On the Role of the Pauli Antisymmetry Principle in Pericyclic Reactions

Michael C. Böhm and Johannes Schütt

Institut für Physikalische Chemie, Physikalische Chemie III, Technische Hochschule Darmstadt,
Petersenstr. 20, D-64287 Darmstadt

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

In the present work we discuss the role of the Pauli antisymmetry principle (PAP) in synchronous pericyclic reactions. These reactions are allowed in the electronic ground state whenever the PAP does not act as a quantum constraint in the transition state. The possible suppression of the influence of the PAP is a peculiarity of π electron systems. The PAP is a hidden (= deactivated) variable in the π electron subspace of polyenes and $(4n + 2)$ annulenes ($n = 0, 1, 2,...$). In $4n$ annulenes ($n = 1, 2, 3,...$) it leads to minority signs in the kinetic hopping matrix of the π electronic wave function and thus to an energetic destabilization. The quantum statistical difference between the above families of π systems renders possible a microscopical definition of the quantities "aromaticity" and "antiaromaticity". The sign behaviour of the kinetic hopping elements is used in the discussion of pericyclic reactions. The present quantum statistical description of these reactions is related to the Dewar-Zimmermann and Woodward-Hoffmann rules.

Key words: π Electron Systems, Pericyclic Reactions, Quantum Statistics, Pauli Antisymmetry Principle.

1. Introduction

In recent publications we have discussed the quantum statistical origin of the special electronic properties of cyclic π systems [1 - 5]. Our approach rendered possible a microscopical explanation of the non-additivities of electronic expectation values like normalized π energies or binding energies in mono- and polycyclic π systems as a function of the electron count. In contrast to this peculiar behaviour of cyclic π systems, a regular variation of electronic expectation values is observed in homologous series of saturated hydrocarbons and polyenes. In the polyene family this effect has been reproduced numerically more than two decades ago [6 - 8]. In our quantum statistical contributions we have demonstrated that the non-additivities of bond increments in cyclic π networks are caused by the Pauli antisymmetry principle (PAP) which acts as some kind of electronic switch. In π Hamiltonians formulated in the tight-binding approximation and an interaction of the density-density type, the influence of the PAP occurs in some matrix elements of the hopping type only. The descriptor "π Hamiltonian" implies a restriction to one atomic orbital (AO) per atomic site and the descriptor "tight-binding approximation" implies that the π electron moves under the influence of the kinetic energy part of the Hamiltonian are restricted to nearest-neighbour centers. In this case the influence of the PAP is easy to identify when working in a basis of atomic electronic occupation numbers. The PAP acts as an electronic constraint whenever a π electron move is accompanied by an odd number of electronic interchanges per spin direction; see the discussion in [5]. The activation or suppression of the PAP is determined by a sensitive interplay between molecular topology and electron count [3-5]. Although quantum chemical approaches of different degrees of sophistication have been very successful to reproduce these electronic peculiarities of cyclic π systems in terms of calculated electronic energies, the quantum statistical origin of this behaviour seems to be unrecognized. An early success of quantum chemical methods for the understanding of π electronic properties has been the Hückel molecular orbital (HMO) model [9] which has lead to a famous π electron counting rule, i. e. the discrimination between Hückel annulenes with $m = (4n + 2)$

π electrons (n = 0, 1, 2,...) and anti-Hückel annulenes with m = 4n π electrons (n = 1, 2, 3,...). "Aromatic" $(4n + 2)$ rings exhibit high stability (= low reactivity) while "antiaromatic" $4n$ rings exhibit low stability (= high reactivity). The quantity which determines the electronic properties of (monocyclic) π systems is the electron count m and not the number M of π centers. M annulenes with $M = 4n$ and an electron count of $(4n + 2)$ are stable, while monocycles with $4n$ π electrons and $M = (4n + 2)$ are unstable.

In the present contribution we transfer the quantum statistical classification of π electron systems we have developed recently [3 - 5] to pericyclic reactions. Subsequently we show that these reactions can be interpreted by a single descriptor, the Pauli antisymmetry principle. We wish to point out that the present theoretical approach does not lead to quantitative numerical results. This is the domain of quantum chemical calculations with steadily increasing effort. In the present work we want to emphasize an electronic effect which seems to be the common origin of theoretical conceptions developed in the past years to explain the reactions of π systems. Different models have been reported in the literature to rationalize these reactions theoretically. A first suggestion goes back to the end of the thirties. Evans [10] pointed out the importance of six-membered "aromatic" transition states in Diels-Alder reactions, a first attempt to use elements from the Hückel counting rule for chemical reactions. The idea of an aromatic transition state has been a central element in the approach of Dewar and Zimmermann (DZ) [11 - 14]. Their rule for pericyclic reactions can be summarized as follows: A pericyclic reaction is thermally allowed if the transition state is aromatic, i. e. monocyclic and of the $(4n + 2)$ electron type. The most prominent approach to predict pericyclic reactions is due to Woodward and Hoffmann (WH) [15, 16]. Their method is based on the conservation of the orbital symmetry. The WH rules have been derived on the basis of correlation techniques where the orbitals of the reactant(s) are correlated with the orbitals of the product(s). For some other theoretical concepts to explain pericyclic reactions we refer to [17 - 19]. The cited concepts have been developed at a time where elaborate electronic structure calculations of chemical reactions have not been feasible. Nowadays many reactions can be studied with high accuracy by the methods of (molecular) quantum chemistry. Despite the powerful tools of computational chemistry there

is still the necessity to find general ordering principles for classes of chemical reactions without performing an explicit calculation for each system. The provision of such a general applicability has been one of the reasons of the large success of the DZ and WH rules. The present approach follows the philosophy of these methods to formulate a non-numerical access. Similarities and differences in the key-elements of these non-numerical procedures will be emphasized in the following discussion. In recent contributions we have adopted the technique touched in the next section to derive fully correlated ground state energies of π systems [1 - 5]. These calculations require the same effort as conventional high-quality approaches of molecular quantum chemistry. In the present work we have restricted our discussion to topics which are beyond numerical aspects, i. e. which are of general nature.

The organization of the present article is as follows. In Sect. 2 we recapitulate some key-elements of the electronic structure approach adopted in the present study. The π electronic structure of some polyenes and annulenes under special consideration of quantum statistical aspects as well as pericyclic reactions are then discussed in Section 3. The article ends with a short resume.

2. Theoretical Background

The decisive role of the Pauli antisymmetry principle in pericyclic reactions will be considered in the following section. In the present section we explain quantum statistical elements of the theory suggested. It is the aim of the present work to demonstrate a general quantum statistical effect which leads to an overall understanding of the corresponding reactions and which does not depend on specific model assumptions such as the orbital (= one-electron) picture or symmetry considerations. Nevertheless we have to accept other idealizations and simplifications which will be commented below. In the course of our discussion we will also touch the DZ and WH rules. Electrons as fermions obey the Pauli principle which imposes constraints on their degrees of freedom. In the present theoretical framework it is the PEP which controls the on-site behaviour of the electons while the PAP controls their intersite behaviour. In the majority of quantum chemical approaches (= conventional determinantal schemes) a fragmentation of the Pauli principle into the Pauli antisymmetry principle and the Pauli exclusion principle (PEP) is not possible. They are

taken into account simultaneously. In many representations of the electronic wave function, the PEP follows from the PAP which – in this context – is the more general principle. In the single-determinantal scheme this is easy to show. An investigation of the individual influence of the PAP and PEP on electronic properties is not possible by computational methods where both occur as coupled constraints. In many-electron bases of atomic occupation numbers, however, the PAP (= intersite constraint) and PEP (= on-site constraint) can be treated as two decoupled variables [1 - 5]. Their consideration or non-consideration has to be defined by external instructions. Such many-electron bases are employed in quantum Monte Carlo (QMC) simulations of electronic problems [1 - 5, 20 - 24] and configuration interaction (CI) calculations of the valence bond (VB) type [25, 26]. In many-electron approaches of the QMC or VB CI type the PAP and PEP have to be taken into account by two anticommutators; see the discussion in [5]. In the present work only the implications of these anticommutators are explained in terms of transparent pictures. The difficulties to take into account the PAP in these many-body calculations has been described in large detail in [20 - 23]. Unfortunately most of these articles have been published in journals which – frequently – are not refereed by chemists. The PEP prevents electronic configurations with more than one electron of the same spin coordinate in the same atomic orbital. The PAP acts on the electrons of one spin direction only where it leads to a negative (= minority) sign in the matrix of the electronic hoppings whenever the sequence of two electrons of the same spin is interchanged. Such changes in the ordering can occur during electronic jump processes over the atoms of the molecule under the influence of the kinetic energy (= hopping) part of the Hamiltonian. In chemistry the matrix elements describing these jumps are denoted as "resonance" integrals. They measure the so-called interatomic sharing which is the driving force for the formation of covalent chemical bonds [27, 28]. It is the large conceptual advantage of many-electron bases in the occupation number representation that the influence of the PAP on the corresponding electron moves (= sign of the hopping element) becomes transparent immediately; see below. Of course the same energetic information is implicitly taken into account in any conventional determinantal description of the many-electron wave function. But here the PA-based influence on the electronic degrees of freedom cannot be identified on the

basis of single matrix elements. To achieve an intelligible interpretation of the influence of the PAP on pericyclic reactions we have to consider one spin space only as the PAP is operative between electrons of the same spin coordinate.

Up to now we have mentioned one type of π electronic moves only, i. e. processes which lead to a change in the ordering of two electrons of the same spin. In this case the prefactor pf of the corresponding element of the hopping matrix in the occupation number representation is negative whenever the AOs overlap in-phase. In short, the here called prefactor pf measures the combined influence of the PAP which takes into account an electronic ensemble effect and of the sign/phase of the corresponding basis integral which is determined by the overlap of the corresponding AOs. In the next section the superposition of an AO basis integral effect and an ensemble effect will be explained via some simple examples. Without loss of generality we can write $pf = pf_{PAP} \times pf_{BI}$ with pf_{PAP} monitoring the ensemble effect due to the PAP and pf_{BI} symbolizing the sign of the basis integral. In other words, f_{PAP} takes into account the effect of the quantum statistics, which is a function of the electron count, while f_{BI} is a function of the molecular topology. The interchange of two electrons is a special case of an odd permutation p, i. e. $p = 1$. According to the laws of quantum statistics of fermion systems a negative pf_{PAP} in the hopping matrix occurs for any odd number of permutations p of electrons within one spin direction. pf_{PAP} is positive whenever an electronic jump process is not accompanied by an interchange in the ordering or when the number of permutations p per spin direction is even [4, 5]. Below we will explain these general quantum statistical principles of fermion systems on the basis of some simple examples.

The electronic ordering within a molecule has to be defined via atomic site indices; see Fig. 1 which is discussed in the next section. Of course any numbering scheme of the atoms is allowed. But a preselected choice must be kept fixed within a calculation. This is an important technical aspect of QMC simulations of fermion problems [1, 2, 22] and CI calculations in a VB basis [25, 26]. Different many-electron configurations in these bases of atomic occupation numbers are discriminated by the occupation and non-occupation of the different atomic centers. At the end of this short theoretical section we want to summarize the idealizations and simplifications of our approach which
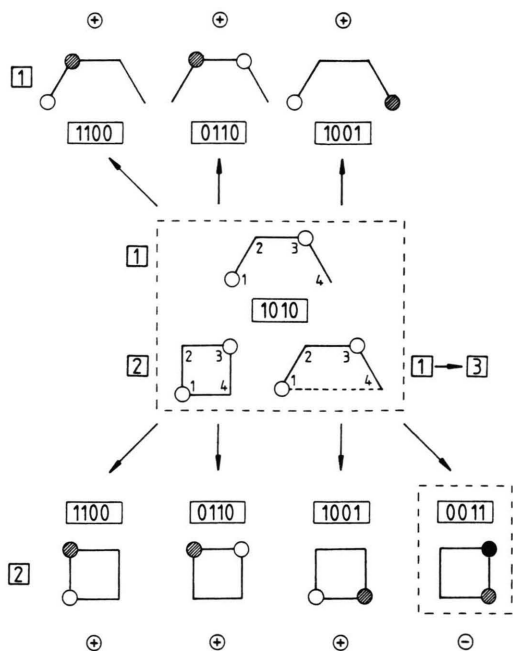
Fig. 1. Nearest-neighbour π electron jumps in one spin direction of butadiene **1** and cyclobutadiene **2** starting from a π configuration with atomic occupation numbers 1010 (center of the diagram). We have also symbolized the "transition state" of the intramolecular cycloaddition from butadiene **1** to cyclobutene **3**. By analogy with the cyclobutadiene molecule **2** 1 → 4 jumps contribute to the transition state wave function **1** → **3**. The electron which has been moved to create the final configuration is labeled by a shaded circle. The electron which has been passed by is indicated by a full circle. Each configuration is indicated by the corresponding atomic occupation numbers. Final configurations which are reached by any $p \neq 0$ are surrounded by a box of broken lines. Jump processes without electronic permutation p or an even p lower the electronic energy while jump processes with an odd number of permutations are destabilizing. This is symbolized by a + and – sign in the final configuration.

makes use of the topology of the systems under consideration.

i) Only one π-type AO per atomic center is taken into account. The σ AOs are neglected in the quantum statistical classification of the non-saturated hydrocarbon systems. π/σ separation – or more generally, restriction to one AO per center – has been the prerequisite to derive a simple quantum statistical subclassification of π electron systems. We wish to point out that both the DZ [11 - 14] and WH [15, 16] methods make use of such a single-AO-per-site approximation. Our intention is to win a deeper insight into the interplay between π electronic properties on the one hand and molecular topology and π electron

count on the other. The restriction to a single AO per atom has been guided by the model assumption that pericyclic reactions of π systems can be rationalized non-numerically in terms of a restricted Hilbert space confined to those electrons that are changed in their bonding character in course of a reaction. Such dramatical changes do not occur in the σ frame. We are aware of the fact that such a selection of an active space corresponds to an approximation preventing the evaluation of any numerical expectation values. But as will be shown in the following discussion this restriction is irrelevant in connection with the aims of our analysis.

ii) In the subsequent discussion the interatomic π electron moves are restricted to bonded nearest-neighbour atoms or to centers where new bonds are formed (in the transition state of pericyclic reactions). By analogy with topic i) this has been necessary to come to a transparent microscopical differentiation of π systems. Model calculations have shown that the consideration of next-nearest (= 1 ↔ 3) hoppings in alternant π systems does not lead to any noticeable effect; note that the elements of the first-order density matrix between these centers are zero. Hoppings between centers that are separated by two or more than two C atoms may lead to small non-zero matrix elements. They are, however, unimportant for the understanding of principal effects.

iii) The interpretation of many-electron results is particularly simple if the two-electron interaction is of the density-density type. This topic has been touched in [1 - 5]. For the present general argumentation further consideration of these numerical fine-effects is not necessary. Finally we should mention the energetic window which is covered by the selective switch operation of the PAP as a function of the electron count. In our previous investigations we have shown that we discuss energetic effects between 1 and 4 eV in the π systems studied in the next section. For more details we refer to [1 - 5].

3. Results and Discussion

To rationalize the peculiarities in the quantum statistics of π electron systems we first consider some annulenes and polyenes before treating pericyclic reactions. A detailed discussion of this topic has been given in our foregoing article [5]. In order to achieve a transparent representation of the theoretical background we compare nearest-neighbour moves within

one spin direction of homologous polyene-annulene pairs. In Fig. 1 we have portrayed such nearest-neighbour moves in the two-electron spin space of butadiene **1** and cyclobutadiene **2**. In the initial configuration, which is shown in the center of the diagam, the atoms 1 and 3 are occupied. In the occupation number representation this configuration is denoted as 1010. From it three nearest-neighbour moves are possible in the polyene molecule **1**. They lead to the final configurations 1100, 0110, and 1001 (top row of Figure 1). As can be seen the electronic ordering is conserved in all processes. Under these circumstances the PAP is without influence on the electronic properties of the π system. With respect to the interatomic interaction the sign of the π electronic wave function is conserved; there are no minority signs in the matrix of the kinetic hoppings. In the schematical representation of Fig. 1 this behaviour has been symbolized by a "+" sign. In polyenes we have the general situation that nearest-neighbour moves, which would lead to an interchange of the ordering per spin direction, are prevented by the PEP.

In cyclobutadiene **2** one additional nearest-neighbour move can take place when starting from the same initial configuration 1010 as in the butadiene case. This is the terminal $1 \rightarrow 4$ π electron jump which is accompanied by an interchange in the π electron ordering as the electron at center 3 has been surpassed by the transferred one to reach the final configuration 0011. We have adopted the label "terminal" to symbolize that the first (= 1) and last (= M = 4) atom of an M annulene participate in the corresponding transfer process. Note that these terminal $1 \leftrightarrow M$ π electron moves are the only nearest-neighbour jumps in annulenes which are accompanied by a change in the π electron ordering. By analogy with polyenes all "inner" $2 \leftrightarrow (M-1)$ π electron jumps in M annulenes conserve the ordering within the given spin direction. In contrast to all other moves symbolized in Fig. 1 the terminal $1 \rightarrow 4$ jump in cyclobutadiene **2** is destabilizing as a result of a PA-based node in the electronic wave function ($pf_{PAP} = -$). In Fig. 1 this destructive interference has been symbolized by a "−" sign. The odd character of the π electron wave function of $4n$ annulenes is well-known from VB calculations which predict a ground state of ^1B symmetry [29].

A collection of all nearest-neighbour moves within one spin direction of butadiene **1** and cyclobutadiene **2**, which are allowed by the PEP, is given in Table 1a and 1b. The +,− indices symbolize the prefactor pf

Table 1. Prefactor pf (+,−) of the non-vanishing elements of the π electron hopping matrix in the many-electron basis of atomic occupation numbers per spin direction. pf is defined by $pf = pf_{PAP} \times pf_{BI}$. The first term measures the influence of the Pauli antisymmetry principle and the second one the phase of the corresponding basis integral. In a) we have collected the non-zero matrix elements of butadiene **1**. In b) we have given the non-zero entries of cyclobutadiene **2** and of the transition state of the disrotatory intramolecular cycloaddition $1 \rightarrow 3$. In c) the non-zero entries of cyclobutadiene in a Möbius-type arrangement and of the conrotatory transition state $1 \rightarrow 3$ are given. The different electronic configurations are labeled by occupation numbers (0 or 1) confined to the π centers 1 to 4. The atoms 1 and 4 are the terminal butadiene and "transition state" atoms. The interaction between the different configurations is provided by nearest-neighbour jumps of the π electrons which are allowed by the PEP. The two transition states $1 \rightarrow 3$ are characterized by non-zero $1 \leftrightarrow 4$ jumps.

	1100	1010	1001	0110	0101	0011
a)						
1100		+				
1010	+		+	+		
1001		+			+	
0110		+			+	
0101			+	+		+
0011					+	
b)						
1100		+			−	
1010	+		+	+		−
1001		+			+	
0110		+			+	
0101	−		+	+		+
0011		−			+	
c)						
1100		+			+	
1010	+		+	+		+
1001		+			+	
0110		+			+	
0101	+		+	+		+
0011		+			+	

of the non-vanishing elements of the hopping matrix. Entries $\neq 0$ are the result of an interaction of two many-electron configurations via a transferred electron. The distribution of the +,− signs reflects the interplay between molecular topology and electron count. On the one hand the magnitude of the entries is a function of the π Hamiltonian employed. On the other it is a function of the geometry. But as emphasized above we are not interested in absolute numbers in the present non-numerical analysis. In one-electron Hamiltonians of the HMO type the lowest eigenvalue of the hopping matrix in the occupation number representation yields
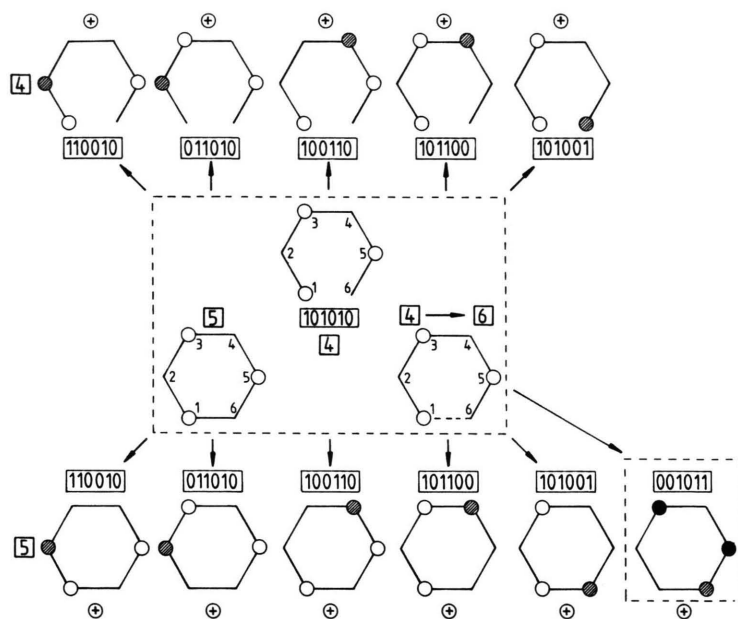
Fig. 2. Nearest-neighbour π electron jumps in one spin direction of hexatriene **4** and benzene **5** starting from the configuration portrayed in the center of the display. Right to benzene we have symbolized the "transition state" of the intramolecular cycloaddition from hexatriene to cyclohexadiene **6**. See legend to Figure 1.

the π energy of one spin direction. Note that the two spin spaces are decoupled here [1, 2]. In theoretical approaches, where the electron-electron interaction is taken into account, the off-diagonal hopping matrix is supplemented by the two-electron part which is diagonal for an interaction of the density-density type. The analytic structure of these matrix elements has been described in a recent article of one of us [22]. In butadiene **1** we have 12 non-zero entries in Table 1. As emphasized above all contribute with a prefactor "+" as the electronic ordering is conserved throughout (elimination of the influence of the PAP). Four additional non-zero entries due to the terminal 1 ↔ 4 processes occur in the cyclobutadiene example **2** (Table 1b). The prefactor "−" is a consequence of the PAP ($pf_{PAP} = -$). To reemphasize; the π electron wave functions of polyenes and $4n$ annulenes differ with respect to their sign behaviour in the nearest-neighbour hoppings. In polyenes no minority signs due to odd permutations are found. Such minority elements, however, occur in $4n$ annulenes.

On the basis of the results of Fig. 1 and Table 1 we have suggested a quantum statistical definition of antiaromaticity [3 - 5]. In $4n$ and $(2n + 1)$ annulenes antiaromaticity is an outcome of Pauli antisymmetry constraints in the electronic wave function. Remember that the PAP forces a negative pf_{PAP} in the matrix of the hoppings whenever a π electron move is accompanied by an odd number of permutations within the given spin direction. The resulting "antiaromatic

destabilization energy" can be measured by the so-called fermionic energy loss which is the energy difference between the electronic energy of the conventional fermionic ensemble and of an ensemble where the PAP has been suppressed. Of course it is possible to adopt this quantum statistical definition of antiaromaticity also for π molecules of other cyclic topologies. With increasing complexity of the molecular structure (i. e. central bonds in polycyclic molecules, exocyclic π fragments, etc.) other types of transfer processes are feasible which are accompanied by an odd number of interchanges. In these molecules the antiaromatic destabilization energy is even larger than the one of an isoelectronic $4n$ anti-Hückel system. For further details we refer to our recent discussion [4, 5]. Nevertheless let us give a concise comment to clarify the relation between a node in the π electronic wave function due to minority hoppings and antiaromatic destabilization. A node in the wave function leads to a reduced spatial uncertainty of the electrons which become more localized. According to the Heisenberg uncertainty principle this reduced spatial uncertainty implies an enhanced momentum uncertainty, i. e. larger momenta of the electrons become of higher probability. They raise the electronic energy. To recapitulate, antiaromaticity can be traced back to an enhanced localization of the π electrons in cyclic molecules under the influence of the PAP.

A second polyene-annulene pair we consider is hexatriene **4** and benzene **5**. In Fig. 2 we have dis-

played all nearest-neighbour moves within one spin direction when starting from the initial configuration 101010 which is given in the center of the diagram. In total 20 of these three-electron configurations per spin direction of hexatriene and benzene can be formed. In hexatriene **4** five nearest-neighbour moves occur. They lead to the following final configurations 110010, 011010, 100110, 101100, 101001 which are reached under conservation of the electron ordering. By analogy with the 4π electron pair in Fig. 1 one additional nearest-neighbour jump is possible in the cyclic system **5**. In benzene, however, the terminal 1 $\rightarrow$ 6 jump is accompanied by an even number of permutations p (= 2) as the two electrons at centers 3 and 5 have been passed by the transferred electron. But any even number of electronic permutations p leads to a positive pf$_{PAP}$ element in the hopping matrix. So, the PAP does not act as an electronic constraint. In contrast to terminal 1 $\leftrightarrow$ 4 processes in cyclobutadiene **2** the 1 $\leftrightarrow$ 6 processes in benzene **5** are stabilizing. $(4n + 2)$ annulenes and polyenes coincide in so far that their hopping matrix is free of non-zero elements with a minority sign; all hoppings are stabilizing. Nevertheless they differ in their electronic localization properties. In polyenes one has a topological localization of the π electrons at the terminal atoms which is absent in cyclic molecules [4, 5]. The quantum statistical peculiarities of $(4n+2)$ annulenes (= suppression of the PAP, absence of topological localization centers) motivated us to suggest a microscopical definition of aromaticity which is the pendant of our quantum statistical definition of antiaromaticity given above. From a quantum statistical point of view aromaticity can be identified with a suppression of the influence of the PAP in cyclic π systems. In molecules where the PAP is suppressed completely the quantum statistics of the electronic ensemble is of a mixed type. It has conventional fermionic character for the intraatomic part of the electronic interaction. This is guaranteed by the PEP. But the quantum statistics is bosonic with respect to the interatomic interaction. Note that the PAP is then a hidden variable only. The quantum statistics of these mixed ensembles has been discussed in some detail in theoretical physics [30]. The corresponding quantum particles each having a spin of 1/2 are denoted as hard core bosons (hcb). We have adopted this label as descriptor of some π systems [3 - 5].

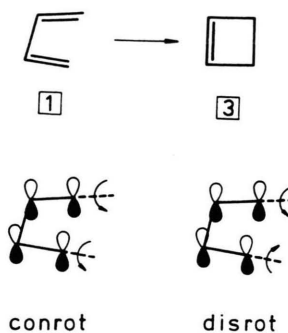On the basis of the above arguments it is straightforward to rationalize pericyclic reactions quantum

Fig. 3. Schematical representation of the disrotatory and conrotatory rotation of the two methylene groups of cis-butadiene **1** in the intramolecular cycloaddition to cyclobutene **3**.

statistically. The schematical representations in Figs. 1 and 2 as well as Table 1 indicate that some elements we are using have their origin in the classical VB theory. In this context we wish to point out that a VB analysis of pericyclic reactions has been published already at the end of the sixties [31]. But the PA-based "sign problem" has not been commented in this work. We first consider the intramolecular cycloaddition of (cis-)butadiene **1** to cyclobutene **3**; see Figure 3. All information that is required to interpret this reaction quantum statistically has been given already in Fig. 1 and Table 1. In the transition state **1** $\rightarrow$ **3** terminal 1 $\leftrightarrow$ 4 moves contribute to the wave function, i. e. they are taken into account via non-zero entries in the kinetic hopping matrix. In butadiene they do not. For the intramolecular cycloaddition two coupled methylene rotations have to be discriminated, i. e. the disrotatory and conrotatory ring closure; for the definition see Figure 3. Both cyclobutadiene **2** and the transition state **1** $\rightarrow$ **3** for the disrotatory ring closure show the same distribution of pf elements in the hopping matrix (Table 1b). The matrix elements of both systems differ only in magnitude. The disrotatory transition state **1** $\rightarrow$ **3** is antiaromatic. Remember that this notion symbolizes the influence of the PAP on the terminal electron moves. We wish to point out that the prefactor "–" in Fig. 1 and Table 1b is an electronic ensemble effect caused by the PAP (pf$_{PAP}$ = –); it is not a basis integral effect: pf$_{BI}$ = +, because the two AOs at the cerminal atoms overlap in-phase in the case of the disrotatory move. So, in the many-electron basis of atomic occupation numbers adopted in the present work the intramolecular cycloaddition of butadiene **1** to cyclobutene **3** would transfer a π electron wave function of the reactant

without minority hoppings into a transition state wave function with minority hoppings if the reaction takes place via the disrotatory route. In course of the reaction the transferred electrons (= electrons performing terminal moves) would feel a constraint due to the PAP which is absent in the educt wave function. Consequently the disrotatory reaction $1 \rightarrow 3$ is forbidden in the electronic ground state. It is however allowed in the excited state as the nodal structure of the transition state wave function correlates with the nodal structure of the wave function of the excited reactant. Please note that the excited state of a nodeless ground state has at least one node.

We next consider the conrotatory reaction path $1 \rightarrow 3$. The non-zero entries in the corresponding hopping matrix are given in Table 1c. As can be seen the $1 \rightarrow 4$ hoppings in the transition state contribute with the same prefactor "+" as all other elements. For the conrotatory route the negative sign of the four $1 \rightarrow 4$ elements due to the PAP (= ensemble effect, $pf_{PAP} = -$) is compensated by the negative sign of the corresponding overlap integral (= basis integral effect), i.e. the π-type AOs at centers 1 and 4 overlap out-of-phase ($pf_{BI} = -$). The conrotatory route of the cycloaddition $1 \rightarrow 3$ conserves the nodeless structure of the educt wave function in the transition state. The reaction is thus allowed in the electronic ground state. By analogy with $(4n + 2)$ Hückel annulenes the PAP is a hidden variable in this intramolecular cycloaddition. The transition state is aromatic. It is clear that the phenomenological DZ rules [10 - 14] have a well-defined microscopical (= quantum statistical) origin. The notion of Dewar and Zimmermann (= aromatic transition state) can be identified with a quantum statistical peculiarity of π systems, i.e. the possibility to suppress the influence of the PAP under certain conditions. Let us next correlate the present approach with the WH rules [15,16]. Woodward and Hoffmann have shown that the shape of orbital correlation diagrams for intramolecular cycloadditions is determined by the symmetry of the highest occupied molecular orbital (HOMO) of the reactant. In cis-cyclobutadiene it is of a_2 symmetry. Its node would yield a negative (= out-of-phase) overlap between the terminal AOs for the disrotatory route while the conrotatory process leads to an in-phase overlap. We have the situation that the number of nodes in the butadiene HOMO with respect to the mirror plane cutting the central bond (one node) coincides with the number of permutations ($p = 1$) of the π electrons of one spin direction accompany-

ing terminal $1 \leftrightarrow 4$ moves; i.e. the orbital picture of WH and the present many-electron approach lead to the same conclusion. In contrast to the WH rules symmetry considerations do not enter our quantum statistical classification of pericyclic reactions. The only descriptor employed in the present approach is the number of electronic permutations per spin direction. Therefore the same explanation as developed for the intramolecular cycloaddition of butadiene 1 is valid for isovalent molecules of lower symmetry. For such systems the consideration of symmetry arguments cannot be justified a priori. By analogy with the WH rules the present concept can be applied to synchronous reactions only. The validity of an orbital picture, however, is not required. In this context it is of some interest to point out that the many-electron basis in the occupation number representation coincides with a simple one-electron model if the (diagonal) two-electron part of the π Hamiltonian is set equal to zero. In this case π electronic effects are determined by the one-electron hopping only. This flexibility of the occupation number representation has been discussed in our recent papers [2, 3].

Let us reconsider Table 1c, i.e. the prefactors pf encountered in the hopping part of the Hamiltonian for the conrotatory cycloaddition $1 \rightarrow 3$. The hopping matrix coincides with the cyclobutadiene hoppings in a Möbius-type arrangement. The "+" entries indicate that Möbius rings with a π electron count of $4n$ are aromatic. $(4n + 2)$ Möbius rings, however, are antiaromatic. For a discussion of Möbius topologies in annulene systems we refer to the literature [32]. It is well-known that Hückel-type resonance integrals t_H and the associated Möbius-type values t_M of neutral $4n$ electron rings behave as $t_M = \cos(\pi/M)t_H$ ($M =$ number of π centers). This formula expresses the reduced interatomic sharing in Möbius-type topologies in comparison to Hückel-type arrangements.

The generalization of the intramolecular cycloaddition $1 \rightarrow 3$ to higher polyenes is very simple. Polyenes with an even number of "CC double bonds" (= π electron count of $4n$) reproduce the butadiene behaviour as all electron moves between the terminal atoms in the transition state are accompanied by an odd number of permutations per spin direction. In combination with a disrotatory move ($pf_{BI} = +$) this leads to a PA-based minority sign in the hopping matrix ($pf_{PAP} = -$) in the electronic wave function of the transition state. The reaction is forbidden in the ground state but allowed in the excited state; vice versa for conrotatory
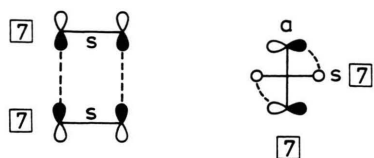
Fig. 4. Schematical representation of the suprafacial (s) and antarafacial (a) participation of a π system in cycloaddition reactions. Two ethylene molecules **7** are chosen to visualize the two stereochemistries.
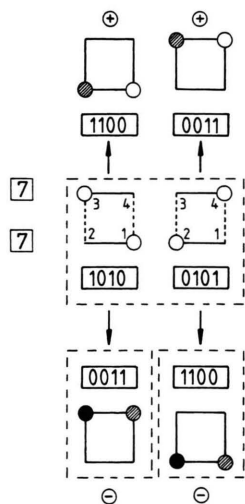

Fig. 5. Intermolecular π electron jumps in two weakly coupled ethylene molecules **7** starting from the two configurations (particle-hole pair) displayed in the center of the diagram 1010 and 0101. Four jump processes are possible. Note the analogy with the cyclobutadiene example in Figure 1. See legend to Figure 1.

processes. In polyenes with an odd number of "CC double bonds" (= π electron count of $(4n+2)$), see the hexatriene example **4** in Fig. 2, the terminal π electron jumps lead to an even number of permutations per spin direction ($p = 2$ in the hexatriene case). The PAP is a deactivated variable ($pf_{PAP} = +$). Now the ground state reaction can take place via the disrotatory route and the excited state reaction via a conrotatory route.

The quantum statistical classification of π systems which has been explained in detail for intramolecular cycloadditions, can be adopted for any other pericyclic reaction as well. We consider the (2+2) cycloaddition of two ethylene molecules **7**. Let us start with the suprafacial approach of the two π systems. See Fig. 4 for the definition of suprafacial (s) and antarafacial (a) processes [16]. To understand the influence of the PAP on the stereochemistry of this reaction

in the ground state we move to Fig. 5 where we have shown two initial configurations in one spin direction of two "weakly coupled" ethylene molecules (center of the diagram). One configuration reads 1010, the other 0101 (= particle-hole pair). From both initial configurations two intermolecular π electron jumps are possible. The processes which lead to the final (= product) configurations in the top row of the diagram are not accompanied by any permutations; they are not influenced by the PAP. The intermolecular moves, however, which yield the "product" configurations in the bottom row, are accompanied by one permutation ($pf_{PAP} = -$). By analogy with the intramolecular cycloaddition **1** → **3** via the disrotatory route a nodeless educt wave function of two ethylenes would be transferred into a transition state wave function which has a node if both ethylenes participate in suprafacial manner. So the suprafacial (2+2) cycloaddition (= $4n$ electron process) is forbidden in the ground state. The prefactors "–" in the hopping matrix due to the PAP, however, can be compensated by a negative phase (= out-of-phase overlap of the AOs) in the basis integral ($pf_{BI} = -$) if one ethylene molecule participates as antarafacial component; see Figure 4. In the terminology of Woodward and Hoffmann [16] this cycloaddition is denoted as $\left[\pi_s^2 + \pi_a^2\right]$. This process is allowed in the ground state. In cycloadditions with a net π electron count of $4n$ two processes are possible in the excited state: $\left[\pi_s^2 + \pi_s^2\right]$ and $\left[\pi_a^2 + \pi_a^2\right]$. We wish to point out however, that an unequivocal experimental support for a concerted $\left[\pi_s^2 + \pi_a^2\right]$ reaction is missing still. Although allowed in the electronic ground state the spatial constraints of this reaction seem to be rather large.

Intermolecular electron jumps occuring in $(4n+2)$ Diels-Alder reactions are not accompanied by an odd number of permutations. This is shown schematically in Fig. 6 where we have symbolized the intermolecular moves accessible in the configurations 101010 and 010101 of the butadiene-ethylene system. We have two processes which are permutation-free; they lead to the product configurations displayed in the top row. The other two moves are accompanied by two permutations (bottom line of Figure 6). Note the difference to the particle-hole pair symbolized in Figure 5. The comparison of Figs. 1 and 5 on the one hand and 2 and 6 on the other shows the quantum statistical similarities between $4n$ annulenes and $4n$ cycloadditions as well as between $(4n + 2)$ annulenes and $(4n + 2)$ cycloadditions. $(4n + 2)$ cycloadditions conserve the
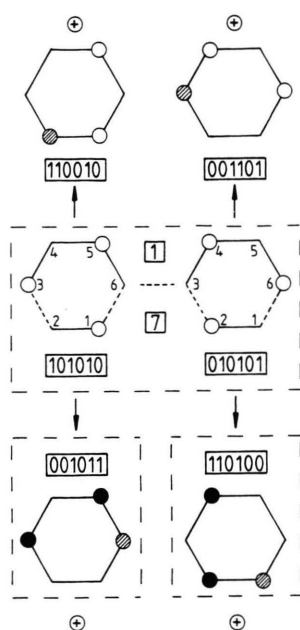
Fig. 6. Intermolecular π electron jumps in the Diels-Alder reaction of butadiene **1** and ethylene **7** starting from the two configurations (particle-hole pair) shown in the center of the diagram 101010 and 010101. Four jump processes are possible. Note the analogy with the benzene example in Figure 2. See legend to Figure 1.

Fig. 7. Cope rearrangement via a chair or boat transition state. Top and bottom arrangement of two allyl units in the middle of the diagram.

nodeless educt wave function in the transition state if both components contribute in suprafacial manner. This reaction is allowed in the electronic ground state. There is also no change in the nodal structure of the wave function of the educts in the transition state if both π molecules contribute as antarafacial components. $(4n + 2)$ cycloadditions in the excited state occur via a transition state with one suprafacial and one antarafacial component.

As last example we discuss the transition state encountered in the Cope rearrangement symbolized in Figure 7. The chair transition state structure has been verified experimentally [33] and has been explained theoretically by the DZ and WH rules [16,17]. Dewar and Zimmermann have argued that the chair form is reminiscent of an aromatic structure while the boat form resembles an aromatic one. Woodward and Hoffmann have used an orbital correlation diagram which shows a correlation between an occupied MO of the educt and a virtual MO of the product when both are interconverted via the boat form. By analogy with the examples discussed above knowledge of the MOs is
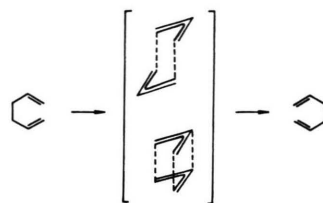
not necessary to explain the stereochemical course of the reaction. "Intermolecular" electron jumps of the 1 $\leftrightarrow$ 6 type are either permutation-free or accompanied by an even number of permutations. Note the analogy with the benzene molecule in Fig. 2 and the butadiene-ethylene pair in Figure 6. Then the nodeless character of the educt wave function is conserved in the transition state. There are no electronic constraints due to the PAP. These 1 $\leftrightarrow$ 6 processes occur both in the chair and boat transition state. In the chair form they are the only "intermolecular" contacts. Electronic moves over the central "intermolecular" contact in the boat form of the transition state configuration (= 1 $\leftrightarrow$ 4 processes), however, cause a prefactor "–" in the hopping matrix and thus a PA-based electronic destabilization ($pf_{PAP} = -$). Under these circumstances the transition state wave function is not nodeless. In order to attenuate this PA-based destabilization in a reaction one expects a transition state with a large interatomic separation between the atoms 1 and 4. Without quantitative calculation it is difficult to estimate the energy difference between both reaction routes. In any case we expect an higher activation energy in the boat form. But it is also well-known that the boat transition state can be stabilized in strained substrate molecules like semibullvalenes [34]. This example shows that topological and electron count criteria may be overrided by other factors. These may be both geometrical constraints and increasing geometrical flexibilities in large molecules. Finally let us mention the formal analogies between antiaromatic $4n$ annulenes or $4n$ cycloadditions and the boat structure of the transition state in Figure 7. To summarize, it is again the PAP which controls the stereochemistry of the Cope rearrangement symbolized in Figure 7.

4. Final Remarks

In the present contribution we have demonstrated that synchronous pericyclic reactions are controlled

by the Pauli antisymmetry principle (= number of electronic permutations per spin direction accompanying the hopping processes). Pericyclic reactions are allowed in the electronic ground state whenever the PAP (= intersite constraint) has the character of a hidden (= suppressed) variable. In this case the electronic degrees of freedom are restricted only the the Pauli exclusion principle (= on-site constraint) as quantum constraint and by topological factors. The suppression of the influence of the PAP on π electronic properties does not become evident in the majority of quantum chemical methods. We were able to recognize this influence by performing many-electron calculations of π systems in the basis of an atomic occupation number representation. In course of our work we have suggested quantum statistical definitions of aromaticity and antiaromaticity. The π electrons in aromatic compounds do not feel the influence of the PAP. In antiaromatic compounds the PAP has a strong influence. It leads to a suppression of the electronic delocalization and thus to an energetic destabilization.

To relate the present quantum statistical analysis of pericyclic reactions to the popular models described in the literature we have chosen examples which have been discussed in large detail. We are convinced that it is the PAP which is a hidden key-parameter in the DZ and WH approaches to pericyclic reactions. The aromatic transition state which has been adopted as descriptive label in the DZ model has its microscopical origin in the suppression of the influence of the PAP. This suppression requires an even number of electronic permutations or the conservation of the electron ordering in the transition state. Then the nodeless wave function of the educts is conserved in the transition state. A correlation of the present approach with the WH rules has shown the following. According to the Woodward-Hoffmann rules a pericyclic reaction is allowed if the orbital symmetry is conserved. This "orbital conservation" has a quantum statistical pendant in the conservation of the number of

electronic permutations per spin direction in the reactants and the transition state. The large success of the simple orbital model of Woodward and Hoffmann may have the following origin: The determinantal form of the electronic wave function guarantees the simultaneous consideration of the PAP and PEP. CI effects beyond the one-electron approximation do not contain any phase information as long as the interaction is of the density-density type, so they are of minor importance in comparison to a dominant effect due to the PAP. Simply speaking, in the case of one-electron Hamiltonians the influence of the PAP on the hoppings is not filtered. It is filtered in the Hartree-Fock approximation with its mean-field potential and in CI methods with correlated electrons. Under the premisis that pericyclic reactions are controlled by the PAP, the remarkable success of orbital models of the WH type is comprehensible. In our theoretical setup, however, orbital symmetry arguments (= group theoretical constraints) are not necessary.

Above we have given a quantum statistical classification of π systems in non-numerical form. It has been our intention to provide a general explanation of pericyclic reactions which is decoupled from any details of the methods of computational chemistry. As already poined out in [1 - 5], there is no specific Hamiltonian needed to obtain these results.

[1] J. Schütt, J. Schulte, M. C. Böhm, and Z. G. Soos, Mol. Phys. **84**, 1127 (1995).
[2] J. Schütt and M. C. Böhm, Mol. Phys. **85**, 1217 (1995).
[3] J. Schütt and M. C. Böhm, Phys. Lett. A **219**, 79 (1996).
[4] M. C. Böhm and J. Schütt, Phys. Lett. A **232**, 105 (1997).
[5] M. C. Böhm and J. Schütt, Z. Naturforsch. **52a**, 717 (1997).
[6] M. J. S. Dewar and C. deLlano, J. Amer. Chem. Soc. **91**, 789 (1969).
[7] B. A. Hess and L. J. Schaad, J. Amer. Chem. Soc. **93**, 205 (1971).

[8] B. A. Hess and L. J. Schaad, J. Org. Chem. **36**, 3418 (1971).
[9] E. Hückel, Z. Physik **76**, 628 (1932).
[10] M. G. Evans, Trans. Faraday Soc. **35**, 824 (1939).
[11] M. J. S. Dewar, Tetrahed., Suppl. 8, Part I, 75 (1966).
[12] M. J. S. Dewar Angew. Chem. **83**, 859 (1971).
[13] H. E. Zimmermann, J. Amer. Chem. Soc. **88**, 1564 (1966).
[14] H. E. Zimmermann, Acc. Chem. Res. **4**, 272 (1971).
[15] R. B. Woodward and R. Hoffmann, J. Amer. Chem. Soc. **87**, 395, 2046, 2511 (1965).
[16] R. B. Woodward and R. Hoffmann, Die Erhaltung der Orbitalsymmetrie, Verlag Chemie, Weinheim 1972.
[17] N. Trong Anh, Die Woodward-Hoffmann Regeln und ihre Anwendung, Verlag Chemie, Weinheim 1972.
[18] A. V. Bellamy, An Introduction to Conservation of Orbital Symmetry – A Programmed Text, Longmans, London 1974.
[19] E. A. Halevi, Orbital Symmetry and Reaction Mechanism, Springer, Berlin 1992.
[20] M. A. Lee, K. A. Motakabbir, and K. E. Schmidt, Phys. Rev. Lett. **53**, 1191 (1984).
[21] W. von der Linden, Phys. Rep. **220**, 53 (1992).
[22] M. C. Böhm, J. Schulte, and L. Utrera, Mol. Phys. **79**, 1239 (1993).

[23] B. L. Hammond, W. A. Lester, and P. J. Reynolds, World Scientific Notes in Chemistry – Vol. 1, Monte Carlo Methods in ab initio Quantum Chemistry, World Scientific, Singapore 1994.
[24] J. B. Anderson, in: Understanding Chemical Reactivity: Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy, S. R. Langhoff (ed.), Kluwer, New York 1995.
[25] Z. G. Zoos and S. Ramasesha, Phys. Rev. B **29**, 5410 (1984).
[26] S. Kuwajima and Z. G. Soos, J. Amer. Chem. Soc. **109**, 107 (1987).
[27] K. Ruedenberg, Rev. Mod. Phys. **34**, 326 (1962).
[28] M. J. Feinberg, K. Ruedenberg, and E. L. Mehler, Adv. Quantum Chem. **5**, 27 (1970).
[29] D. J. Klein, Pure Appl. Chem. **55**, 299 (1983).
[30] E. Fradkin, Field Theories in Condensed Matter Systems, Addison-Wesley, New York 1991.
[31] W. T. A. M van der Lugt and J. Oosterhoff, J. Amer. Chem. Soc. **91**, 6042 (1969).
[32] E. Heilbronner, Tetrahedron Lett. 1923 (1964).
[33] W. von E. Doering and W. R. Roth, Tetrahedr. **18**, 67 (1962).
[34] N. L. Allinger, M. P. Cava, D. C. de Jongh, C. R. Johnson, N. A. Lebel, and C. L. Stevens, Organische Chemie, de Gruyter, Berlin 1980.