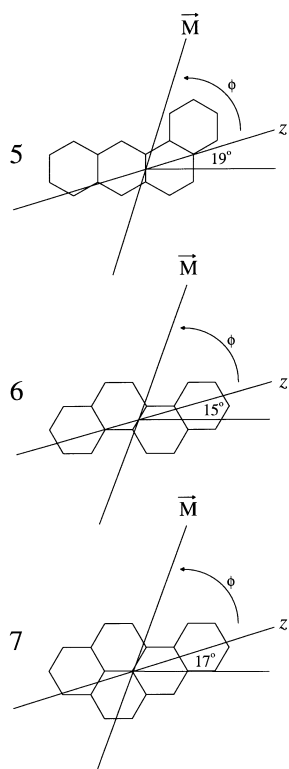
Fig. 2. Definition of π–π^* transition moment angles ϕ for benz[*a*]anthracene (**5**), chrysene (**6**), and benzo[*a*]pyrene (**7**). ϕ is measured anti-clockwise relative to the axis z, the assumed molecular orientation axis in a stretched polyethylene matrix; see [26–28] for details
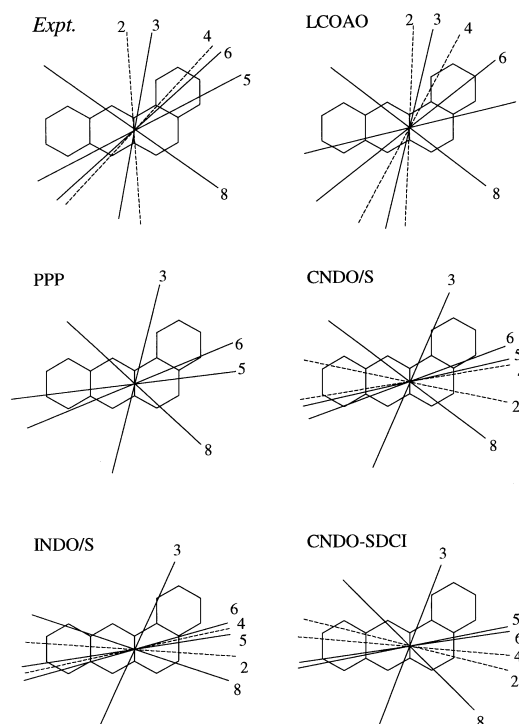

Fig. 3. Experimental π–π^* transition moment directions for benz[*a*]anthracene (**5**) and directions computed with different approximate theories, numbered according to the term labels in Table 6. *Dashed lines* indicate moment directions for states with approximate minus-state symmetry, i.e., 2 and 4 (strictly forbidden by perfect pairing in case of PPP). Experimental and calculational details are given in Ref. [26]

Table 6. Calculated and observed transitions for benz[*a*] anthracene (**5**) (see legend to Table 2)

Term	LCOAO				Observed[a]			
	$\tilde{v}$	ϕ[b]	f	B	$\tilde{v}$	ϕ[b]	f	B
2 $^1A'^-$ (L_b)	27.2	+69	10^{-4}	+0.09	*26.0*	+73	10^{-3}	+0.1
3 $^1A'^+$ (L_a)	29.3	+57	0.18	−0.11	*27.4*	+60[c]	0.1	−0.2[c]
4 $^1A'^-$	34.8	+42	10^{-3}	−1.1	*33.3*	+28	0.1	
5 $^1A'^+$ (B_b)	35.4	−6	2.13	+2.9	*34.3*	+11	1	>0
6 $^1A'^+$ (~B_a)	38.1	+19	0.58	+2.5	*38.8*	+24	0.3	
7 $^1A'^-$	39.5	+82	0.08	−5.9	38[d]			<0
8 $^1A'^+$ (~B_a)	40.0	−57	0.42	+2.7	*39.9*	−54	0.2	>0
9 $^1A'^-$	42.9	−25	0.02	−0.3				
10 $^1A'^-$	44.6	+80	0.03	−1.7	42.7[d]			<0
11 $^1A'^+$	46.1	−8	0.48	+7.6	43.5	±17[e]	0.3	>0
12 $^1A'^+$	46.4	+66	0.34	−4.6	45.5	±64[e]	0.2	<0

[a] Refs. [26]
[b] Transition moment angle ϕ is defined in Fig. 2
[c] Estimated on the basis of fluorescence polarization data [81], yielding $|\phi_1 - \phi_2| = 13$ deg
[d] MCD feature
[e] Sign of angle uncertain [26]

weak transitions that are near-forbidden by approximate pairing symmetry, i.e., 2 and 4 in Fig. 3. The results for NDO-based theories are seriously at error for these transitions because of the breakdown of this symmetry; the CNDO/S moment angle for the L_b transition of **5** is off by as much as 80° [26]. The situation is similar in the case of **6** and **7** [27, 28]. The transitions predicted with LCOAO are in general agreement with observed absorption, polarization, and MCD data (Tables 6–8). Caution is justified, however, since prediction of moment angles for weak transitions like L_b may be sensitive to CI expansion and other calculational details, as observed for **6** [27, 28]. A relatively large, positive ΔHL

value is predicted for **7**, indicating a positive-hard MCD chromophore. This is reflected in the increased intensity and large positive B-term of the computed L_b transition, in agreement with the experimental trends [28].

3.1.2 Non-benzenoid compounds

The electronic transitions and MCD B-terms of the 4N-perimeter π-systems biphenylene (**8**) and *sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne (**9**) will be the subject of detailed analyses in forthcoming publications [86, 103]; some aspects of the LCOAO results for these species are considered here. **8** and **9** are formally alternant π-

Table 7. Calculated and observed transitions for chrysene (**6**) (see legend to Table 2)

Term	LCOAO				Observed[a]			
	$\tilde{v}$	ϕ^b	f	B	$\tilde{v}$	ϕ^b	f	B
$1\ ^1B_u^-\ (L_b)$	29.2	$+83^c$	10^{-5}	$+0.11$	27.6	$+73$	10^{-3}	$+0.38$
$2\ ^1B_u^+\ (L_a)$	31.6	-36	0.41	$+0.05$	31.0	-36	0.3	$+0.53$
$2\ ^1A_g^-$	35.0	$-$	0	0				
$3\ ^1B_u^+\ (B_b)$	38.3	-1	2.33	$+3.1$	36.9	0	1.1	$+3.9$
$3\ ^1A_g^-$	38.7	$-$	0	0				
$4\ ^1A_g^+$	39.7	$-$	0	0				
$4\ ^1B_u^+\ (B_a)$	40.7	$+83$	0.69	-1.1	37.4	$\pm65^d$	0.3	-1.3
$5\ ^1B_u^-$	43.8	$+79^c$	0.01	-2.3	41.1^e	$\pm40^d$	0.1	-4.9
$5\ ^1A_g^-$	44.6	$-$	0	0				
$6\ ^1A_g^+$	46.4	$-$	0	0				
$6\ ^1B_u^-$	45.7	-1	0.18	-1.1	44.4	~0		
$7\ ^1B_u^+$	47.8	$+1$	0.49	$+2.8$	45.5	~0	0.5	$+4$
$7\ ^1A_g^+$	49.3	$-$	0	0				

[a] Ref. [27]
[b] Transition moment angle ϕ is defined in Fig. 2
[c] Sensitive to calculational details [27, 28]
[d] Sign of angle uncertain [27]
[e] Assigned to $6\ ^1B_u^-$ in [82]

Table 8. Calculated and observed transitions for benzo[a]pyrene (**7**) (see legend to Table 2)

Term	LCOAO				Observed[a]			
	$\tilde{v}$	ϕ^b	f	B	$\tilde{v}$	ϕ^b	f	B
$2\ ^1A'^-\ (L_b)$	26.1	-44	0.02	$+5.1$	24.8	-45	0.01	$+1.00$
$3\ ^1A'^+\ (L_a)$	26.9	-34	0.61	-5.4	25.8	-30	0.3	-0.42
$4\ ^1A'^-$	33.4	-53	10^{-3}	-0.1				
$5\ ^1A'^+$	35.6	$+24$	0.10	$+3.0$				
$6\ ^1A'^+\ (B_b)$	35.9	$+19$	1.53	$+0.3$	33.5	$+18$	0.6	$+4.0$
$7\ ^1A'^-$	37.0	$+25$	0.10	$+1.6$				
$8\ ^1A'^+$	38.4	$+59$	0.11	$+3.4$				
$9\ ^1A'^-$	38.5	$+70$	0.04	-3.8				
$10\ ^1A'^+\ (B_a)$	39.0	-27	1.31	-3.8	37.5	-30	0.7	-1.5
$11\ ^1A'^-$	40.8	$+9$	0.01	$+0.2$				
$12\ ^1A'^-$	43.8	-24	0.04	-0.4				
$13\ ^1A'^+$	45.6	-19	0.14	-0.9	43.9	~0	0.2	-0.1
$14\ ^1A'^-$	46.5	-21	0.05	$+2.0$				
$15\ ^1A'^+$	47.1	$+11$	0.02	-0.9				

[a] Ref. [28]
[b] Transition moment angle ϕ is defined is Fig. 2

systems (discounting the in-plane π-components of the triple bonds in **9**), but as discussed in Sect. 2.2.2, the presence of a 4-membered ring in **8** and an 8-membered in **9**, with bond angles deviating strongly from 120°, leads to the prediction of next- neighbour elements $^\lambda f_{13}^\circ$ that differ substantially from zero [1]. Significant breakdown of the orbital pairing symmetry is thus predicted.

The CNDO/S and LCOAO MO energy diagrams for **8** are compared in Fig. 4. The level patterns obtained with the two methods differ in the expected manner: relative to LCOAO, CNDO/S predicts larger spacing in energy of the bonding π MOs and smaller spacing of the antibonding π^* MOs. The computed electronic transitions of **8** are sensitive to the predicted MO level pattern, and CNDO/S and LCOAO obtain different orderings of the $2\ ^1B_{1u}^+$ and $1\ ^1B_{2u}^-$ states, leading to divergent assignments of the experimental spectrum [1, 84b, 103]. As shown in Table 9, the LCOAO results are in agreement with observed MCD B-terms for transitions in the low-energy region. **8** is correctly predicted to be a positive-hard MCD chromophore [1]: a large positive B-term is predicted for the $1\ ^1B_{1u}^-$ state (perimeter state label N_1 [86, 103]), in contrast to earlier attempts that lead to disagreement with experimental findings [38]. The sign of the computed B-term can be explained as a result of weakly negative next-neighbour elements $^\lambda f_{13}^\circ$ in the region of the 4-membered ring, a consequence of the small bond angles [1]. In the case of **9**, the corresponding next-neighbour terms in the 8-membered ring are weakly positive because of the large bond angles, leading to the prediction of a negative B-term for the $1\ ^1B_{1u}^-\ (N_1)$ state. Again, this is in agreement with the observed sign [86], as indicated in Table 10.

sym-Dibenzo-1,7-cyclododecadiene-3,5,9,11-tetrayne (**10**) contains a $4N$ π-system with a planar 12-membered ring [87] but its MCD spectrum has apparently not been published. LCOAO (Table 11) predicts a large negative B-term for the $1\ ^1B_{1u}^-\ (N_1)$ state, as in the case of **9**. However, in contrast to the case of **8** and **9**, a large negative B-term is also obtained for the intense $2\ ^1B_{1u}^+$ (P_1) transition. The predicted absorption data are consistent with the observed UV-VIS data, but the experimental spectrum is complex with a wealth of fine structure [87]; an analysis by LD and MCD spectroscopy would probably be rewarding.

It should be mentioned that the prediction of B-terms in the high energy region seems problematic, at least in the case of **8**. This is most likely due to limitations of the CIS approximation; inclusion of doubly excited configurations has a significant impact on the results of
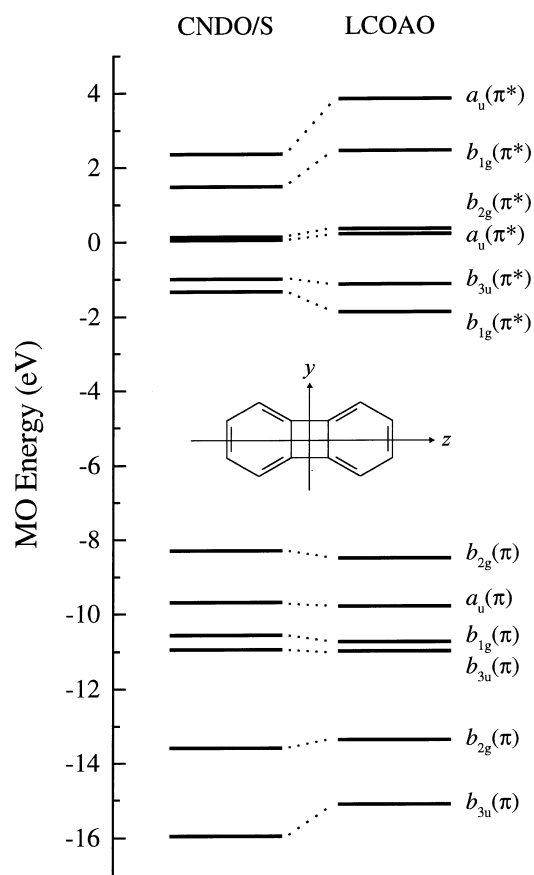
Fig. 4. π and π^* molecular orbital energies for biphenylene (**8**) computed with CNDO/S [23c] and LCOAO

CNDO/S calculations on **8** in the region above $40\,000\,\text{cm}^{-1}$ [85].

3.2 Non-alternants

We conclude this survey with the presentation of results for some characteristic non-alternant systems, **11–16**. These compounds tend to be hard MCD chromophores and theoretical prediction of their MCD B-terms is usually less problematic [18, 19, 38, 48, 49]. The LCOAO results are given in Tables 12–17. Within the limits of the perturbation theoretical approach (Sect. 2.5) the computed MCD B-terms are in general agreement with the observed data. Unreasonably high values are computed in a few cases of accidentally near-degenerate states, i.e., for acenaphthylene (**13**) and fluoranthene (**15**) (Tables 14, 16).

The results for 6,6-dimethylfulvene (**11**) in Table 12 deserve comment. LCOAO correctly predicts negative and positive B-terms for the two π-π^* transitions in the near-UV, $^1B_2$ and $^1A_1$. However, the B-term predicted for the $^1B_2$ state is unusual in that it is strongly dominated by the contribution B_0 due to coupling with the *ground state*: $B_0 = -1.13$, $B_F = +0.21$ in units of $10^{-3}\,\beta_e\text{D}^2/\text{cm}^{-1}$ (see Sect. 2.5; largest single contribution is the direct coupling term between $|0\rangle$ and $|^1B_2\rangle$, amounting to -1.19). The B-term for the $^1A_1$ state is dominated by B_F, but B_0 is still significant: $B_0 = -0.33$, $B_F = +0.64$. Michl and Warnick [48] have discussed the MCD of the fulvene chromophore in detail, analysing in graphical terms the magnetic coupling between excited states; however, the simple picture seems to be complicated by unusually strong, negative

Table 9. Calculated and observed transitions for biphenylene (**8**) (see legend to Table 2)

Term	LCOAO				Observed[a]			
	$\tilde{v}$	pol.	f	B	$\tilde{v}$	pol.	$\log\varepsilon$	B
$1\ ^1B_{3g}^+\ (S)$	25.7	–	0	0	*25.1*	*(z)*	1.6	$+(w)$
$1\ ^1B_{1u}^-\ (N_1)$	30.7	z	0.06	$+0.76$	27.8	z	4.0	$+0.5$
$2\ ^1A_g^-$	38.0	–	0	0	(38)	*(z)*	3.1	
$2\ ^1B_{1u}^+\ (P_1)$	41.6	z	2.06	$+2.1$	40.3	z	5.0	$+3$
$1\ ^1B_{2u}^-\ (N_2)$	45.8	y	0.06	-3.3	45.9	*(y)*	3.8	>0
$2\ ^1B_{3g}$	48.0	–	0	0				
$2\ ^1B_{2u}^-\ (P_2)$	49.2	y	0.08	-0.05	50.0	y	4.0	

[a] Refs. [38, 83, 84]

Table 10. Calculated and observed transitions for *sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne (**9**) (see legend to Table 2)

Term	LCOAO				Observed[a]			
	$\tilde{v}$	pol.	f	B	$\tilde{v}$	pol.	f	B
$1\ ^1B_{3g}^+\ (S)$	22.6	–	0	0	24.0	*(z)*	<0.009	$+0.03$
$1\ ^1B_{1u}^-\ (N_1)$	30.0	z	0.03	-1.1	28.3	z	0.02	-0.11
$2\ ^1A_g^-$	34.8	–	0	0	33.5	*(z)*	<0.02	$+0.01$
$2\ ^1B_{1u}^+\ (P_1)$	38.5	z	3.1	$+2.3$	36.8	z	1.2	$+3.0$
$1\ ^1B_{2u}$	42.9	y	0.06	$+3.4$				>0
$2\ ^1B_{2u}$	43.9	y	0.30	-5.4	44	y		
$2\ ^1B_{3g}$	45.1	–	0	0				

[a] Refs. [83, 85, 86]

Table 11. Calculated and observed transitions for *sym*-dibenzo-1,7-cyclododecadiene-3,5,9,11-tetrayne (**10**) (see legend to Table 2)

Term	LCOAO				Observed[a]	
	$\tilde{v}$	pol.	f	B	$\tilde{v}$	$\log \varepsilon$
1 $^1B_{3g}^+$ (S)	20.9	–	0	0	23.0	2.9
1 $^1B_{1u}^-$ (N_1)	28.9	z	0.04	−2.8	27.6	3.8
2 $^1A_g^-$	33.3	–	0	0		
2 $^1B_{1u}^+$ (P_1)	35.1	z	4.2	−5.8	32.9	5.1
1 $^1B_{2u}$	36.9	y	0.45	+19.9	35.1[b]	4.8
2 $^1B_{2u}$	40.3	y	0.26	−11.5	37.2[b]	4.3

[a] Refs. [83, 87]
[b] Possibly vibronic components of the intense transition with origin at 32 900 cm^{-1} [87]

Table 12. Calculated and observed transitions for 6,6-dimethyl-fulvene (**11**) (see legend to Table 2)

Term	LCOAO				Observed[a]		
	$\tilde{v}$	pol.	f	B	$\tilde{v}$	f	B
1 $^1B_2$	29.6	y	0.05	−0.92	*27.0*	0.01	−0.05
2 $^1A_1$	37.7	z	0.61	+0.31	*37.0*	0.3	+0.05

[a] Ref. [48]

contributions due to coupling with the ground state. Moreover, the methyl groups in **11** are predicted to have a significant impact on the MCD. For unsubstituted fulvene [59b], LCOAO predicts transitions to $^1B_2$ and $^1A_1$ states at 28 200 and 43 000 cm^{-1} with negative B-terms for both transitions, −0.63 and −0.34 (these values are similar to those obtained with PPP SCI-MN: −0.66 and −0.20 [48]). For the $^1B_2$ state, B_0 and B_F are both negative, $B_0 = -0.31$, $B_F = -0.32$. The negative B-term for the $^1A_1$ state is due to coupling with the ground

Table 13. Calculated and observed transitions for azulene (**12**) (see legend to Table 2)

Term	LCOAO				Observed[a]			
	$\tilde{v}$	pol.	f	B	$\tilde{v}$	pol.	f	B
1 $^1B_2$	17.4	y	0.02	+0.54	*14.5*	y	0.009	+0.17
2 $^1A_1$	29.3	z	0.01	−1.04	*28.0*	z	0.06	−0.26
2 $^1B_2$	36.3	y	0.21	+6.2	*33.5*	y	0.03	+2
3 $^1A_1$	40.2	z	2.24	−7.5	*35.0*	z	∼ 1	< 0
3 $^1A_1$					*∼ 40.5*	w		< 0
3 $^1B_2$	47.7	y	0.37	+5.2	*42.0*	y	m	+1.5

[a] Refs. [88, 89]

Table 14. Calculated and observed transitions for acenaphthylene (**13**) (see legend to Table 2)

Term	LCOAO				Observed[a]			
	$\tilde{v}$	pol.	f	B	$\tilde{v}$	pol.	f	B
1 $^1B_2$	24.6	y	0.01	+0.08	*21.4*	y	0.005	−0.05
2 $^1A_1$	31.6	z	0.26	−97	*29.3*	z	0.1	−2.2
2 $^1B_2$	31.8	y	0.13	+97	*31.0*	y	0.2	+2.8
3 $^1A_1$	38.7	z	0.01	+0.5	*36.3*	z	0.1	+0.5
3 $^1B_2$	44.6	y	1.40	−4.7	*43.0*	y	1.1	−1

[a] Refs. [90–92]

Table 15. Calculated and observed transitions for pleiadiene (**14**) (see legend to Table 2)

Term	LCOAO				Observed[a]			
	$\tilde{v}$	pol.	f	B	$\tilde{v}$	pol.	f	B
1 $^1B_2$	21.3	y	0.03	+1.3	*17.9*	y	0.01	+0.2
2 $^1A_1$	28.6	z	0.38	+18	*25.8*	z	0.2	+4
2 $^1B_2$	30.1	y	0.09	−16	*29.3*	y	0.05	−1
3 $^1A_1$	37.1	z	0.02	−1.2	*33.7*	z	0.1	−2
3 $^1B_2$	42.0	y	0.83	+8	*40.3*	y	∼ 0.3	+(s)
4 $^1A_1$	43.9	z	0.26	−18	*40.8*	z	0.3	−(s)
4 $^1B_2$	45.3	y	0.38	+8	*43.1*	y	∼ 0.2	+(s)
5 $^1B_2$	46.9	y	0.06	+6				
5 $^1A_1$	47.8	z	0.64	−23	*∼ 46.5*			−(s)

[a] Refs. [92, 93]

Table 16. Calculated and observed transitions for fluoranthene (**15**) (see legend to Table 2)

Term	LCOAO				Observed[a]			
	$\tilde{v}$	pol.	f	B	$\tilde{v}$	pol.	f	B
1 $^1B_2$	26.7	y	0.006	−0.4	*24.8*	y	0.012	−0.2
2 $^1A_1$	29.0	z	0.38	−6.1	*27.8*	z	0.17	−2.7
2 $^1B_2$	31.7	y	0.05	+3.6	*31.0*	y	0.05	+0.6
3 $^1A_1$	36.3	z	0.45	+2.7	*34.7*	z	0.55	+5.3
4 $^1A_1$	39.5	z	0.01	+0.4	*38.0*	z	(0.14)	
3 $^1B_2$	40.6	y	0.002	−0.4	*38.4*	y	(0.08)	+
4 $^1B_2$	43.1	y	1.19	−240	*42.2*	y	0.44	−
5 $^1A_1$	43.1	z	0.74	+240	*43.5*	z	(0.13)	+
6 $^1A_1$	47.8	z	0.83	+6	*46.9*	z	0.26	+

[a] Refs. [94–96]

Table 17. Calculated and observed transitions for dicyclohepta [cd, gh] pentalene (**16**) (see legend to Table 2)

Term	LCOAO				Observed[a]			
	$\tilde{v}$	pol.	f	B	$\tilde{v}$	pol.	f	B
1 $^1B_{3g}$	14.4	−	0	0	*14*	−	0.002	+
1 $^1B_{1u}$	22.1	z	0.11	+1.7	*19.9*	z	0.04	+0.5
2 ^1A_g	23.4	−	0	0	*23.6*	−	0.002	+0.02
1 $^1B_{2u}$	27.8	y	0.02	−2.2	*25.7*	y	0.09	−1.0
2 $^1B_{1u}$	29.7	z	10^{-5}	+0.1	*26–29*	z		
2 $^1B_{3g}$	34.4	−	0	0				
2 $^1B_{2u}$	34.5	y	0.68	+14	*31.2*	y	0.26	+2.7
3 ^1A_g	36.2	−	0	0				
3 $^1B_{1u}$	38.8	z	3.7	−23	*34.9*	z	1.2	−2.9
3 $^1B_{2u}$	44.1	y	0.7	+10	*37.5*	(y)		+1.5

[a] Ref. [97]

state: $B_0 = -0.53$, $B_F = +0.19$. The MCD of fulvene has apparently not been investigated experimentally.

4 Concluding remarks

This paper describes the construction of an all-valence electrons theory for the prediction of electronic absorption and MCD spectra of organic π-systems. The method is based on an approximate LCOAO procedure going beyond the NDO approximation [9]. Kinetic energy and penetration terms are evaluated explicitly in the Löwdin OAO basis from parameterized expressions valid for AOs, while the two-electron repulsion terms are treated according to conventional NDO theory. The procedure is parameterized explicitly on reproduction of the observed alternant pairing properties for the π-systems of benzene and naphthalene. Within the limits of the CIS approximation, it accounts successfully for the MCD of benzenoid hydrocarbons where traditional NDO theories fail and it yields much improved results for transition moment directions in low-symmetry compounds. It also predicts in a straightforward manner the MCD signs for various non-benzenoid compounds, such as $4N$-perimeter π-systems with different ring sizes. Using canonical ensemble CI theory, it reproduces the spectra of conjugated hydrocarbon radicals; the relative ordering of so-called Koopmans' and non-Koopmans' configurations in radical ions is adequately described, leading to excellent predictions of "shake up" ionization processes as observed in photoelectron spectroscopy [99]. In contrast, to be useful for radical ions, the CNDO/S method requires an empirical scaling of the relative energies of Koopmans' and non-Koopmans' configurations [29b–d].

The present version of the LCOAO theory is based on standard atomic parameters and Slater exponents, and applies essentially four molecular parameters, namely the constants d_s and d_p used in the evaluation of penetration terms (Eq. 14) and a and b appearing in the expression for off-diagonal elements of $f°$ (Eq. 27). For calculation of MCD B-terms a fifth parameter k is applied in the expression for matrix elements of the magnetic dipole operator (Eq. 49, using Linderberg's relation [51]). The parameters are adapted to the description of π-π* transitions and little attention has been paid to the properties of σ-systems, but hyperconjugative σ–π interactions with alkyl substituents and in non-planar π-systems seem well described, e.g. [99]. σ* MOs are predicted to be more strongly antibonding than in NDO theories (a similar trend is observed in related work by Kollmar and Böhm [30b]). The procedure is not specifically parameterized for the description of heteroatomic systems. Successful applications have been performed on hetero-systems containing nitrogen, oxygen, and fluorine [99,103], using pertinent atomic parameters and the same set of molecular parameters as derived for hydrocarbons, but no systematic investigation of the applicability of this approach has been carried out.

The results of this study demonstrate that substantial improvements in the semi-empirical description of valence-electronic systems can be achieved by incorporation of orbital overlap effects in a simple fashion. The LCOAO procedure may thus serve as inspiration for future work in this field.

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