Quantum Constraints in π Systems: The Role of the Pauli Antisymmetry Principle for π Electronic Properties

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Dedicated to Prof. Dr. K. G. Weil on the Occassion of his 70th Birthday.

It is demonstrated that the Pauli antisymmetry principle (PAP) is without influence in the π electron subspace of polyenes and $(4n + 2)$ annulenes (n = 0, 1, 2...) as long as the hoppings are restricted to nearest-neighbour centers. Here the π electrons behave like a hard core bosonic (hcb) ensemble where fermionic on-site and bosonic intersite properties are combined. In $4n$ and $(2n + 1)$ annulenes (n = 1, 2, 3...) π electron jumps between the first and last ring atom lead to a Pauli antisymmetry-based destabilization. The second quantum constraint in fermionic systems is the Pauli exclusion principle (PEP). In the many-electron basis adopted in the present work it is possible to treat the PAP and PEP as two decoupled constraints. The electronic destabilization due to the PEP is enhanced with increasing size of the system. The influence of the PAP and PEP on the π electrons is discussed in terms of π energies and charge fluctuations. The model Hamiltonians adopted are of the Hückel molecular orbital (HMO) and Pariser-Parr-Pople (PPP) type. We suggest quantum statistical definitions of the quantities "aromaticity" and "antiaromaticity", qualitative descriptors which are widely employed in the chemical literature.

Key words: π Electronic Properties, Quantum Statistics, Pauli Antisymmetry and Exclusion Principle, Green's Function Quantum Monte Carlo Simulations, Aromaticity vs. Antiaromaticity.

1. Introduction

Homologous series of mono- and polycyclic π systems exhibit strong non-additivities in their bonding properties which do not occur in polyenes, where a constant variation of electronic increments is observed. The non-additivities of bond increments in annulenes, e. g., is reproduced by the popular Hückel counting rule [1]. High stability is predicted for $(4n+2)$ annulenes ($n = 0, 1, 2...$), while low stability is predicted for $4n$ and $(2n+1)$ annulenes ($n = 1, 2, 3...$). It is well known that the transition from butadiene to cyclobutadiene is accompanied by a destabilization of the π system, while the transition from hexatriene to benzene is accompanied by a stabilization. Phenomenologically, this behaviour can be described by so-called "resonance energies" where π energies of cyclic networks are correlated to π energies of properly defined reference molecules [2]. Note in this context that M annulenes (M = number of π centers) with $M = 4n$ and a π electron count of $(4n + 2)$ (= dianions) are stable. It is the number of electrons which determines the bonding properties of cyclic π systems and not the number of atoms M. Although quantum chemical calculations of different degrees of sophistication have been very successful to reproduce these energetic effects, it seems that the microscopic origin of the peculiarities of cyclic π systems is still unrecognized. We have adopted the descriptor "microscopic origin" to denote a quantum statistical effect which acts as driving force for energetic shifts in electronic structure calculations. In the present work we will show that even the popular Hückel counting rule for annulenes has a quantum statistical basis.

In the present manuscript we evaluate the influence of quantum statistics on the aforementioned special electronic properties of cyclic π molecules. The indistinguishability of electrons leads to characteristic prerequisites in the fermionic quantum statistics. The

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electronic degrees of freedom are restricted by two "quantum constraints", the Pauli antisymmetry principle (PAP) which states that the many-electron wave function changes sign whenever the ordering of two electrons of the same spin is changed and the Pauli exclusion principle (PEP) which prevents configurations with more than one electron of the same spin in the same atomic orbital (AO). Changes in the electron ordering can occur during electron transfer processes under the influence of the kinetic hopping part of the corresponding Hamiltonian. With this information it is straightforward to generalize the physical implications of the PAP. A sign change in the electronic wave function occurs for any odd number of permutations p of electrons within one spin direction. The change of the ordering of an electron pair corresponds to $p = 1$. In the chemical literature it is a common practice to consider the PAP physically quivalent to the PEP. In conventional computational methods of molecular quantum chemistry it is the PEP which – from a formal mathematical point of view – follows from the PAP, i. e. the PAP is the more general principle. In the single-determinantal approximation this is trivial to show. Moreover it is almost impossible in these methods to separate the PAP and PEP into two individual constraints acting on the electronic ensemble. In many-electron bases of atomic occupation numbers it is however straightforward to treat the PAP and PEP as two individual electronic constraints. In this degree of sophistication it is possible to perform electronic structure calculations where either the PEP or the PAP are taken into account. In determinantal descriptions both constraints occur as some kind of mathematical prescription. Electronic structure approaches beyond the conventional determinantal framework are widely used in quantum Monte Carlo (QMC) simulations of fermion problems [3 - 10] and in configuration interaction (CI) methods in a valence bond (VB) basis [11, 12]. In these numerical schemes it is however necessary to consider the quantum constraints of fermionic ensembles via external conditions. In the present work we make use of the degree of freedom of many-electron bases to decouple the PAP from the PEP. This step is the prerequisite to quantify the influence of the quantum constraints PEP and PAP on the electronic properties of π systems. In addition to these quantum constraints we have topological constraints in molecules that act on the electronic degrees of freedom such as the number of nearest neighbours of a given "reference" atom. For an electron at a terminal atom, only one hopping process is – at least in principle – accessible, while two jumps may be allowed for an electron at an atom with two neighbours, etc..

Below we evaluate π electron energies of polyenes and annulenes according to four different quantum statistics which will be defined in the next section. In addition to the fermionic (fe) statistics we consider a so-called hard core bosonic (hcb), soft core fermionic (scfe) and the bare bosonic (b) statistics. The π energies calculated in the framework of these statistics are abbreviated as E_{fe}, E_{hcb}, E_{scfe}, and E_{b}. A priori E_{hcb}, E_{scfe} and E_{b} should be accepted as some kind of "reference energies" which do not have a physical meaning by their own. The comparative discussion of these energies, however, leads to an understanding of the significance of the PAP and PEP in π electron systems. In addition to these simple model systems we discuss miscellaneous π compounds which have been studied in many experimental and theoretical contributions. The π Hamiltonians employed are defined in the next section.

The organization of the present work is as follows. The theoretical background and the computational conditions adopted are described in Section 2. The numerical results are then discussed in Section 3. We end with a short resume.

2. Theoretical Background and Computational Conditions

At the beginning of this section we briefly introduce the aforementioned quantum statistics. They differ in the consideration or non-consideration of the PAP and PEP as quantum constraints. In quantum mechanics, the consideration of a constraint is described by an anticommutator relation (–), while a commutator relation (+) symbolizes the non-consideration of the corresponding constraint. In a many-electron basis of atomic occupation numbers we have an on-site relation which refers to the PEP and an intersite relation associated to the PAP. This simple one-to-one correspondence (i. e. on-site characteristics ↔ PEP, intersite characteristics ↔ PAP) is possible for all electronic Hamiltonians based on a one orbital per atomic site description. Subsequently we express the on- and intersite commutator-anticommutator properties of the quantum ensembles by a short-hand notation $(\pm,\pm)$ where the first parameter in parenthesis describes the on-site properties and the second the intersite properties. The fermionic quantum statistics is defined by two anticommutators (–,–) which refer to the PEP and PAP. The quantum statistics of the hcb and scfe ensembles is of a mixed type which is defined by one anticommutator and one commutator relation. In the hcb ensemble both relations are combined as (–,+) which denotes that the PEP is conserved while the Pauli antisymmetry based anticommutator has been replaced by a commutator. Hard core bosonic ensembles with quantum particles of spin 1/2 are well-known in theoretical physics [13]. The hard core character is due to the on-site anticommutator (= PEP). It is of interest to mention that the Pauli spin matrices obey a mixed quantum statistics of the hcb type. The many-particle wave functions of a fe and hcb ensemble can be interconverted by the Jordan-Wigner transformation [14]. In the scfe ensemble an on-site commutator is combined with an intersite anticommutator (+,–). Here the PEP is no longer conserved. Note however that the indistinguishability of the electrons is incompatible with this quantum statistics. As a consequence electronic ensembles and scfe properties rule out each other. This is simple to explain. The on-site commutator (= soft core character) does not prevent electronic configurations with two quantum particles of the same spin in the same AO. The fermionic intersite characteristics, however, forces a sign change of the wave function whenever the sequence of two electrons of the same spin is interchanged in a transfer process starting from a hypothetical configuration with two electrons of the same spin in the same AO. But in order to decide whether or not the sequence of the two electrons is changed as response to a transfer process, distinguishability of the two particles would be necessary. Otherwise the computational result remains undefined. For the hcb ensemble such an a priori exclusion cannot be formulated. Finally we mention the bosonic ensemble where both fermionic anticommutators have been replaced by commutators (+,+). Here neither the PEP nor the PAP are conserved. By analogy with the scfe ensemble a quantum statistics of this type can be ruled out a priori for electronic systems. In summary we have introduced four quantum ensembles whose on-site and intersite commutator (+) and anticommutator (–) properties can be abbreviated as follows.

Ensemble:	fe	hcb	scfe	b
Defined by:	(–,–)	(–,+)	(+,–)	(+,+)

We have two quantum constraints in the fe ensemble (PEP, PAP), always one quantum constraint in the hcb (PEP) and scfe (PAP) ensembles and none in the b ensemble. In the next section we evaluate π electronic properties of hydrocarbons which are due to the PEP and PAP. This proceeding is possible by comparing E_{fe} with E_{hcb}, E_{scfe} and E_{b}.

In electronic models where the two-electron interaction is of the density-density type the four quantum statistics differ only in their influence on the hopping part of the (π) Hamiltonian. In the occupation number representation adopted in the present study the hopping matrix is completely off-diagonal while the interaction matrix is diagonal [7, 9]. This block structure of the Hamiltonian offers the possibility to adopt a simple one-electron model of the Hückel molecular orbital (HMO) type [1] in an analysis of the influence of the PEP and PAP on the energy of π electrons. In the following we combine the HMO model with the four types of quantum statistics described above. This simple electronic model has the didactical advantage that the two spin spaces are decoupled, a condition which simplifies an intelligible visualization of the theoretical results. The computational effort (= many-electron basis of atomic occupation numbers) adopted in connection with the HMO model is of course not necessary to derive the standard HMO energies of fermionic ensembles. The corresponding HMO energies can be found in many tables [15, 16]. They are feasible via an eigenvalue problem of dimension $M * M$. The present many-electron basis leads to a matrix of dimension $\{M!/[(M/2)!]^2\}^2$ (neutral π systems with an identical number of electrons in both spin spaces). The necessity to adopt a theoretical method without matrix diagonalization in the case of larger π systems is thus evident. The computational strategy we have adopted has been guided by the combination of the HMO model with other quantum statistics. Let us touch the point to observe the effects of statistics in the single-particle spectrum of a one-body Hamiltonian. Without external constraints these effects are not reflected in one-body Hamiltonians. In the present setup they are taken into account via the consideration and non-consideration of the π configurations accessible (PEP) and via the consideration or non-consideration of the parity p (= even or odd) of electronic permutations per spin direction (PAP). In a second series of calculations we combine the popular Pariser-Parr-Pople method [17, 18] with the fe and hcb quantum statistics. In addition to energetic considerations, the PPP operator has been employed also to calculate the electronic charge fluctuations $\langle(\Delta n_i)^2\rangle$.

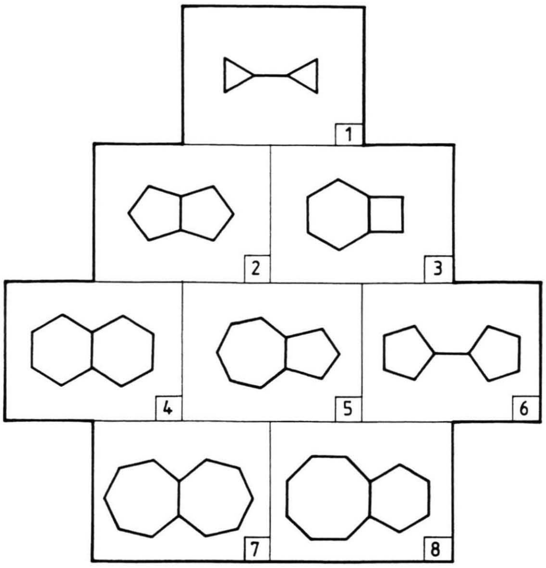

Fig. 1. Molecular graphs of the molecules **1** to **8**.

They measure the mean square deviation of the electron density at center i around the respective mean value $\langle n_i \rangle$. In previous publications we have shown that the $\langle (\Delta n_i)^2 \rangle$ are a convenient measure of the electronic delocalization (= interatomic sharing) [19, 20].

As one computational tool we have adopted a Green's function quantum Monte Carlo (GF QMC) algorithm. GF QMC simulations of fermionic systems are still a non-trivial task as a result of the fermionic sign problem which may prevent the definition of electronic transition probabilities [5, 6, 21, 22]. In the present work we have used the GF QMC implementations described in detail in [8, 9] where we have developed techniques to circumvent the sign problem in π molecules of any topology. As mentioned in Sect. 1, the GF QMC method makes use of many-electron configurations defined in the atomic occupation number representation. Different configurations are coupled by allowed nearest-neighbour moves. A nearest-neighbour approximation has been employed both in the HMO and PPP models. The PPP parametrization adopted in the present contribution coincides with the one of our previous GF QMC studies [8 - 10]; see also the CI studies [11, 12] in a VB basis for the definition of the matrix elements. The PPP hopping integral of –2.4 eV has been used also in the HMO part of our work. The polyene geometries are of the all-trans type. For M annulenes we have adopted the point symmetry D_{Mh}. Regular geometries as portrayed in Fig. 1 have been chosen for the miscellaneous π systems discussed in Section 3. In all molecules a CC standard bondlength of 140 pm has been adopted. The π systems with an even number of electrons are singlets, while the ground state is doublet in molecules with an odd number of electrons.

In the case of molecules with up to 8 π electrons we have performed supplementary CI calculations in a VB basis of atomic occupation numbers to have an additional test of the accuracy of the statistically determined π energies. Numerical techniques to enhance the accuracy of the statistical approach have been discussed in [23]. The charge fluctuations $\langle (\Delta n_i)^2 \rangle$ have been derived by complete π CI calculations. The $\langle (\Delta n_i)^2 \rangle$ numbers in the next section refer to the PPP Hamiltonian as the HMO model would yield the standard mean-field results [19, 20]. In neutral alternant systems, e. g., one has $\langle (\Delta n_i)^2 \rangle = 0.5$ at any center i.

3. Results and Discussion

We start the discussion of the theoretical results with HMO energies of annulenes and polyenes by using the fe, hcb, scfe, and b quantum statistics. As emphasized above, the hcb, scfe, and b values should be acepted as some kind of "reference energies". They are without physical significance whenever $E_x < E_{\mathrm{fe}}$ (x = hcb, scfe, b) does hold. The inequality symbolizes that the quantum ensemble x is not accessible for the electronic system. The difference between E_x and E_{fe}, however, has a transparent physical meaning. It measures the "energy loss" of the electronic system under the influence of the PEP and PAP. E_{b} and E_{scfe} in Table 1 are much lower than E_{fe} and E_{hcb}, as the interatomic sharing is not attenuated by either the PEP (b, scfe ensembles) or the PAP (b ensemble). The rather large difference between E_{b} and E_{scfe}, on the one hand, and E_{fe} and E_{hcb}, on the other, is caused by the neglect of the two-electron interaction in the HMO model.

For polyenes and annulenes with $(4n+2)$ electrons a degeneracy between E_{fe} and E_{hcb} is observed. $4n$ annulenes are the only molecules in Table 1 where the hcb energy is below the fermionic one. The coincidence of E_{fe} and E_{hcb} in polyenes and $(4n+2)$ annulenes indicates that the π energy of these molecules is not influenced by the PAP. Here it has the character of a deactivated quantum constraint. In these molecules the difference between the conventional electronic fermionic ensemble and a hypothetical hard core

Table 1. π electron energies of annulenes and polyenes in the framework of the fe, hcb, scfe, and b quantum statistics (E_{fe}, E_{hcb}, E_{scfe}, E_{b}). The bosonic and scfe energies of systems containing more than four π electrons have been estimated by using m times (m = number of electrons) the energy of the lowest occupied molecular orbital. In parentheses we have given the commutator (+) or anticommutator (−) behaviour with respect to the on-site and intersite interactions. The energies correspond to the simple HMO model with a nearest-neighbour resonance integral t of −2.4 eV. M symbolizes the number of π centers; all values are given in eV. For annulenes with $M = 4n$ (n = 1, 2) π centers we have also studied the corresponding dianions 4^{2-} and 8^{2-}, which are of the $(4n + 2)$ Hückel-type. To derive the scfe energies we have raised E_{b}, by the difference in the energy between the hcb and fe ensembles. This choice was necessary to fix the phase of the wave function (problems caused by the electronic indistinguishability).

M	E_{fe} (−,−)	E_{hcb} (−,+)	E_{scfe} (+,−)	E_{b} (+,+)
Annulenes				
4	−9.600	−13.577	−16.690	−20.667
4^{2-}	−9.600	−9.600	−28.800	−28.800
6	−19.200	−19.200	−28.800	−28.800
8	−23.177	−25.048	−36.529	−38.400
8^{2-}	−23.177	−23.177	−48.000	−48.000
10	−31.066	−31.066	−48.000	−48.000
Polyenes $C_{2n}H_{2n+2}$ ($M = 2n$)				
4	−10.733	−10.733	−16.794	−16.794
6	−16.771	−16.771	−25.949	−25.949
8	−22.843	−22.843	−35.077	−36.077
10	−28.927	−28.927	−46.056	−46.056

bosonic ensemble is removed. In short, the fermionic electrons reproduce hcb properties which correspond to a superposition of fermionic on-site and bosonic intersite properties. Only in $4n$ annulenes the PAP has an explicit destabilizing influence on the electronic degrees of freedom.

In the many-electron basis adopted in the present study the suppression of the influence of the PAP in polyenes and $(4n + 2)$ annulenes is easy to explain. A convenient schematic representation of this behaviour is possible in the HMO picture where the two spin spaces are decoupled; see above. To elucidate the quantum statistical effects leading to the results in Table 1 we have portrayed (Figs. 2 to 4) allowed π electron moves within one spin direction of polyene and annulene pairs. The atomic site indices in the diagrams define the electronic ordering. They must be kept fixed within a calculation. This is an important technical point in CI calculations in of the VB type [11, 12] and in QMC simulations of fermion problems [8 - 10]. Let us consider first a two-electron configuration of butadiene and cyclobutadiene with

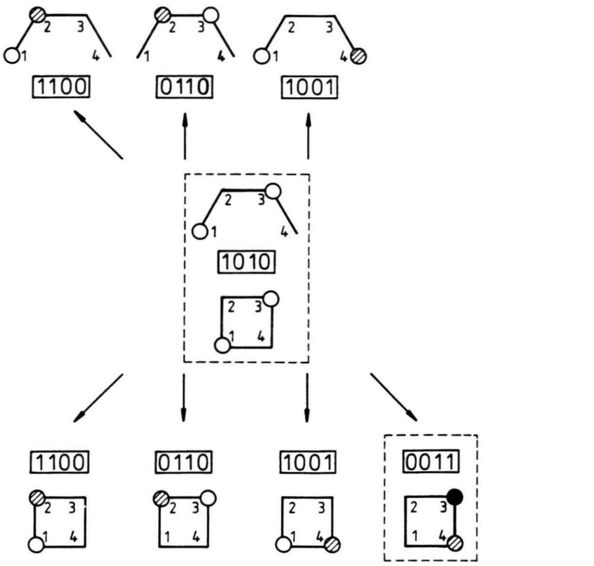

Fig. 2. Nearest-neighbour jumps in one spin direction of butadiene and cyclobutadiene starting from a π configuration with atomic occupation numbers 1010 (center of the diagram). The electron which has been moved to create the new configuration is symbolized by a shaded circle. The electron which has been passed by is labeled by a full circle. Each configuration is characterized by the corresponding atomic occupation numbers.

atoms 1 and 3 occupied; center of Figure 2. In the occupation number representation this configuration reads 1010. For both two-electron systems six different configurations can be defined, i.e. there are six possibilities to distribute two indistinguishable particles over four atomic sites. In butadiene these configurations are coupled by 12 allowed nearest-neighbour jumps. In cyclobutadiene four additional 1 ↔ M (M = 4) jumps occur. From the configuration 1010 three nearest-neighbour moves are possible in butadiene. None leads to an interchange of the electron ordering. In polyenes jump processes which would be accompanied by electronic interchanges are prevented by the PEP. The somewhat arbitrary statistics of electrons in a line has been recognized by Jordan and Wigner already in the early days of quantum mechanics [14]. In polyenes, any discrimination between the fe and hcb quantum statistics becomes irrelevant. Physically it is the PEP which suppresses any influence of the PAP in polyenes. In cyclobutadiene, one additional nearest-neighbour move is possible when starting from the same configuration as in the cyclobutadiene case. This is the "terminal" 1 ↔ 4 process. The label "terminal" symbolizes that the first and last

(= M) π centers of the annulene under consideration are involved in the corresponding π electron move. In contrast to the three remaining jumps, the 1 $\leftrightarrow$ 4 hopping in cyclobutadiene is accompanied by an interchange in the π electron ordering. The π electron at center 3 has been surpassed by the transferred electron. The Hückel-type resonance (= hopping) integral associated with this jump process must be considered with a negative sign in the many-electron basis. This negative sign causes a node in the electronic wave function which is well-known from VB investigations of $4n$ annulenes [11]. These calculations predict a ground state of ^{1}B symmetry. The negative sign is a consequence of the PAP. In the hcb ensemble, where the PAP is not taken into account, 1 $\leftrightarrow$ M processes with an odd number of electronic interchanges within a given spin direction are as nodeless as all other nearest-neighbour moves are. The PAP leads to an additional electron localization in the fermionic ground state of cyclobutadiene or – more generally – in all annulenes with an even number of π electrons in one or both spin directions. According to the Heisenberg uncertainty principle [24], this enhanced π electron localization (= suppressed spatial uncertainty) causes an enhanced momentum uncertainty; larger momenta become more probable. As a matter of fact the π electronic energy is raised (= destabilization).

In Fig. 3 we have shown the allowed nearest-neighbour moves per spin direction for one initial configuration (= 1110) of the butadienyl and cyclobutadienyl dianions. The additional electron per spin direction relative to the neutral parents butadiene and cyclobutadiene restricts to four the number of configurations allowed by the PEP. In the polyene dianion these configurations are interconnected by six nearest-neighbour hoppings. In the cyclic dianion two additional terminal 1 $\leftrightarrow$ 4 jumps occur. In the starting configuration 1110 of the acyclic network only one π electron jump is allowed by the PEP while two processes are possible in the cyclic system. In contrast to the neutral annulene in Fig. 2, the terminal 1 $\leftrightarrow$ 4 process in the cyclobutadiene dianion is now accompanied by an even number of electronic interchanges in this spin direction. By analogy with all "inner" 2 $\leftrightarrow$ (M − 1) π electron moves in annulenes and all moves in polyenes, this process is of the hcb type; two interchanges conserve the sign of the matrix element in the hopping matrix (= elimination of a PA-based constraint). The same conservation of the phase of the many-electron wave function in connection with "terminal" π jumps is symbolized in Fig. 4 where we show all allowed π electron moves from one initial configuration of hexatriene and benzene. In total 20 of such configurations can be formed for the two 6π systems. In hexatriene they are coupled by 60 allowed nearest-neighbour moves. In benzene, 12 additional terminal 1 $\leftrightarrow$ 6 moves can take place. Five processes are possible in the polyene configuration portrayed in Figure 4. In benzene we have the additional 1 $\leftrightarrow$ 6 process where the electrons at centers 3 and 5 have been passed by the transferred one. By analogy with the 1 $\leftrightarrow$ 4 hopping in Fig. 3, the sign of the Hückel-type resonance integral is conserved. The PAP is a passive electronic constraint only. Figures 3 and 4 indicate that the "deactivation" of the PAP in polyenes and for the terminal jumps in ($4n$ + 2) annulenes is of different origin. In polyenes it is the PEP which prevents any interchanges of electrons of one spin direction. The same PE-based mechanism of course is operative for all inner 2 $\leftrightarrow$ (M − 1) moves in annulenes which are "polyene-like". In annulenes, electronic interchanges within one spin direction are not forbidden principally. But in ($4n$ + 2) annulenes the 1 $\leftrightarrow$ M processes are always accompanied by an even number of interchanges p per spin direction, a sequence which eliminates the PA-based minus sign in the hopping matrix (p = even).

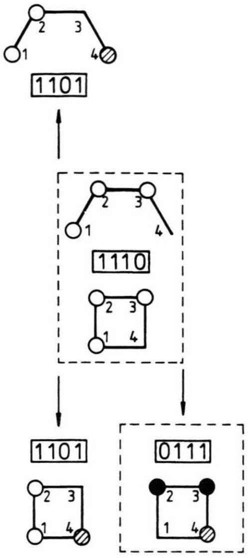

Fig. 3. Nearest-neighbour jumps in one spin direction of the butadienyl and cyclobutadienyl dianion starting from the π configuration shown in the center of the diagram. See legend Figure 2.

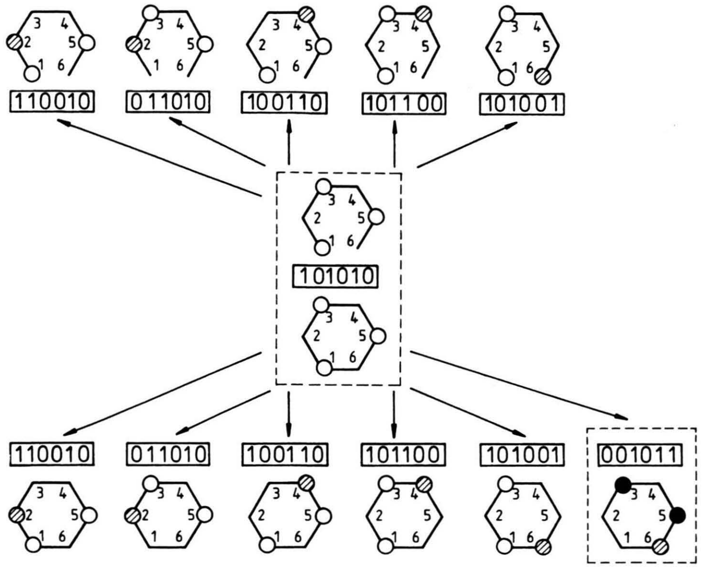

Fig. 4. Nearest-neighbour jumps in one spin direction of hexatriene and benzene starting from the π configuration shown in the center of the diagram. See legend Figure 2.

Table 2. Normalized π energies of neutral annulenes with M carbon atoms in the fermionic and hard core bosonic ground state E_{fe}/M, $E_{\mathrm{hcb/M}}$ according to fully correlated PPP calculations. Additionally we have given the normalized fermionic energy loss $|\Delta E|/M$ and the parameter Q (= $E_{\mathrm{fe}}/E_{\mathrm{hcb}}$ in %). All energy values are given in eV. The experimental status of the unsubstituted systems has been taken from [25].

M	E_{fe}/M	E_{hcb}/M	$\lvert\Delta E\rvert/M$	Q	Status
3	–1.708	–2.472	0.764	69.1	unknown
4	–1.814	–2.588	0.774	70.1	unstable
5	–2.016	–2.281	0.265	87.9	transient intermediate
6	–2.338	–2.338	–	100.0	stable
7	–2.089	–2.226	0.137	93.8	short lived species
8	–2.094	–2.261	0.167	92.6	high reactivity
9	–2.112	–2.194	0.082	96.3	stable in inert atmosphere
10	–2.203	–2.203	–	100.0	stable
11	–2.131	–2.171	0.040	98.2	
12	–2.110	–2.182	0.072	96.7	polyolefinic character
13	–2.152	–2.178	0.004	98.6	
14	–2.175	–2.175	–	100.0	stable
15	–2.163	–2.173	0.010	99.5	
16	–2.128	–2.172	0.044	98.0	polyolefinic character
17	–2.162	–2.171	0.009	99.6	
18	–2.162	–2.162	—	100.0	stable
19	–2.151	–2.157	0.006	99.7	
20	–2.132	–2.159	0.027	98.5	

In the following we replace the simple HMO model [1] by the more sophisticated PPP Hamiltonian [17, 18]. As the scfe and b quantum ensembles are not accessible for any electronic system, we concentrate on the fe and hcb quantum statistics. In Table 2 we have summarized fully correlated normalized π energies E_{fe}/M and E_{hcb}/M of annulenes. The parameter $|\Delta E|/M = |E_{\mathrm{fe}} - E_{\mathrm{hcb}}|/M$ measures the energy loss in the electronic system under the influence of the PAP, and Q is the ratio $E_{\mathrm{fe}}/E_{\mathrm{hcb}}$. In the last column we have given the experimental status of the unsubstituted annulenes [25]. Note, however, that the idealized D_{Mh} geometries considered in the calculations are not realized experimentally in higher annulenes. But the differences between the idealized model geometries and the experimental ones are without influence on the present discussion, which is prevailingly of topological nature. The key parameter of our analysis is the parity p of electronic permutations within one spin direction which occur as response to nearest-neighbour jumps. The destabilizing influence of the PAP is clearly seen in the data collection. In $4n$ annulenes the PAP is operative in both spin spaces, while it is operative in only one spin space in doublet rings (in the spin space with an even electron count). The enhancement of the $|\Delta E|/M$ elements in Table 2 (= decreasing Q ratios) correlate with a decreasing stability of the corresponding π systems. Two interesting effects can be extracted from Table 2: i) The destabilizing influence of the PAP in $4n$ and $(2n + 1)$ rings is attenuated with increasing electron number. This is a typical "dilution effect" as the weight of the $1 \leftrightarrow M$ moves is reduced with increasing number of stabilizing $2 \leftrightarrow (M - 1)$ π electron jumps. ii) The influence of the PEP is enhanced with increasing electron numbers. The normalized π energies in both ensembles are raised with increasing electron count. In the fe ensemble, this effect is superimposed by switch operations of the PAP as a function of the electron count. The observed PE-based destabilization is caused by an increasing number of many-electron configurations with "locked" electrons with increasing M. In cyclobutadiene, which is a system with two electrons per spin direction, it is not possible to "lock" an electron completely. There is always one hopping process that is not forbidden by the PEP. Benzene is the first closed shell system where such a locking due to the PEP can occur. The central electron in the configuration 001110 is locked. The number of hopping allowed by the PEP follows a simple $f = 0.5M/(M - 1)$ law (neutral M annulenes). The denominator reflects the maximum number of final atoms accessible for nearest-neighbour jumps when starting from a preselected initial atom. The numerator reflects the number of jump adresses allowed by the PEP. In cyclobutadiene we have $f = 2/3$. With increasing number of π centers, f converges towards 0.5. The raise of normalized π energies with increasing electron count is caused by the PEP.

The present theoretical analysis suggests that "aromaticity" can be identified with an hcb character of the π electron wave function in the limit of smaller electron counts. hcp properties indicate that the PAP is not operative and small electron numbers reduce constraints due to the PEP. "Antiaromaticity" in π systems is an outcome of the Pauli antisymmetry constraint in the fermionic wave function. Small electron numbers in antiaromatic π systems enhance the relative weight of the destabilizing $1 \leftrightarrow M$ moves.

After having discussed the normalized π energies of annulenes in the fully correlated PPP limit, we next analyze the PPP-based electronic charge fluctuations $\langle(\Delta n_i)^2\rangle$. The $\langle(\Delta n_i)^2\rangle$ measure the probability to find two, one or no electrons at the i'th center and thus the probability of nearest-neighbour jumps. According to the uncertainty principle, increasing $\langle(\Delta n_i)^2\rangle$ implies an increasing stabilization of the π system. In Fig. 5 we have portrayed the atomic $\langle(\Delta n_i)^2\rangle$ of some annulenes and polyenes. For the two $4n$ rings we have given the $\langle(\Delta n_i)^2\rangle$ values of the fe (–,–) and hcb (–,+) ensembles. The schematical display shows the topological electron localization at the terminal atoms of polyenes. At these centers the charge fluctuations are strongly suppressed. This spatial localization of carriers has some formal analogies to the Anderson localization of electrons at defect sites in solids [26]. The spatial localization of the electrons at the terminal atoms of polyenes explains that the transition from polyenes to $(4n + 2)$ annulenes is stabilizing. Nevertheless we see that the topological effect is rather weak in comparison to the electron localization in $4n$ annulenes, which is caused by the node in the wave function (= PA effect). Figure 5 visualizes large differences in the electronic localization properties of $4n$ annulenes in the hcb and fe ensemble.

We have demonstrated that $|\Delta E| = 0$ (= aromatic stabilization in annulenes) or $|\Delta E| > 0$ (= antiaromatic destabilization) depends on the number of electronic interchanges p per spin direction accompanying the π electron hoppings over the atomic sites. With this quantum stastistical descriptor it is straightforward to extend the present microscopical classification scheme to π molecules of any topology. In Table 3 we have summarized fully correlated PPP energies of the molecules **1** to **8** portrayed in Figure 1. The π energies have been calculated for the fe and hcb ensembles. Additionally we have given $|\Delta E|$ and Q (see above) as well as the experimental status of the bare π systems [27]. By analogy with annulenes stable molecules are found in the vicinity of $|\Delta E| = 0$, i. e. in the absence of strong fermionic antisymmetry effects (= odd number of electronic interchanges as response to π electron moves). With increasing electronic constraints due to the PAP the stability of the system is reduced. The large $|\Delta E|$ element in molecules **2** and **3** with a total π electron number of 8 is a result of a superposition of an "outer" negative hopping (note the analogy with 8 annulene) and an

Table 3. π energies of the molecules **1** to **8** of Fig. 1 in the fermionic and hcb ground state according to fully correlated PPP calculations; see legend of Figure 2. For the experimental status of the unsubstituted π systems see [27].

Molecule	E_{fe}	E_{hcb}	$\lvert\Delta E\rvert$	Q	Status
1	–12.669	–15.892	3.223	79.7	unstable
2	–17.886	–20.166	2.280	88.7	unstable
3	–18.190	–20.471	2.281	88.9	unstable
4	–24.172	–24.347	0.175	99.3	stable
5	–23.748	–24.171	0.423	98.2	stable
6	–22.28	–24.25	1.97	91.9	unstable
7	–26.76	–28.32	1.56	94.5	unstable
8	–27.42	–28.48	1.06	96.3	unstable

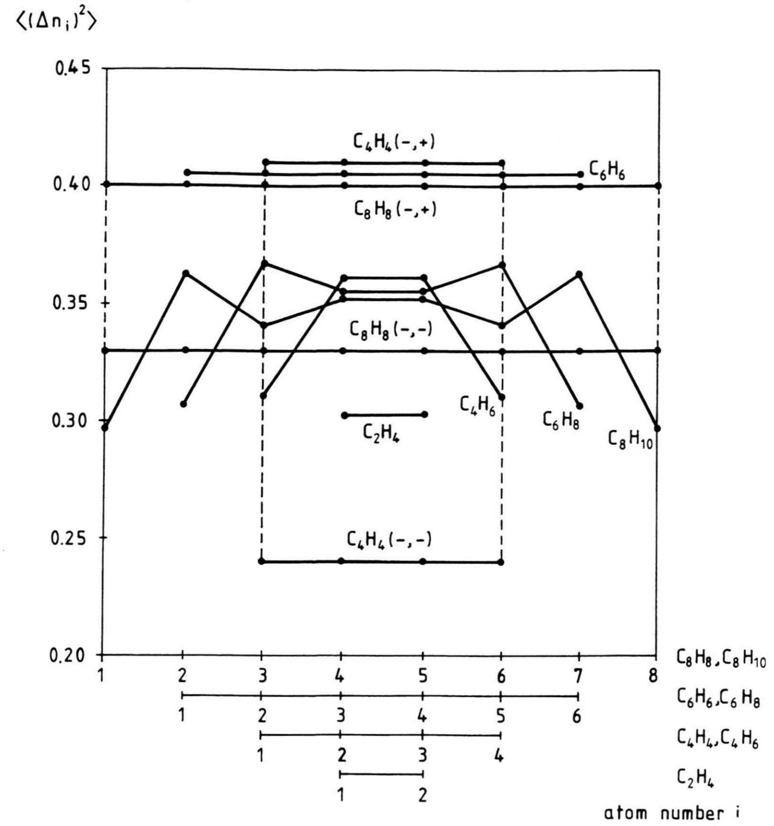

Fig. 5. Mean square deviations of the π electron density $\langle(\Delta n_i)^2\rangle$ at the different centers i of polyenes and annulenes according to fully correlated PPP calculations. For the two $4n$ annulenes we have given the mean square deviations in the fermionic (-,-) and hcb (-,+) state.

"inner" jump over the central carbon bridge. The latter process is accompanied by an odd number of electronic interchanges, too. Let us compare the energy loss $|\Delta E|$ of pentalene **2** (= 2.28 eV) and 8 annulene (= 1.291 eV). These numbers indicate that PA-based constraints in **2** are roughly doubled in comparison to 8 annulene. The "inner" π electron moves in naphthalene **4**, on the other hand, are not accompanied by an odd number of interchanges as long as the configurations are symmetrical with respect to the central CC bond (= covalent configurations). The energy loss $|\Delta E|$ in this molecule is thus rather small. Deviations from $|\Delta E| = 0$ are due to central π electron moves in configurations with three electrons per spin direction in one ring and only one electron in the second. Now the central jumps are accompanied by an odd number of interchanges and PA-based fermionic effects occur. The difference in $|\Delta E|$ calculated for the 8π systems **2** and **3**, on the one hand, and the 12 π systems **7** and **8**, on the other, is a manifestation of the aforementioned size effect. The PAP is of larger influence in (poly-)cyclic π networks with smaller M.

4. Resume

The results of the present theoretical investigation can be summarized as follows. We have shown that the Pauli antisymmetry principle is without influence in the π electron subspace of polyenes and $(4n + 2)$ annulenes as long as the hoppings are restricted to nearest-neighbours and the interaction is of the density-density type. In this case the wave function of the corresponding π system behaves like the wave function of a so-called hard core bosonic ensemble. The intersite interaction in this quantum ensemble is bosonic, while the on-site interaction is fermionic. We want to reemphasize that we do *not* doubt the fermionic character of electrons. In the most general case the quantum statistics of electrons is defined by two constraints, the PEP and PAP. Polyenes and $(4n + 2)$ annulenes can be considered as exceptions where molecular topology and electron count interact cooperatively. This cooperativity eliminates the influence of Pauli antisymmetry constraints in the many-electron wave function. We have derived a theoretical result which shows that the minimum prerequisite that has to be fulfilled by an electronic wave function is the conservation of the Pauli exclusion principle. We wish to point out that the fermionic energies discussed in the present work can be derived by any conventional method of electronic structure theory. In most of the widely used programs of molecular quantum chemistry it is however impossible to extract the influence of the PAP on the electronic energy. This degree of freedom has been the conceptional advantage of the adopted many-electron basis in the occupation number representation.

On the basis of the present quantum statistical findings it is possible to suggest a microscopical definition of "aromaticity" and "antiaromaticity". The restriction of both qualitative descriptors to smaller electron numbers is a Pauli exclusion effect (in the case of aromaticity) or some kind of "dilution" effect (in the case of antiaromaticity). The influence of the negative phase in the many-electron wave function of antiaromatic compounds is attenuated with increasing electron count. Furthermore, we have shown that the concepts derived for annulenes can be transferred to polycyclic π molecules. The quantum statistical origin leading to low stabilities of polycyclic compounds is the same as encountered in monocycles, i.e. hoppings accompanied by an odd number of electronic interchanges per spin direction. In addition to the quantum constraints PEP and PAP we have mentioned a third constraint on the electronic ensemble which is of topological nature. The interplay of these three constraints has been considered in the discussion of the electronic charge fluctuations $\langle(\Delta n_i)^2\rangle$.

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