On a Direct Superconducting Pairing Mechanism

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Dedicated to Prof. Dr. Helmut Witte on the Occasion of his 90th Birthday

We suggest that superconductivity can be traced back to a first-order interaction between the charge carriers which does not necessarily involve second-order electron-phonon coupling. For small molecular model systems it is demonstrated that the formation of Cooper pairs can lead to an attenuation of the destabilizing influence of the Pauli antisymmetry principle (PAP). We suggest that this attenuation of a fermionic quantum constraint is the driving force for the superconducting transition. Whenever the PAP is activated in single-particle hoppings of electrons, the corresponding moves reduce the electronic delocalization; they raise the ensemble energy. The stability of a fermionic system is enhanced with decreasing influence of the PAP. Moves of Cooper pairs are not influenced by any quantum constraint of the intersite type. This behaviour differs from the well-known fermionic constraints. The quantum statistics of Cooper pairs is of a mixed type combining a fermionic on-site and a bosonic intersite behaviour. It coincides with the quantum statistics of so-called hard core bosonic ensembles. In the present work Cooper pair formation has been studied for smaller molecular models. The electronic Hamiltonian employed is of the two-parameter Hubbard-type. The solid state phenomenon superconductivity is correlated with the molecular concepts of "antiaromaticity" and "aromaticity". Arguments are given which support the present interpretation.

Key words: Superconductivity; Possible First-Order Pairing Interaction; Quantum Statistics; Pauli Antisymmetry Principle; Superconductivity vs. Antiaromaticity and Aromaticity.

1. Introduction

Superconductivity is one of the most fascinating and challenging low-temperature properties of solids [1, 2]. But despite many years of intensive theoretical efforts is it impossible still to predict whether a material will be superconducting or not at low temperatures by measuring its physical properties at high temperatures. A priori attempts to estimate the magnitude of the superconducting transition temperature T_c on the basis of measurements or calculations of normal-state properties have remained unsuccessful as well. It seems to be an irony that rough estimates of transition temperatures are feasible only if T_c has been measured before it has been calculated. In other words, theoretical evaluations of T_c numbers published so far, are of bare a posteriori character. Since the middle of the 1950s it is quite generally believed that the superconducting pairing is caused by a second-order interaction, i. e. the phonon-mediated coupling between electrons [3 - 5]. The theoretical derivation of the electron-phonon coupling mechanism by Bardeen, Cooper, and Schrieffer (BCS) has been guided strongly by the measured isotope dependence of T_c [3 - 5]. For a rather long time systematical theoretical research on alternative pairing mechanisms including first-order interactions between the charge carriers has been an exception. In the present work we have adopted the label "first-order interaction" to denote all expectation values provided by the electronic Hamiltonian.

Several new families of non-conventional superconductors have been characterized in the past two decades. For the majority of these new super-

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conductors it is generally believed that the BCS electron-phonon coupling is unapplicable. Examples of such non-conventional superconductors are organic charge-transfer (CT) salts, high-T_c cuprates, non-cuprate oxides such as BaKBiO or BaPbBiO as well as alkali- and alkaline-earth-doped fullerides. We are confronted with the problem that one or even more new pairing mechanisms in addition to the BCS electron-phonon coupling are required to explain the properties of all families of superconducting materials. It is not necessary, however, to quote these families of non-conventional superconductors in order to recognize the conceptual problems and several inconsistencies of the BCS theory. It is known that this approach even has difficulties to explain experimental observations in conventional superconductors. Some of these problems are mentioned below.

In many conventional superconductors [1, 2] it has been found that the measured isotope dependence of T_c differs from the expectations of the BCS theory. Such differences between experiment and theorerical expectations have been found in high-T_c cuprates as well [6]. Matthias has established an empirical rule according to which the magnitude of T_c depends on the average number of valence electrons per atom [7 - 9]. Although such regularities have been verified in a large number of compounds, they never have been rationalized convincingly within the BCS theory of superconductivity. Other deficits of the BCS approach become evident when considering measurements of the Hall coefficient. Experimentally it has been found that the pairing in the majority of superconductors is due to holes [10 - 12]. Again this behaviour has not been explained within the BCS theory. Finally we want to mention that superconductivity is not restricted to crystalline solids [1, 2]. Amorphous superconductors have been described in detail. In contrast to this variety in the morphology of superconducting solids, the BCS electron-phonon approach has been derived for crystalline materials only, where the wave vector $\boldsymbol{k}$ is a well-defined quantum number. The shape of Fermi surfaces is a key-element of the BCS model [3 - 5].

Doubts on the validity of the electron-phonon second-order coupling in conventional superconductors are supported strongly by a recent study of Hirsch [13]. On the one hand this author has demonstrated that properties assumed to be important within the BCS approach rank lowest in the predictive power regarding whether a material is a superconductor or not. On the other hand, Hirsch has shown that properties which are irrelevant in connection with the electron-phonon coupling, exhibit the highest predictive power in this respect. In Fig. 1 we have reviewed the basic results of [13]. This diagram visualizes the degree of association of normal-state properties with superconductivity, here measured by the Kolmogoroff-Smirnoff index D which covers a range from 0 to 1. $D = 0$ refers to complete statistical independence while $D = 1$ represents complete statistical dependence of the attributes. Figure 1 is a slightly modified version of Fig. 15 of [13]. It shows that quantities such as the Debye temperature T_D, the electronic specific heat or the electrical conductivity, which are important within the BCS theory, rank rather low in their degree of association with superconductivity. A quantity such as the Hall coefficient, however, is the normal state property that is by far the most closely related to the existence or nonexistence of superconductivity. [13] can be considered as a focus in which the limitations of the BCS theory become noticeable most clearly. Guided by comprehensive results derived from a statistical point of view, Hirsch has suggested to call into question electron-phonon theories of superconductivity. We wish to point out that conventional elemental superconductors have been studied in [13].

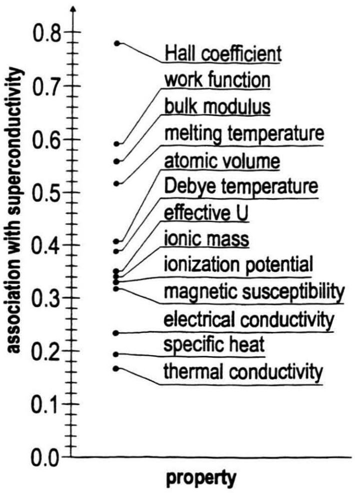

Fig. 1. Degree of association of normal-state properties with superconductivity as measured by the Kolmogoroff-Smirnoff index D. The data have been taken from [13]. They have been sampled over 44 metallic elements.

On the basis of the above information one can understand the theoretical attemps over the past years to suggest alternative superconducting pairing mechanisms [14 - 22]. When compared with the number of studies based on the BCS formalism, these non-BCS approaches are by far in the minority. In some of these models the electron-phonon coupling has been accepted as one component of the pairing interaction. Other models have favoured a direct first-order interaction under exclusion of second-order effects such as the electron-phonon coupling. We cannot summarize all non-BCS pairing mechanisms in detail which have been suggested in the past. Nevertheless we want to mention the rather popular resonating valence bond (VB) models developed for high-T_c materials, excitonic mechanisms, spin wave formalisms and approaches favouring hole pairing. In this context several theoretical contributions are of particular interest where the superconducting pairing has been correlated with a fractional quantum statistics intermediate between a bare bosonic (b) and a bare fermionic (fe) statistics [23 - 26]. The quantum particles, which obey the fractional statistics of [23 - 26], are denoted as "anyons" [27, 28]. Anyon superconductivity and its relation to the fractional quantum Hall effect has been studied in [29].

It is the purpose of the present contribution to discuss the influence of the Pauli antisymmetry principle (PAP) on the superconducting transition and to suggest possible direct electron-electron or hole-hole interactions as pairing mechanisms. An early suggestion of a bare electronic pairing interaction in low-dimensional solids with special molecular topologies has been reported already in the 1960s [30]. Our approach should be accepted as a first step towards a possible first-order pairing mechanism and not as a closed theory where all aspects of superconductivity have been treated and clarified finally. We hope that our impetus may be helpful to understand experimental facts such as the empirical findings of Matthias [7 - 9] or the preference of hole superconductivity [10 - 12]. In this first presentation of our theory we have accepted simplifications and idealizations in order to facilitate a transparent derivation of the basic ideas. Thus we have chosen small model clusters for the numerical calculations and an electronic Hamiltonian with a simple setup. The computational results discussed in Sect. 5 have been derived in the framework of the two-parameter Hubbard Hamiltonian where the nearest-neighbour matrix elements t and t' compete with the two-electron on-site repulsion U [31, 32]. In the present study we have adopted the label t to denote the nearest-neighbour hoppings of the single-particle type, while t' is associated to the superconducting pairs. We suggest to identify t' with a correlated pair hopping; see below for further details. With the theoretical tools employed in this work, calculations of T_c numbers of superconducting materials are not feasible. We hope that it will be possible in future investigations to enhance both the theoretical and computational effort of our approach.

In analogy to the quantum statistical publications cited above [23 - 26] we have employed elements of quantum statistics to discuss the driving force for the superconducting pairing. In the derivation of the present theory we have used the experience, one of us has gained in electronic structure investigations of π systems under special consideration of quantum statistical problems [33 - 36]. In these contributions we have analyzed the quantum constraints experienced by a fermionic ensemble as a function of the electron count and the molecular topology. In a many-electron basis of atomic occupation numbers, the fermionic quantum constraints decompose into a formal on-site and a formal intersite constraint. The on-site (= diagonal or density-density) constraint can be equated with the Pauli exclusion principle (PEP) and the intersite (= off-diagonal or hopping) constraint can be equated with the Pauli antisymmetry principle. In our recent works we have demonstrated that fermionic intersite constraints can be attenuated and even suppressed by a constructive interference between electron count and molecular topology [33 - 36]. If the PAP influence is suppressed completely, the conventional fermionic statistics of electron systems coincides with a mixed quantum statistics which is characterized by fermionic on-site and bosonic intersite properties. We have used the descriptor hard core bosons (hcb) [37] to denote the quantum particles of such mixed ensembles. A quantum statistics of the hcb type in electronic structure problems occurs in the absence of interatomic hopping processes with an odd number of permutations p per spin direction [33 - 36]. The PAP is neither activated for hoppings under conservation of the electron ordering per spin direction ($p = 0$) nor for hoppings with p = even. The idea of a mixed quantum statistics in electronic ensembles goes back to the 1920s where Jordan and Wigner have analyzed the statistical peculiarities of electrons in a line, i. e. electronic systems with one-dimensional (1D) ordering [38]. Here the PEP prevents any electronic interchanges within one spin direction.

In [23 - 26] prerequisites have been studied which allow to rewrite the conventional "integral" quantum statistics of electronic systems with the two phases +1 and –1 in terms of the fractional quantum statistics of anyons. In the case of neutral annulenes with a π electron count of $4n$ (n = 1, 2, 3,...) we have shown that the integral phases +1 and –1 with a ratio $(4n - 1)/1$ can be replaced by a common fractional phase factor $\cos(\pi/4n)$ in the derivation of the π electron energy [39, 40]. When preparing [39, 40] we have been unaware of the publications on the fractional statistics of anyons [23 - 26].

Next we should mention that the commutator-anticommutator relations for the quantum particles of hcb ensembles [34, 36, 38] exhibit surprising similarities with the commutator-anticommutator relations of Cooper pairs [41]. The quantum statistical properties of superconducting pairs have been investigated by Bardeen, Cooper, and Schrieffer [4, 5] as well as by Anderson [42, 43]. Unfortunately it seems that these authors have been unaware of the findings of Jordan and Wigner [38] who emphasized the peculiarity of a mixed quantum statistics of electrons in a line. Below it will be shown that some knowledge of the mixed quantum statistics of hcb ensembles is useful for the understanding of the superconducting pairing. In the most general case the quantum statistics of Cooper pairs does not depend on the details of the pairing mechanism. The quantum statistics discussed in connection with the electron-phonon coupling of the BCS theory [3 - 5] coincides with the statistics of the present pairing interaction. For reasons of completeness we should mention that a bare bosonic statistics of the pairs in superconductors has been suggested by Schafroth, Butler, and Blatt [44 - 46]. But then one would expect a Bose-Einstein condensation with all "bosons" in the lowest state. However, such processes do not occur in the superconducting transition.

Let us come back to our recent theoretical contributions on quantum statistical peculiarities of π electron systems where we have shown that the popular molecular concepts of "aromaticity" and "antiaromaticity" [47, 48] can be traced back to a quantum statistical origin [35, 36]. Aromaticity is caused by the absence – or at least by an attenuation – of fermionic intersite constraints (= suppression of the PAP influence) in molecules with cyclic topologies. Antiaromaticity is an outcome of large fermionic intersite constraints (= large influence of the PAP) in cyclic systems. In the present study we demonstrate that the molecular concept of antiaromaticity and partially also the concept of aromaticity can be correlated with the solid state property superconductivity. A possible interrelation between aromaticity and antiaromaticity, on the one hand, and superconductivity, on the other, had been mentioned briefly by F. London already in the 1930s [49]. However, it has been a pity that this stimulating idea has been reconsidered neither by London in later articles nor by other scientists.

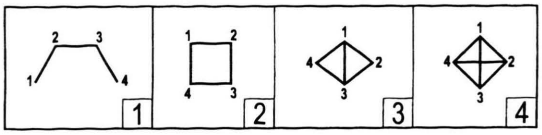

Fig. 2. Molecular graphs of the four-center systems **1** to **4** investigated in the present work. The atomic numbering scheme employed in the theoretical calculations has been given for each network. All systems have been studied for an overall electron count m of two, four and six.

We have given this rather detailed introduction in order to illuminate the disperse background of the present research and to touch upon interrelations between phenomena and properties which have not been recognized in the past. In the following it will be explained that such interrelations might be decisive for the understanding of the phenomenon of superconductivity. The model systems adopted in the numerical simulations have been portrayed in Figure 2. We have chosen four-center problems which have been studied in many electronic structure investigations of π systems. Only one atomic orbital (AO) per center has been taken into account in the Hubbard-like calculations of Section 5. The topology of butadiene **1** simulates 1D order. Note that the two-parameter Hubbard Hamiltonian in connection with the tight-binding approximation does not discriminate between cis and trans configurations of polyenes. As mentioned above, the PEP prevents electronic interchanges within one spin direction in the case of 1D ordering. Hopping processes, which are accompanied by changes of the electron ordering, are accessible in the other model systems **2**, **3**, and **4**. In the present work we have studied the molecules **1** to **4** with an electron count m of two, four and six (formal dications, neutral species and dianions in the terminology of chemists). This choice of finite electron systems implies that we can study only the "molecular" precursor effects of the collective property superconductivity. In the following discussion we adopt the term "superconducting" both for these molecular precursor effects as well as for the thermodynamic limit.

At the end of the introduction we want to reconsider the experimentally observed isotope dependence of T_c [1, 2]. For a long time measured isotope effects have been accepted as unambiguous evidence for a phonon mediated second-order pairing interaction [3 - 5]. In so-called all-quantum simulations we have demonstrated recently that an isotope dependence of T_c does not provide unambiguous information on the nature of the superconducting pairing mechanism [50, 51]. Isotope effects indicate the non-negligible influence of the quantum character of the nuclei on electronic expectation values. Furthermore they demonstrate the limitations of all electronic structure calculations on the basis of a single geometry. In [50, 51] and in our other all-quantum simulations [52, 53] we have calculated shifts of several eV in electronic expectation values (reference state: configuration at the minimum of the potential energy surface) as response to nuclear zero-point fluctuations. The corresponding shifts are a function of the atomic masses. The results reported in [50 - 53] have been derived by a combination of Feynman path-integral simulations for the nuclear fluctuations [54, 55] and electronic structure calculations in different degrees of sophistication. The electronic expectation values in [50 - 53] have been sampled over manifolds of nuclear configurations populated in thermal equilibrium. To sum up; there is no convincing correlation between an isotope effect at T_c and a superconducting pairing mechanism [50, 51].

The organization of the present manuscript is as follows. In Sect. 2 we explain the quantum statistical considerations which initiated the present suggestion of the driving force for the superconducting pairing. In this context we discuss the quantum statistics of fermions and hard core bosons. In Sect. 3 we consider the quantum statistics of Cooper pairs [41] and analyze the influence of the PAP on the pairing. In Sect. 4 we define the Hubbard Hamiltonian in the absence and presence of Cooper pairs. The simulation of Cooper pairs in a real-space representation of the Hamiltonian is a key-element of this section. Remember that Cooper pairs in the BCS theory have been defined in $\boldsymbol{k}$-space [3 - 5]. Model calculations for the compounds displayed in Fig. 2 are reported in Section 5. The article ends with a resume. Here we summarize arguments in favour of our approach. But we also touch upon topics which require future consideration.

2. Quantum Statistical Preliminaries: Fermions and Hard Core Bosons

In the following we summarize some quantum statistical principles which initiated the present considerations on the driving force for the superconducting transition; for these precursor studies of π electron systems see [33 - 36]. But at first we want to comment on a possible difference between the present approach and the majority of previous explanations of the superconducting pairing. This difference concerns the delocalization of the charge carriers in the normal state and the superconducting state. In the literature superconductivity has been studied almost exclusively by so-called reduced Hamiltonians where only those electrons, which are coupled to Cooper pairs, have been taken into account [3 - 5, 13 - 22]. The ensemble of electrons, which are not paired, remains unconsidered in descriptions on the basis of reduced Hamiltonians. In the present theory the whole quantum ensemble, i. e. the Cooper pairs and the unpaired fermionic background, has been taken into consideration. It seems to be a common trend of previous discussions to equate Cooper pair formation with a reduction in the electronic delocalization [1 - 5]. According to the Heisenberg uncertainty principle [56] reduced spatial uncertainty of quantum particles implies enhanced momentum uncertainty, i. e. larger momenta become of higher probability. The enhanced momenta raise the ensemble energy. But such a shift would be in contradiction with the energy gain of superconductors for temperatures $T \leq T_c$. What has been wrong in this argumentation? In the BCS approach the superconducting stabilization has been explained via a second-order potential energy term, the electron-phonon coupling. But if we restrict the pairing interaction to elements of the bare electronic Hamiltonian, the Heisenberg uncertainty principle [56] requests that Cooper pair formation must be accompanied by an enhanced spatial uncertainty of all charge carriers (i. e. Cooper pairs and unpaired single-particle background). It is one aim of the discussion of quantum statistical aspects in this and the following section to reconsider the assertion that pair formation should be accompanied by a reduction in the spatial degrees of freedom of the charge carriers. To simplify the understanding of our argumentation it is necessary to clarify the relation between quantum statistical constraints experienced by an ensemble of quantum particles and carrier delocalization. In previous articles [33 - 36] we have demonstrated that many-electron bases in the occupation number representation are an optimum choice to analyze this relation quantitatively. It is a peculiarity of fermion ensembles that not all interatomic electronic hopping events contribute to the delocalization of the carriers; see below. Many-electron bases of atomic occupation numbers are adopted in configuration interaction (CI) studies of the valence bond type [57, 58] and in quantum Monte Carlo (QMC) simulations of fermion systems [39, 40, 59].

For a problem with M atomic sites with one basis function per site and electron numbers $m_\uparrow$ and $m_\downarrow$ in the two spin directions, the overall configuration count N_C reads

$$\begin{aligned} N_\mathrm{C} &= N_{\mathrm{C}\uparrow} \cdot N_{\mathrm{C}\downarrow} \\ &= \frac{M!}{(M-m_\uparrow)!m_\uparrow!} \cdot \frac{M!}{(M-m_\downarrow)!m_\downarrow!}. \end{aligned} \quad (1)$$

The $N_{\mathrm{C}\uparrow}$ and $N_{\mathrm{C}\downarrow}$ denote the number of many-electron configurations per spin direction. The total number of electrons m is $m_\uparrow + m_\downarrow$. In systems with $M = m$ and $m_\uparrow = m_\downarrow$ (1) reduces to

$$N_\mathrm{C} = N_{\mathrm{C}\uparrow} \cdot N_{\mathrm{C}\downarrow} = \left\{ \frac{M!}{[(M/2)!]^2} \right\}^2. \quad (2)$$

(1) and (2) indicate a technical boundary of electronic structure calculations in such many-electron bases. The number of configurations is a strongly increasing function of M. Note that (1) and (2) define the configuration numbers in the absence of Cooper pairs. For the model systems **1** to **4**, see Fig. 2, we observe overall configuration numbers N_C of 16, 36, and 16 for the dicationic, neutral, and dianionic oxidation states (m = 2, 4, 6; singlet states throughout). The number of configurations per spin direction $N_{\mathrm{C}\uparrow}$ and $N_{\mathrm{C}\downarrow}$ is four, six, and four. All numbers refer to configurations without Cooper pairs. We have mentioned already in the introduction that many-electron bases in the occupation number representation offer the possibility to decompose the quantum constraints of fermionic systems into a formal on-site and a formal intersite constraint which can be equated with the PEP and PAP. Remember that the PAP only occurs in connection with the kinetic hopping part of the (Hubbard) Hamiltonian. For the following argumentation we have to keep in mind that the PEP and PAP only act on the electrons of one spin direction. This condition is implicit throughout the whole paper.

In (3) and (4) we define the quantum statistics of fermionic ensembles in the form of two anticommutator relations. The $a^+_{i,\sigma}$ and $a_{j,\sigma}$ denote single-particle creation and destruction operators of electrons with spin coordinate $\sigma = \uparrow, \downarrow$ at the atomic sites i and j. δ abbreviates the conventional Kronecker delta. The label fe in (3) and (4) has been added to denote the fermionic origin of the two anticommutator expressions.

$$(a^+_{i,\sigma,\mathrm{fe}})^2 = (a_{i,\sigma,\mathrm{fe}})^2 = 0, \quad (3)$$

$$a^+_{i,\sigma,\mathrm{fe}} a_{j,\sigma',\mathrm{fe}} + a_{i,\sigma',\mathrm{fe}} a^+_{j,\sigma,\mathrm{fe}} = \delta_{i,j}\delta_{\sigma,\sigma'}. \quad (4)$$

The on-site anticommutator (3) defines the influence of the PEP. Physically the PEP prevents many-electron configurations with two electrons of the same spin in the same quantum state (= same AO in the present occupation number representation). Note that (3) also manifests the Fermi-hole properties of fe ensembles. It is the intersite anticommutator (4) which leads to a change in the sign of the electronic wave function whenever the parity of the permutations p of interatomic hopping processes is odd. The interchange of two electrons is the most simple case of an hopping event with p = odd; it corresponds to $p = 1$. In the occupation number representation (4) can be equated with the PAP. The parity of p depends both on the electron count per spin direction and on the topology of the fermion system. The PAP is not operative in hoppings with p = even. We wish to reemphasize that only these in-phase moves contribute to the spatial delocalization of the electrons; they lower the ensemble energy [35, 36]. Hoppings with p = odd localize the electrons at the atomic centers. They have a destabilizing influence on the ensemble energy. As a matter of fact fermion systems become unstable if the ratio q between out-of-phase and in-phase hoppings exceeds a critical boundary. For a detailed discussion on the relation between q and the magnitude of the electron (de)localization we refer to [35]. To sum up; the fermionic intersite constraint (4) prevents the blind identification of PEP-allowed hopping processes with electron delocalization. In this work we denote the stabilizing majority hoppings of electrons

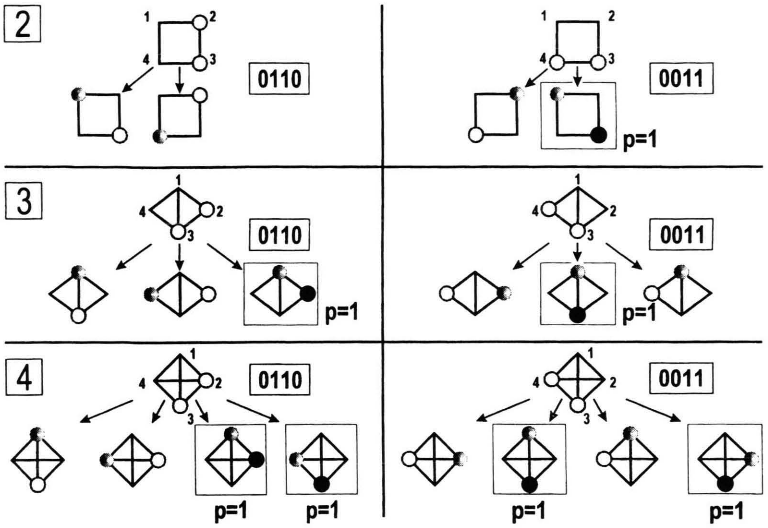

Fig. 3. Nearest-neighbour jumps in one spin direction in the neutral four-electron systems **2**, **3** and **4** (from top to bottom). The electron count per spin direction $m_\uparrow = m_\downarrow$ amounts to two. On the left hand side of the diagram we have chosen an initial two-electron configuration with atomic occupation numbers 0110. The initial configuration chosen on the right hand side is 0011. The atomic numbering scheme has been given for each system. The electron which has been moved to generate a new configuration has been symbolized by a shaded circle. Electrons which have been passed by have been labeled by full circles. p denotes the number of permutations accompanying the hopping process. Moves with $p = 0$ have not been labeled explicitely.

(p = even) by t_+, while the destabilizing minority hoppings (p = odd) are denoted by t_-. In QMC simulations of fermion problems the t_- elements cause the so-called minus-sign problem [40, 60, 61]. Note that such a discrimination between t_+ and t_- hoppings becomes irrelevant for the pair matrix elements t' discussed below. The simultaneous existence of t_+ and t_- hopping entries is a peculiarity of single-particle moves.

In (5) and (6) we define the quantum statistics of hard core bosonic ensembles [35 - 37]. The index hcb in the two relations has been added to denote this origin.

$$(a^+_{i,\sigma,\mathrm{hcb}})^2 = (a_{i,\sigma,\mathrm{hcb}})^2 = 0, \tag{5}$$

$$a^+_{i,\sigma,\mathrm{hcb}} a_{j,\sigma',\mathrm{hcb}} - a_{i,\sigma',\mathrm{hcb}} a^+_{j,\sigma,\mathrm{hcb}} = \delta_{i,j}\delta_{\sigma,\sigma'}. \tag{6}$$

Comparison of (3) and (5) indicates that the fe and hcb ensembles coincide in their on-site behaviour. Both ensembles are characterized by on-site anticommutativity. In analogy to fe ensembles it is again the PEP which prevents configurations with two electrons of the same spin at the same center. This means that it is the PEP which guarantees the hard core character of the quantum particles in hcb ensembles. Comparison of (4) and (6) demonstrates that the fermionic intersite anticommutator (4) has been replaced by an intersite commutator (6) in hcb ensembles. Independent of the parity of p all interatomic moves in hcb ensembles, which are allowed by the PEP, are in-phase. They enhance the delocalization of the quantum particles and lower the ensemble energy. In other words; the quantum statistics of hcb ensembles is not influenced by the PAP. Both the fe and hcb ensembles are formed by quantum particles with spin 1/2 [37]. We wish to point out that the Pauli spin matrices exhibit properties which are defined by (5) and (6) [37].

In the most general case, hcb ensembles are without physical significance in connection with fermionic (= electronic) problems. They define a fictitious state with maximum interatomic delocalization of the quantum particles (= phase coherence). A comparative theoretical analysis of electronic structure properties under the fe and hcb conditions, however, leads to insight into the influence of the PAP in fermionic systems [33 - 36]. Electronic ensembles, where hoppings with p = odd are prevented by a constructive interference between electron count and topology, are of particular interest. Such an interference leads to a coincidence in the characteristics of fe and hcb ensembles. This implies that electrons in systems without odd hoppings show hcb-like properties. We now consider the conditions leading to such a coincidence of two quantum ensembles.

It seems to be convenient to explain the parity p of interatomic electron moves with the help of diagrams. In Fig. 3 we have portrayed all allowed nearest-neighbour moves in neutral **2** to **4** when starting from initial two-electron configurations with occupation numbers 0110 (lhs.) and 0011 (rhs.). As expressed in (1) and (2), the distribution of two indistinguishable particles (per spin direction) over four atomic sites yields six different configurations. The trivial nearest-neighbour

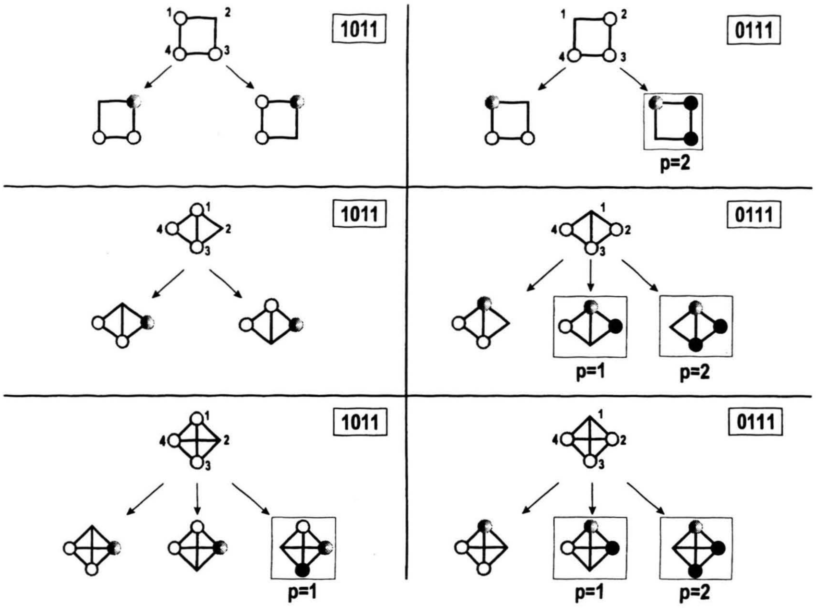

Fig. 4. Nearest-neighbour jumps in one spin direction of the dianionic model systems **2**, **3**, and **4** (from top to bottom). The electron count per spin direction amounts to three, the total electron count is six. On the left hand side of the diagram we have chosen an initial configuration with atomic occupation numbers 1011. The initial configuration chosen on the right hand side reads 0111. For further information see legend to Figure 3.

moves in **1**, where the PEP prevents all processes with $p \neq 0$, have not been considered graphically. To understand the contents of Fig. 3 (and Fig. 4, see below) one has to keep in mind that the sequence of electrons is defined by the atomic numbering scheme. Of course, a chosen numbering has to be kept fixed within a calculation. The proper consideration of the atomic numbering is an important technical aspect of CI calculations in a VB basis and QMC simulations of fermionic problems [39, 40, 57 - 59]. In the top row of Fig. 3 (rhs.) it is demonstrated that so-called "terminal" electron moves in neutral **2** are characterized by $p = 1$ = odd. The descriptor "terminal move" defines hopping processes covering the two "terminal" atoms 1 (= first atom) and $M = 4$ (= last atom) of a given M-center problem. Notice that the electron at center 3 has been passed by the "reference" electron performing the 1 ↔ 4 move. So-called "inner moves" in **2** conserve the electron ordering. The additional central bond(s) in **3** and **4** open new hopping channels which are characterized by $p = 1$ = odd (center and bottom diagram in Figure 3). The number of hopping events with p = odd is enhanced with increasing three-dimensionality of the fermion system (= increasing connectivity of the atoms).

In Fig. 4 we have displayed all nearest-neighbour moves in **2** to **4**, which are allowed by the PEP, when starting from the three-electron configurations 1011 (lhs.) and 0111 (rhs.). In contrast to the terminal 1 ↔ 4 moves in neutral **2** the 1 ↔ 4 moves in the six-electron monocycle are accompanied by $p = 2$ = even (top diagram, rhs.). Now two electrons (at centers 2 and 3) have been passed by the transferred one. But $p = 2$ prevents an influence of the PAP. In recent contributions [35, 36] we have explained in some detail that the difference between aromatic Hückel annulenes with a π electron count m of $(4n + 2)$ (n = 0, 1, 2,...) and anti-Hückel rings with a π electron number m of $4n$ (n = 1, 2, 3,...) [62] is caused by the parity p of the terminal 1 ↔ M hoppings. p is even (= $2n$) in $(4n + 2)$ rings, while it is odd (= $(2n - 1)$) in $4n$ annulenes. As a matter of fact, the π electrons in $(4n + 2)$ Hückel-rings exhibit hcb-like properties while fermionic intersite constraints are operative in $4n$ annulenes. Figure 4 clearly shows that hoppings with p = odd in the six-electron compounds are prevented only in the monocycle **2**. The inner bond(s) in **3** and **4** render possible hoppings with $p = 1$ = odd also for an electron count of six.

The total number of nearest-neighbour moves within one spin direction in dicationic, neutral and dianionic **1** to **4** has been summarized in Table 1. In the upper half we have given the non-zero entries t_+ and t_- for electron moves. In the bottom half the non-zero entries for hole moves have been collected. The abbreviations h_+ and h_- are the hole pendants of the electron hoppings t_+ and t_-. Let us consider first the t_+ and t_- elements. Table 1 demonstrates that the

Table 1. Top half: Number of stabilizing electronic majority hoppings t_+ and destabilizing minority hoppings t_- per spin direction in the model systems **1**, **2**, **3**, and **4** as a function of the overall electron count m. From top to bottom we have given the number of electron hoppings t_+, t_- in the dicationic, neutral and dianionic four-center models. The number of t_+, t_- entries refers to many-electron configurations without pair formation. All electron hoppings are of the uncorrelated single-particle type. $N_{C\uparrow} = N_{C\downarrow}$ denotes the number of configurations per spin direction. Bottom half: Number of hole hoppings per spin direction which are accompanied by an even (h_+) and odd (h_-) number of hole permutations. Note that these entries refer to "unoccupied" levels. Thus they do not have an influence on the ground state energy. m_h is the hole count.

Oxidation state	Hopping element	m	$N_{C\uparrow} = N_{C\downarrow}$	**1**	**2**	**3**	**4**
Dications	t_+	2	4	6	8	10	12
	t_-			–	–	–	–
Neutral	t_+	4	6	12	12	14	16
	t_-			–	4	6	8
Dianions	t_+	6	4	6	8	8	8
	t_-			–	–	2	4

Oxidation state	Hopping element	m_h	$N_{C\uparrow} = N_{C\downarrow}$	**1**	**2**	**3**	**4**
Dications	h_+	6	4	6	8	8	8
	h_-			–	–	2	4
Neutral	h_+	4	6	12	12	14	16
	h_-			–	4	6	8
Dianions	h_+	2	4	6	8	10	12
	h_-			–	–	–	–

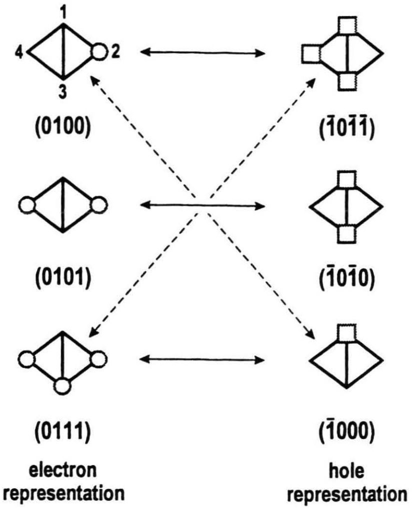

Fig. 5. Electron-hole correspondence in **3** as a function of the electron count. Electron configurations have been portrayed on the lhs, hole configurations on the rhs. The diagonal broken lines symbolize a formal correspondence in the quantum statistical constraints of electron and hole ensembles; see Table 1.

number of allowed nearest-neighbour moves in the neutral systems exceeds the nearest-neighbour moves in the two ionic configurations by a factor of two. In the six-electron systems this graduation in the number of hoppings is a direct consequence of the PEP (= deficit of vacant centers). In the two-electron systems it reflects the lack of electrons. The $m = 2$ results in Table 1 are trivial; all non-zero entries in the kinetic hopping matrix are of the t_+ type. The transition from neutral butadiene **1** to the $4n$ ($n = 1$) annulene **2** leads to four t_- elements which are caused by the terminal $1 \leftrightarrow 4$ hoppings; see above and Figure 3. According to Table 1 an equivalence in the type (t_+ versus t_-) and number of the non-zero hopping entries only occurs for the dication-dianion pairs of **1** and **2**. In the case of the butadiene pair it is the PEP which prevents any nearest-neighbour moves with $p \neq 0$. In the dianion of **2** it is the cyclic topology which causes $p = 2 =$ even for the $1 \leftrightarrow$ M hoppings. With exception of the trivial dicationic two-electron configurations of **1** to **4**, the cyclobutadiene dianion **2** is the only non-linear example considered in the present study, where the electrons exhibit a hcb-like statistics. To summarize; only for the dication-dianion pairs of **1** and **2** we observe identical hopping matrices. The particle-hole symmetry of polyenes as well as $(4n + 2)$ and $4n$ annulenes belongs to an old experience of π electron theoreticians [63]. Note, that this symmetry is violated for the ion-pairs of **3** and **4** which are considered next. Here only the overall number of the non-zero hopping entries coincides. The two ions, however, differ in the number of t_+ and t_- elements; see Table 1. In the dianion of **4** the ratio $q = t_-/t_+$ coincides with q of the neutral system ($t_-/t_+ = 0.5$). This implies that the number of electrons (four versus six) has no influence on the strength of the PAP in the case of the tetrahedral topology. Such a conservation of the q ratio does not exist in neutral and dianionic **3**. In the neutral bicyclic system q amounts to $6/14 \approx 0.429$; in the dianion q is reduced to 0.250. The topology of **3** renders possible a PAP influence which depends on the electron count. As already touched upon in the introduction, electronic systems with a coexistence of t_+ and t_- hoppings can be related to quantum ensembles with a fractional statistics; see [23 - 26, 39, 40]. In the present work, however, this topic is not commented in larger detail.

In the lower half of Table 1 we have given the number and the type of the nearest-neighbour jumps of holes (h_+, h_-). We are aware of the fact that such a hole representation of many-particle configurations might be unfamiliar in connection with ground state properties of molecules. In the electronic structure theory of solids, however, hole states are of importance [64, 65]. Remember the discussion of the Hall coefficient in Sect. 1 [10 - 12]. Holes are fictitious quantum particles of charge +e (the electronic charge is –e) which fill the states (= atomic sites in the present occupation number representation) not occupied by electrons. In Fig. 5 we have visualized the correspondence between electron and hole representations of many-particle states in the occupation number representation. As an example we have chosen the bicyclic system **3** with an overall electron (hole) count of two (six), four (four) and six (two); from top to bottom. In analogy to Figs. 3 and 4 only the quantum particles within one spin space have been displayed in Figure 5. The schematical drawing shows that the electron configuration 0100 has its hole pendant in the configuration $\bar{1}0\bar{1}\bar{1}$. The other electron-hole pairs correlated in Fig. 5 are: 0101 ↔ $\bar{1}0\bar{1}0$ and 0111 ↔ $\bar{1}000$.

The t_+, t_- and h_+, h_- elements of the two- and six-electron systems in Table 1 are related by particle-hole symmetry. This means that the h_+, h_- entries of the dications coincide with the t_+, t_- entries of the dianions while the hole entries of the dianions coincide with the electron entries of the dications. Electron-hole symmetry, here defined by the number and type of the kinetic hopping matrix elements, is fulfilled for the neutral four-electron systems. The observed correlation between t_+ and t_- elements, on the one hand, and h_+ and h_- elements, on the other, has been indicated schematically in Fig. 5 (broken diagonal lines). Note however, that the magnitude of the t_+ and t_- elements can differ from the magnitude of the h_+ and t_- elements; see [66] for a discussion of possible inequivalences. Thus the correlation shown schematically is only a qualitative one. To reemphasize; the electronic ground state energy is determined by the t_+ and t_- entries. The h_+ and h_- elements are irrelevant in this context. In the presence of an applied electrical field, the equilibrium distribution of electrons (and holes) of solids is perturbed and the electrical current can be transported by electrons and/or by holes. In the latter case the quantum statistics of hole states plays an active role in the material properties of the ensemble. Hole pairing is observed in the majority of superconducting materials [10 - 12]. On the basis of the theoretical tools adopted in the present work it is not possible to derive numerical results for hole pairing. Therefore we have transferred our considerations, which have been derived for electrons, to many-particle configurations of the hole type; see Section 6.

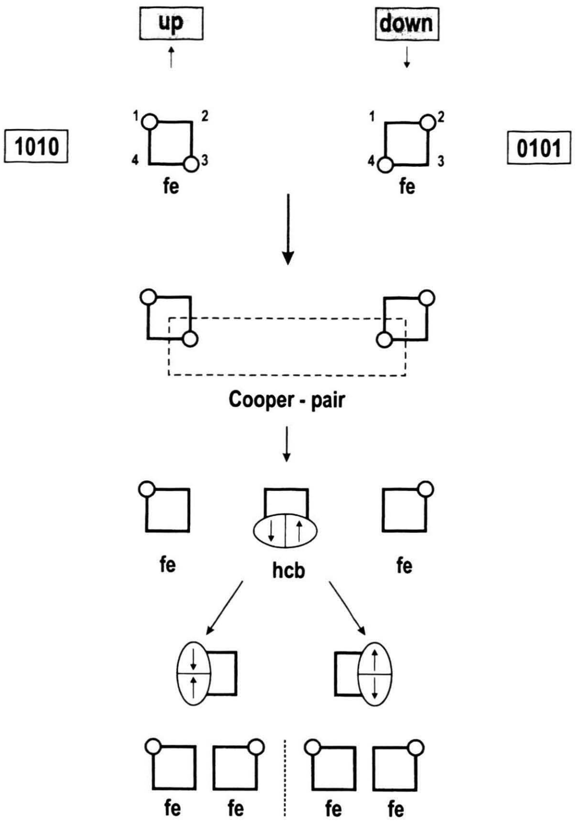

Fig. 6. Schematical representation of the formation of a Cooper singlet pair of the nearest-neighbour intersite type in neutral cyclobutadiene **2**. The initial single-particle configurations in the two spin spaces ↑, ↓ are 1010 (lhs.) and 0101 (rhs.). Note that the pair formation leaves one unpaired electron per spin space, i. e. a fermionic configuration without destabilizing PAP influence. Nearest-neighbour hopping processes of the Cooper pair have been displayed in the lower part of the diagram. The index hcb has been added to denote the quantum statistics of Cooper pairs. The unpaired background obeys the conventional fe statistics. In the example given, fe constraints do not occur as a result of the electron count.

The analysis of quantum statistical constraints, which are operative in fermion systems, has shown that the destabilizing influence of the PAP depends both on the topology of the quantum system and the electron count. High stability of an electron system requires hcb-like properties and thus the suppression – or at least the attenuation – of PAP effects. The instability of many molecules and solids is caused by a large number of out-of-phase hoppings. But note that these processes are still of the minority type. Aromaticity and antiaromaticity [47, 48] are molecular manifestations of a variable PAP influence on the electronic structure of mono- or polycyclic hydrocarbon π systems [35, 36]; see above. How is it possible to reduce the destabilizing influence of the PAP in fermion systems? The chemical answer is simple and well-known: By reduction or oxidation, i. e. by a change in the number of electrons. This degree of freedom has been discussed in detail in connection with Figs. 3 and 4 as well as Table 1. But is there also a physical process which can lead to an attenuation of the PAP influence? The answer is *superconductivity*, which – due to the formation of Cooper pairs – changes the number of unpaired electrons and thus the influence of the PAP. Up to now we have presupposed that the PAP is operative only in the unpaired fermionic background but not in the sea of Cooper pairs. The theoretical justification of this statement is derived in Section 3. Figure 6 gives a schematical real-space representation of a Cooper pair formation in the four-membered cyclobutadiene ring **2**; see the following section for a more detailed discussion of this diagram.

3. Quantum Statistics of Cooper Pairs and Suggestion of a Possible First-Order Pairing Interaction

To explain our suggestion of a PAP-controlled pairing mechanism, which has been touched upon at the end of the foregoing section in more detail, we have to consider the quantum statistics of Cooper pairs. The statistics summarized below concurs with the theoretical findings of [4, 5, 42, 43]. But in contrast to the $\boldsymbol{k}$-space representation employed in the literature [1 - 5], we have chosen a real-space representation to describe Cooper pairing. It is only in this adoption of a real-space representation of the pairing, that the present approach coincides with the theory of Schafroth, Butler and Blatt [44 - 46]. We define the creation and destruction operators $b^+(\Delta)_i$ and $b(\Delta)_i$ for pairs in terms of the conventional fermionic single-particle operators $a^+_{i,\sigma,\text{fe}}$ and $a_{i,\sigma,\text{fe}}$ by

$$b^+(\Delta)_i = a^+_{i,\sigma,\text{fe}} a^+_{i+\Delta,\sigma',\text{fe}}, \tag{7}$$

$$b(\Delta)_i = a_{i,\sigma,\text{fe}} a_{i+\Delta,\sigma',\text{fe}}. \tag{8}$$

Singlet pairing is characterized by $\sigma \neq \sigma'$. The parameter Δ counts the number of atomic centers between the two quantum particles forming a Cooper pair with site i denoting the reference center. Once Cooper pair formation has fixed the value of the Δ parameter, all pair elements t', see following section, are described by a common "phase" difference Δ. In Fig. 6 we have sketched a singlet pair in the cyclobutadiene molecule **2** with $\Delta = 1$. $\Delta = 0$ defines on-site pairing. In the bottom part of this diagram some nearest-neighbour pair hoppings t' have been displayed. The pairon operators $b^+(\Delta)_i$ and $b(\Delta)_i$ satisfy the anticommutator and commutator relations

$$\left(b^+(\Delta)_i\right)^2 = \left(b(\Delta)_i\right)^2 = 0, \tag{9}$$

$$b^+(\Delta)_i b(\Delta)_j - b(\Delta)_i b^+(\Delta)_j = 0, \; i \neq j. \tag{10}$$

(9) and (10) indicate that the quantum statistics of Cooper pairs coincides with the quantum statistics of a hcb ensemble which has been defined in (5) and (6). It is the on-site anticommutator (9) which ruins a simple bosonic statistics for the quantum ensemble of pairs. Constraint (9) prevents a Bose-Einstein condensation for temperatures $T \leq T_c$. In contrast to the on-site anticommutators (3) and (5) confined to a single atomic center, the diagonal anticommutator (9) covers two atomic sites i and $i + \Delta$. (10) shows that the moves of Cooper pairs are not influenced by the PAP. They are in-phase and lower the ensemble energy. This suppression of the fermionic antisymmetry constraint is decisive for the energy of configurations with charge carrier pairing. To recapitulate; the quantum statistics expressed in (9) and (10) is well-known in connection with superconductivity [4, 5, 42, 43]. Possible energetic consequences of these quantum statistical peculiarities of Cooper pairs, however, have not been analyzed in the past. Remember that only the ensemble of Cooper pairs has been considered explicitly in previous theoretical studies. This restriction in the active space has been a result of the adoption of reduced Hamiltonians.

In contrast to these models we take into account the whole ensemble of quantum particles. But this requires the consideration of two types of quantum statistics as well as the consideration of commutativity and/or anticommutativity between the two ensembles. We express the diagonal pendant ($i = j$)

of (10) in the presence of a fermionic single-particle background by

$$b^+(\Delta)_i b(\Delta)_i - b(\Delta)_i b^+(\Delta)_i = 1 - (n_{i,\uparrow} + n_{i,\downarrow}). \quad (11)$$

The $n_{i,\uparrow}$ and $n_{i,\downarrow}$ denote the spin-dependent number operators confined to atomic site i. They are defined by fermionic single-particle creation and destruction operators $a^+_{i,\sigma,\mathrm{fe}}$ and $a_{i,\sigma,\mathrm{fe}}$; we have $n_{i,\sigma} = a^+_{i,\sigma,\mathrm{fe}} a_{i,\sigma,\mathrm{fe}}$. The spin-independent number operators are defined as follows: $n_i = n_{i,\uparrow} + n_{i,\downarrow}$. The $n_{i,\uparrow}$, $n_{i,\downarrow}$ parameters on the rhs. of (11) arise from the effect of the PEP due to single-particle configurations. In short, the on-site statistics of the whole ensemble is controlled by the PEP. It is operative in both ensembles.

Next we have to consider the influence of the fermionic background on the off-diagonal pair hoppings expressed in (10). We have to ask whether or not the hoppings in both sub-ensembles can be treated independently in order to derive the influence of the PAP. In other words, do the off-diagonal operators (4) and (10) commute or anticommute? Remember the bosonic intersite character of (10). Quantum statistics tells us that (hard core) boson operators commute with all other second-quantized operators [67]. This implies that the fermionic background has no influence on the off-diagonal statistics (= hcb behaviour) of the Cooper pairs. It only remains to take into account the intersite anticommutativity within this fe background. In addition to this formal criterion a more pragmatical argument can be given which suggests commutativity between both off-diagonal hopping terms. Without loss of generality one has to accept that the phase difference Δ in the pairon operators prevents an unambiguous definition of the ordering of the quantum particles in an ensemble formed by Cooper pairs and unpaired fermions. The ordering of particles can be defined unambiguously only for ensembles of the single-particle type.

On the basis of the above statistical considerations we suggest that the superconducting transition can be driven by a possible reduction of fermionic intersite constraints (= PAP effect). For temperatures $T \leq T_c$ this stabilization overcompensates a possible classical Coulomb repulsion between the charge carriers and the reduction in the number of single-particle moves. It favours correlated pair-wise hoppings. The number of Cooper pairs formed should depend on the strength of the PAP. With a decreasing number of destabilizing single-particle hoppings t_-, the tendency to form Cooper pairs should be reduced. The experimental observation to have all Cooper pairs in the same quantum state [1, 2] is fulfilled by a common phase factor Δ for all pairs. In the next section it is suggested that the leading contributions to the pair elements t' should be of the hopping type. If this is accepted the corresponding elements differ from zero only if the two interatomic hoppings of a given pair move are identical, a prerequisite which prevents electron-hole coupling. The present explanation of the zero-dc electrical resistance in superconducting configurations coincides with previous theories [1 - 5].

It has been a central topic of the above theoretical discussion to emphasize that the influence of the PAP on fe ensembles depends on the electron count and the atomic building principles. Cooper pair formation is one way to change the number of fermions. Thus we feel that our suggestion of a first-order pairing is in line with the empirical rule of Matthias [7 - 9] who has verified a correlation between the magnitude of T_c and the average number of valence electrons per atom. Pair formation should be favoured in systems, where the PAP influence is strong, a fermionic constraint leading to a sizeable localization of the carriers and thus to strong electronic correlations. Again it seems, that this implication of our theory is in line with experimental experience [1, 2]. Many superconductors are in the vicinity of an instability threshold which is caused by strong correlation effects. Let us come back to the molecular concepts of aromaticity and antiaromaticity [47, 48] and thus to an old suggestion of London [49]. It is our opinion that the superconducting transition can be equated with an avoidance of antiaromaticity and thus with an inclination towards aromaticity.

Within the present model suggesting an attenuation of the PAP as driving force for the superconducting pairing it seems to be straightforward to explain the large spatial separation between the two carriers of a Cooper pair. In the majority of superconductors this length covers many interatomic spacings. Such distances are much too large to render possible a sizeable overlap between the two single-particle wave functions of a pair state. The BCS explanation of the pair interaction is well-known [3 - 5]. In this theory it is argued that one electron polarizes a lattice position and that a second electron, many interatomic spacings apart, is attracted by this polarized lattice position. It seems, that such a description has difficulties to explain the exclusion of hopping processes of near-by electrons. In the present theory the spacing between the carriers of a Cooper pair is not necessarily related to a direct physical interaction. The particles "feel" each other (i. e. they are coupled) via their response on the single-particle background (= PAP attenuation). It is our opinion that the coupling between the carriers of a pair has remarkable similarities with the hyperfine interaction in NMR spectra where the direct overlap between the two nuclear wave functions is zero. The nuclei "feel" each other due to their coupling to the electron ensemble. In connection with the present topic the nuclear wave functions in the NMR case have to be replaced by the wave functions of the carriers of a Cooper pair and the electronic wave functions in NMR problems by the electronic wave functions of the single-particle background. To summarize; Cooper pair formation should be accompanied by a reduction of the PAP influence on the overall quantum ensemble. It is the fermionic phase-modulation via the PAP which can establish the long-range interaction between the carriers of a Cooper pair. In consideration of the large interparticle spacing it seems to be rather unlikely that the two carriers of a pair feel each other via an overlap of the two single-particle wave functions or via classical Coulomb effects. The PAP effect discussed is a peculiarity of fe ensembles. We suggest that the mean spatial separation between the carriers of a Cooper pair is a bare ensemble-size effect determined by the ratio between the number of paired carriers and the number of unpaired electrons per unit volume. We assume that this ratio reflects the competition between the PAP influence on the one hand and the restriction in the number of uncorrelated single-particle moves, on the other. The finite molecular models adopted, see Fig. 2, unfortunately prevent the simulation of long-range effects. The factors favouring intersite or on-site pairing in small molecules differ from the factors which are decisive in solids; see the discussion in Section 5.

Let us come back to a possible difference between the present approach and the electron-phonon mechanism of the BCS theory. The superconducting stabilization in the second-order BCS method is explained via a gain in the potential energy which overcompensates the increase of the kinetic energy of the pairs. As an implicit assumption this approach equates Cooper pair formation with reduced spatial uncertainty of the carriers. We favour a mechanism where Cooper pair formation might be accompanied by a reduction in the kinetic energy of the whole quantum ensemble and thus by an enhanced spatial uncertainty (PAP attenuation). It seems that this interpretation is more appealing to explain the zero-dc electrical resistance for temperatures $\leq T_c$.

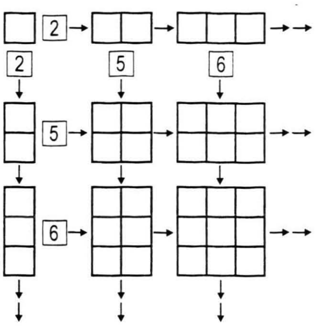

Fig. 7. Schematical representation of the condensation of a solid formed by four-membered rings. On the top left we have portrayed the monocyclic cyclobutadiene unit **2**. With **5** we denote (0,2,2)-hexatriene, with **6** the according tricyclic system. The PAP effects occuring in **2** are conserved in each four-membered ring of the 2D arrangement. The diagram has been chosen for didactical purposes only. The antiaromatic destabilization in each ring as well as ring tension prevent a condensation as shown in the figure.

At the end of this section let us comment on the transferability of arguments formulated for molecular units to macroscopical solids. In this context we wish to point out that the number of majority t_+ and minority t_- hoppings in a quantum ensemble depends on the topology of the building units of a solid and on the average number of valence electrons per atom. With building units we identify the smallest fragments which define the characteristic structural elements of a solid. Whether or not these units are interrelated by perfect translational symmetry is of minor importance only. Remember that superconductivity is not restricted to crystalline solids [1, 2]. Let us consider the cyclobutadiene molecule **2** as a simple example to emphasize the transferability of the quantum statistical constraints experienced by molecules to solids. The transition from **2** to bicyclo-(0,2,2)-hexatriene **5**, see Fig. 7, is roughly accompanied by a doubling of the PAP influence [36]. In the tricyclic system **6** the PAP effect of one cyclobutadiene ring is roughly triplicated, etc. In one of our recent studies we have analyzed the π electronic structure of **2, 5, 6** and of higher annelated four-membered rings [68]. It is the parity of the hoppings in each four-membered ring which controls the antisymmetry constraints experienced by the overall ensemble of fermions. These brief quantum statistical considerations on the condensation of four-membered rings can be transferred to any other building units of solids such as tetrahedra, octahedra, cubes, etc. Note that electronic interchanges are possible in any ensemble which deviates from perfect 1D ordering. Let us postpone the problem of hole superconductivity to a later section. In the next one we explain the real-space simulation of Cooper pairs [41] in the framework of the Hubbard Hamiltonian [31, 32]. Numerical results will be given in Section 5.

4. Electronic Hamiltonian and Pairing Approximation

In (12) we define the two-parameter Hubbard Hamiltonian H_{Hu} [31, 32] employed in the present study. H_{Hu} contains the two-electron on-site repulsion U and the nearest-neighbour hopping integrals t ($= t_+$ and t_-). H_{Hu} has been expressed in the language of second quantization by

$$H_{\text{Hu}} = -t \sum_{i<j(nn),\sigma} a^+_{i,\sigma} a_{j,\sigma} + 0.5 \cdot U \sum_{i=1}^{M} n_i \cdot (n_i - 1). \quad (12)$$

The index nn in the hopping term denotes that the $i < j$ summation over the atomic sites i, j covers all bonded pairs of nearest-neighbours. (12) refers to an electronic ensemble defined by unpaired fermions. All moves are of the single-particle type t ($= t_+$, t_-). In (13) we express the Hubbard Hamiltonian H^{CP}_{Hu} for an ensemble of Cooper pairs. Here the single-particle operators $a^+_{i,\sigma}$ and $a^+_{j,\sigma}$ in the hopping part of the Hamiltonian have been replaced by pairon operators $b^+(\Delta)_i$ and $b^+(\Delta)_j$. The elements t of the matrix of single-particle hoppings can be replaced by pair matrix elements t':

$$\begin{aligned} H^{\text{CP}}_{\text{Hu}} = -t' \sum_{i<j(nn),\sigma} b^+(\Delta)_i b(\Delta)_j \\ + 0.5 \cdot U \sum_{i=1}^{M} n_i \cdot (n_i - 1). \end{aligned} \quad (13)$$

In (13) we have postulated that pairon operators of the type (7) and (8) can be combined with the hopping (i. e. one-electron) part of the Hubbard Hamiltonian. The physical justification of this procedure has been touched upon already in the foregoing section. Nevertheless we have to point out that a simple interpretation of the t' as accessible for the t in (12) might cause some problems in connection with a Hamiltonian where the matrix elements are inserted as parameters. Although we favour an interpretation of the t' in terms of pair hoppings it cannot be ruled out that Coulomb-type interactions or even electron-phonon coupling might contribute to effective t' elements (prerequisite: same combination of creation and destruction operators in these additional matrix elements as encountered in the pair hopping). In consideration of the doubts formulated in connection with the BCS electron-phonon theory, we feel that electron-phonon contributions to effective t' elements should be of minor importance only. A quantitative analysis of this topic, however, would require the evaluation of all matrix elements of the Hubbard-Hamiltonian on the basis of explicit single-particle and pair wave functions. Despite the absence of these calculations we are nevertheless convinced that the present study has provided insight into the influence of the PAP on the superconducting pairing. Although we have defined different Hamiltonians (12), (13), and (14), see below, the analysis of the lowest eigenvalue renders possible a comparison of the energetics of paired and unpaired many-electron configurations. To summarize; the present pairing approximation suggests to consider the hopping processes of Cooper pairs as formal one-electron processes. In the framework of our theory this has been justified by fixing the separation Δ between the two particles of a Cooper pair. Note that a vanishing electron-phonon coupling is the natural outcome of a fixed Δ parameter. Examples for moves of Cooper pairs have been visualized in Figure 6. Let us come back to the definition of the Hubbard Hamiltonian of the unpaired and paired states. Comparison of (12) and (13) shows that the two Hamiltonians coincide in the form of the two-electron on-site parameter. In the framework of the present simplified calculations the two-electron part remains unchanged when going from H_{Hu} to $H^{\text{CP}}_{\text{Hu}}$.

Within the model adopted an unambiguous definition of the ratio between t and t' is difficult. Thus we have considered t' as a variable parameter. If t' is identified with a bare correlated pair hopping, a t/t' ratio of 2 seems to be a physically meaningful choice. In this first presentation of our theory this t/t' ratio has been chosen. Note that the mass of a Cooper pair is twice the electron (or hole) mass. In analogy to the effects mentioned above we also have neglected effective mass phenomena of solids in such a qualitative estimation of the t/t' ratio. We define the Hubbard Hamiltonian $H_{\rm Hu}^{\rm mix}$ for a mixed ensemble containing both Cooper pairs and the unpaired fermionic background by

$$H_{\rm Hu}^{\rm mix} = -t' \sum^{\rm CP} \sum_{i<j(nn),\sigma} b^{+}(\Delta)_i b(\Delta)_j \qquad (14)$$
$$- t \sum^{\rm unp} \sum_{i<j(nn),\sigma} a^{+}_{i,\sigma} a_{j,\sigma} + 0.5 \cdot U \sum_{i=1}^{M} n_i (n_i - 1).$$

In the present theoretical approach, intended to explain the pairing as response to an attenuation of the influence of the PAP, (14) has to be employed. Remember that it is the fermionic background with its residual PAP influence which determines whether or not Cooper pair formation leads to energetic stabilization.

The first hopping summation in (14) is over the Cooper pairs and the second one is over the unpaired (unp) single-particle background. Note that a second summation index (unp) for the single-particle moves has not been neccessary in (12) with only one type of quantum particles. What we have done in (14) is the fragmentation of the overall hopping interaction into a parameter describing the pair moves (with possible contributions from other parts of the Hamiltonian, see above) and a parameter describing the decoupled single-particle moves. As emphasized in the discussion of quantum statistical principles, only the moves of the unpaired quantum particles are controlled by the PAP (prerequisite: odd number of permutations p accompanying a certain jump process). The t' elements are not influenced by the antisymmetry constraint of fermion systems. To sum up; the subdivision of the overall hopping into two different terms in (14) has been the prerequisite to take into account the different quantum constraints (i. e. PAP effect) acting on the two types of quantum particles of the ensemble. The theoretical uncertainties in the quantitative definition of t' in (14) have been discussed already in connection with (13).

Table 2. Number of stabilizing majority hoppings t_+ and destabilizing minority hoppings t_- in both spin directions of the neutral model systems **1**, **2**, **3**, and **4** in the unpaired state as well as the number of single-particle hoppings t_+ and pair hoppings t' in **1** to **4** in the case of a pair state with a single on-site pair. The latter ensemble is formed by two uncoupled electrons with spin coordinates ↑ and ↓ and the on-site singlet pair. The number of configurations in both four-electron ensembles is 36. In the bottom line the total number of non-zero elements in the hopping matrix is given. See Table 1 for further information. In the numerical calculations discussed in Sect. 5 we have adopted the relation $t' = 0.5|t|$. It has been explained in detail that a discrimination between in-phase (+) and out-of-phase (-) moves of the type t' is irrelevant in the paired subspace. Here the PAP is not activated. All t' entries are of the type "t'_+".

Hopping element	Unpaired config.				Paired configuration			
	1	2	3	4	1	2	3	4
t_+	144	144	168	192	72	96	120	144
t_-	–	48	72	96	–	–	–	–
t'	–	–	–	–	24	32	40	48
Total number of non-zero hoppings	144	192	240	288	96	128	160	192

In order to simplify the discussion in the following section we have summarized the t_+, t_- and t' elements in neutral **1** to **4** for the unpaired four-electron state and for a configuration with a single on-site pair. The corresponding matrix elements can be found in Table 2. The data collected for the unpaired four-electron states can be considered as a supplementing of the information summarized already in Table 1. In contrast to Table 1 the matrix elements of both spin directions have been taken into account in Table 2. The number of configurations in the unpaired and on-site paired states of **1** to **4** is identical; it amounts to 36. As explained above the influence of the PAP in the unpaired four-electron states is enhanced in the series from **1** to **4**. In **1** all 144 single-particle moves are of the stabilizing t_+ type. In **4** 192 t_+ elements compete with 96 t_- entries. Table 2 visualizes that the overall number of non-zero entries in the hopping matrix is reduced in the paired states of the systems **1** to **4**. Cooper pair formation in **1** transforms 144 t_+ entries of the unpaired state in 72 t_+ and 24 t' entries. Obviously such a "transition" cannot lead to any energetic stabilization. In the model systems **2** to **4** pair formation renders possible the complete elimination of all t_- entries of fermion ensembles. In other words; the PAP is without influence in the pair states of **1** to **4**; see Figure 6. The minimum prerequisite to observe an influence of the PAP is an electron count > 1 within a given spin direction, a condition which is not fulfilled in the paired configurations considered in Table 2. The 144 t_+ and 48 t_- elements encountered in the unpaired configuration of **2** correlate with 96 t_+ and 32 t' entries in the state with one on-site pair. The suppression of the destabilizing t_- elements is of course strongest in tetrahedral **4**. Formation of two on-site pairs is a very unfavourable process. Here the configuration size is reduced to 6. The number of non-zero pair-hoppings t' in the series **1** to **4** amounts to 6, 8, 10, 12.

In the next section we compare the normalized Hubbard energies of **1** to **4** for different pairing interactions and coupling conditions. Shifts in the ensemble energy as a function of the pairing interaction are a result of the competition between modifications in the PAP constraints acting on the ensemble and the reduction in the number of stabilizing hoppings (t_+, t'). Energy minimization for different configurations shows whether or not Cooper pair formation can lead to a stabilizing first-order pairing interaction.

In the present work we have solved the energy eigenvalue problems of the Hubbard Hamiltonian algebraically in a basis of atomic occupation numbers; see Sects 2 and 3. Thus our approach corresponds to a CI implementation of the VB type [57, 58]. In recent studies of fermionic problems we have adopted this technique in order to check the accuracy of statistical QMC simulations [33 - 36, 59]. In Sect. 5 we have studied the Hubbard Hamiltonian as a function of the on-site repulsion U. The nearest-neighbour hopping t has been fixed to t = 2.4 eV (t' = 1.2 eV), a value frequently used in the π electron theory of hydrocarbon compounds [57, 58]. This choice of the hopping can be considered as a reminiscence to the π electron origin of the molecular models **1** to **4**.

5. Numerical Results and Discussion

In the following we analyze the normalized electronic energy E (= energy per electron) of the four-center systems **1** to **4** for different many-particle configurations (= absence and presence of Cooper pairs) as a function of the electron count m. We have simulated intersite pairing of the nearest-neighbour type as well as on-site pairing. All Cooper pairs studied are of the singlet type. The spin state of the overall ensembles is singlet as well. As pointed out above our choice of molecular model systems prevents an evaluation of T_c numbers. Nevertheless the strategy adopted renders possible a transparent discussion of the influence of the PAP on Cooper pair formation. In Figs. 8 to 10 we have plotted the normalized energies E of **1** to **4** as a function of the two-electron on-site repulsion U. For U = 0 the energy E of the unpaired configurations corresponds to the conventional Hückel molecular orbital (HMO) results [62] which can be found in many text books [69, 70]. In Fig. 8 we have displayed the normalized energy curves of the two-electron problems (dications) of **1** to **4**. Remember that the PAP is without influence in this case (prerequisite: singlet spin states). The energy of the unpaired state is reduced with increasing connectivity of the atomic sites (= increasing number of bonded neighbours). In the absence of Pauli antisymmetry constraints increasing connectivity guarantees increasing electron delocalization. On the basis of the discussion in Sect. 2 and 3 it could be expected already that pair formation cannot lead to any energetic stabilization of two-electron singlet systems. Figure 8 shows that the separation between the unpaired and paired configurations increases from **1** to **4**, i. e. the energy difference increases with the connectivity of the atomic sites. To summarize, Cooper pair formation in a two-electron singlet system is not a favourable

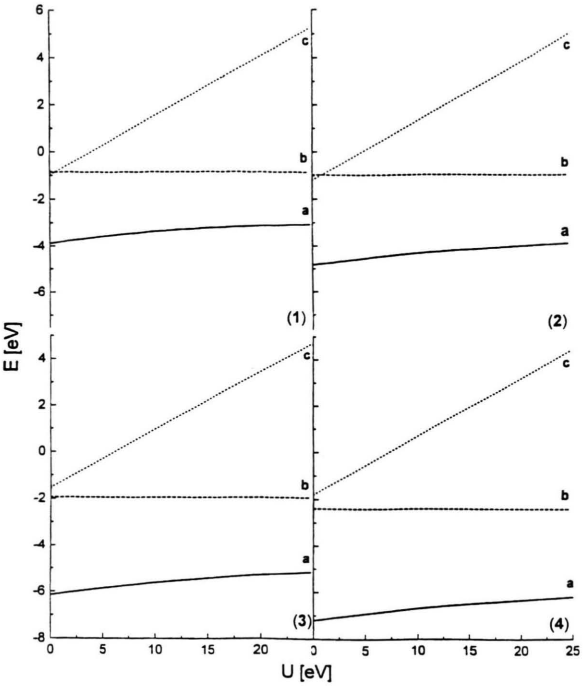

Fig. 8. Normalized electronic energy E (= energy per electron) of the dicationic two-electron systems **1** to **4** as a function of the two-electron on-site term U. All calculations refer to a singlet state. The full curve a corresponds to the single-particle configuration (= absence of Cooper pairs), curve b refers to a configuration with a single nearest-neighbour intersite pair while c refers to on-site pairing. All numbers are given in eV (t = 2.4 eV, t' = 1.2 eV).

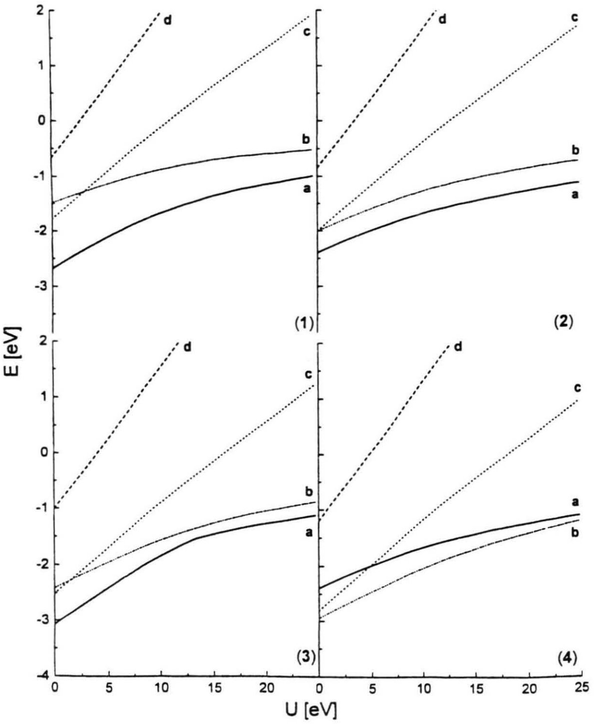

Fig. 9. Normalized electronic energy E of neutral **1** to **4** as a function of the two-electron on-site parameter U (singlet states). Curve a refers to a configuration without pairing, b and c, respectively, correspond to nearest-neighbour intersite and on-site pairing of a single pair and d refers to an ensemble with two on-site pairs; all values in eV (t = 2.4 eV, t' = 1.2 eV).

process. The energetic splitting between the configurations with on-site and intersite pairing at $U = 0$ eV reflects differences in the Hilbert space accessible for the two-electron ensembles. With increasing atomic connectivity the on-site curve is shifted above the intersite curve also in the limit $U \to 0$. We should mention that pair formation in two-electron systems remains a destabilizing process even if t' is shifted towards t. Remember that the t' parameter adopted in all calculations portrayed in Figs. 8 to 10 is only one half of the single-particle hopping element t.

In Fig. 9 we have plotted the E curves of neutral **1** to **4** as a function of the on-site term U. In contrast to the m = 2 series we observe sizeable PAP effects in the four-electron systems **2** to **4**. An exception is the linear butadiene molecule **1** where the PEP prevents an activation of the PAP. Note that the energy difference between unpaired and Cooper paired four-electron configurations corresponds to a maximum in **1**. The computational results in Fig. 9 demonstrate that pair formation in **1** to **3** is not accompanied by an energetic stabilization. The electronic energy of the unpaired ensembles **1** to **3** corresponds to the minimum. In the tetrahedral system **4** the formation of a single Cooper pair leads to a stabilization relative to the single-particle state. Tables 1 and 2 have shown that fermionic PAP constraints are of maximum strength in neutral (and dianionic) **4**. Here Cooper pair formation can successfully compete with the single-particle hoppings. The energy of the intersite pair lies below the E curve of the unpaired state for all values of U considered. The E curves of **4** furthermore indicate that – within the parameter set of the Hubbard Hamiltonian chosen – even the on-site pairing can compete with the unpaired state if U becomes smaller than a critical boundary U_c. The crossing of the two curves occurs at $U_c \approx 4.7$ eV.

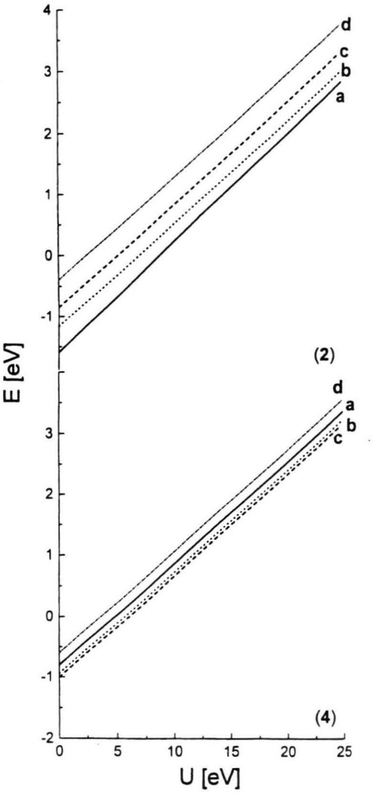

Fig. 10. Normalized electronic energy E of dianionic **2** and **4** (singlet states). The following configurations have been considered; a: absence of pairing, b: single on-site pair, c: two on-site pairs, d: three on-site pairs; all values in eV (t = 2.4 eV, t' = 1.2 eV).

The ensemble energies derived for the four-electron system **4** indicate that Cooper pair formation can lead to an energetic stabilization relative to the unpaired state if the PAP constraints acting on a fermionic ensemble are sufficiently strong. See again the discussion in Sect. 2 and 3. The numerical results in Fig. 9 demonstrate that Cooper pair formation is possible via a first-order interaction between charge carriers. Under certain conditions correlated hoppings of electron pairs render possible energetic stabilization. The energy required to overcompensate the classical Coulomb repulsion – if there is any in pair states with large Δ parameters – and the reduction in the number of single-particle moves, is provided by an attenuation of the PAP influence. Each participation of the PAP in interatomic hoppings causes incoherence and thus electronic localization. We strongly feel that a superconducting pairing approach which predicts enhanced delocalization of the quantum particles in the pair state is more appealing than a second-order mechanism which postulates reduced spatial uncertainty of the carriers in the superconducting state.

Let us reconsider Figure 9. The large energetic destabilization of configurations with two on-site pairs is easy to explain. Remember that the formation of a single Cooper pair leaves a single-particle background with two electrons of different spin. PAP effects do not occur in this background. The strong energetic competition between on-site and intersite pairing with decreasing U is again a molecular size effect caused by the PEP which acts on the whole ensemble. With increasing system size the partial locking of two neighbouring sites in the case of intersite pairing becomes less important. See the analysis of the PEP influence as a function of ensemble size effects in [36]. With increasing system size intersite pairing will be favoured in comparison to on-site pairing. In analogy to the dicationic series presented in Fig. 8 let us touch upon energetic consequences of enhanced pair hoppings t' (i. e. $t' \rightarrow t$) in the four-electron systems of Figure 9. t' enhancement does not change the energetic ordering of the different configurations in linear **1**. For cyclobutadiene **2** we predict an intersite pair which is only slightly above the E curve of the unpaired state. A similar behaviour is derived for the bicyclic four-electron system **3**. In **4** configurations with a single pair strongly profit from the enhancement of t'. But even for $t' = t$ the formation of two Cooper pairs in **4** cannot compete energetically with the other electronic configurations.

In the foregoing sections it has been mentioned already that Cooper pair formation and thus the superconducting transition can be correlated with the molecular concepts of antiaromaticity and of aromaticity [47, 48]. We suggest that the driving force for the superconducting transition is the attenuation of PAP effects in "antiaromatic" configurations. In the present context we equate "antiaromatic" configurations with configurations destabilized by a large number of minority hoppings t_-. If this molecular picture is accepted to explain a solid state phenomenon, the superconducting transition can be identified with an electronic transition from an "antiaromatic" domain to an "aromatic" one. Remember that aromaticity can be identified with an absence or an attenuation of PAP effects in cyclic molecular structures.

Finally we want to discuss the numerical results for configurations with $m = 6$ (dianions). In Fig. 10 we have portrayed the normalized energies E of **2** and **4** as a function of U. We have restricted the analysis to the two systems with four identical atoms where charge shifts and polarization effects are prevented by the corresponding point symmetries. In Fig. 10 we have considered the unpaired configurations of **2** and **4** as well as configurations with one, two and three on-site pairs. The results for the cyclobutadiene dianion, a six π electron system of the Hückel-type [62], have been expected. Pair formation does not lead to an energetic stabilization. Remember that even the PAP attenuation in neutral **2** has been insufficient to render possible pair formation. The results derived for the tetrahedral dianion are of some interest. We see that the configurations with one and two on-site pairs are both below the energy curve of the unpaired state. Remember the strong PAP effects in neutral and dianionic **4**; see Table 1. Only the configuration with three pairs is less stable than the unpaired one.

The computational results in Figs. 8 to 10 indicate that pair formation is enhanced with an increasing connectivity of the atoms. Increasing connectivity opens an enhanced number of hopping channels with p = odd. As explained in detail this is the topological condition for an enhanced influence of the PAP. We feel that this correlation between the connectivity of atoms and the tendency to form a superconducting state is in agreement with experimental experience. Superconductivity is favoured in systems with high coordination numbers [1, 2, 22]. Let us come back to the empirical rule of Matthias [7 - 9]. The numerical results presented, clearly show a correlation between the number of electrons per atom and the tendency to form pairs. From our previous all-quantum simulations reported in [50 - 53] it follows that the different configurations for a given electron count m differ in the virial coefficient r (= ratio between electronic potential and kinetic energy). This imbalance, however, implies that the corresponding ensemble energies (e. g. the energy without and with pair formation) differ in their temperature dependence. The attenuation of the PAP influence due to pair formation is the energy-determining factor in the temperature interval $T \leq T_c$.

6. Conclusions

In the present theoretical study we have suggested that pair formation in molecular model systems might be caused by a first-order interaction without participation of phonons. We have adopted the descriptor "first-order" interaction to denote that only terms of the electronic Hamiltonian have been used to simulate the pairing interaction. The present suggestion of a direct pairing does not mean that phonons are unimportant for the electronic structure properties of solids and molecules as well. On the opposite, we have shown in a series of articles [50 - 53] that the fluctuations of the nuclei have a strong influence on electronic expectation values. Historically – i. e. in the absence of comprehensive calculations – this influence had favoured the development of a phonon-mediated second-order coupling; see the discussion in the introduction. The quantum and classical thermal fluctuations of the nuclei lead to an intrinsic isotope dependence of all (electronic) expectation values. Note that these effects which are a result of an ensemble averaging over manifolds of nuclear configurations, differ from a possible contribution of the electron-phonon coupling to the pairing. In the present study we have suggested to explain Cooper pair formation by an attenuation of the destabilizing influence of the PAP on the fermion ensemble. As emphasized in detail, this PAP effect is both a function of the topology of the structural building units of the solid and a function of the average number of unpaired electrons per atom. Cooper pair formation causes a change of the latter parameter. The present pairing mechanism neither requires a sizeable overlap between the wave functions of the carriers forming a Cooper pair nor an electron-lattice interaction. The pairs are coupled via the phase modulation of the hoppings (= PAP effect) in the fermionic single-particle background.

In the introduction it has been pointed out that the BCS electron-phonon approach leads to conceptual problems already in conventional superconductors. In the past two decades new classes of superconductors have been characterized where the electron-phonon coupling is believed to be not applicable. Let us formulate the following daring hypothesis: Superconductivity in *all* materials is caused by the PAP-attenuation described in the present work which does not neccessarily require an electron-phonon interaction of the second-order type. Can we find arguments which support our hypothesis? Some have been given already in Sects. 2, 3, and 5. Let us sum up the main ones. The discussion has shown that the tendency of pair formation depends both on the number of valence electrons per atom and the topology of the fermion system. Thus we feel that the present approach is in line with the empirical findings of Matthias [7 - 9]. The analysis of the computational results in Sect. 5 furthermore is in line with an enhancement of the tendency of superconducting pairing with increasing coordination numbers of the atoms. In analogy to the Matthias rule this implication following from our theory is in line with experimental experience. The isotope dependence of T_c is a consequence of the non-negligible quantum character of the nuclei; see above. Quantitative insight into the magnitude of this effect would require all-quantum simulations as described in [50 - 53] for each system. The physical explanation of the energy gap in the majority of superconducting materials corresponds to previous theories [1, 2]. In the following we briefly mention other arguments in favour of the present approach.

i) It is well-known that superconducting materials are only poor conductors for temperatures $T > T_c$. Advocates of the electron-phonon approach argue that poor conductivity is the prerequisite to have strong electron-phonon coupling. In the present study we have analyzed the coherence or incoherence of fermionic moves. With increasing incoherence (increasing PAP influence) the localization of the carriers is enhanced and the corresponding materials become poor metals only. Note that this is a first-order effect, while the electron-phonon coupling is a second-order one.

ii) Jahn-Teller (JT) distortions have been observed in many superconductors [1, 2]. Remember that the sizeable JT effects encountered in certain cuprates initiated the research activities finally leading to high-T_c cuprates in the 1980s [71]. In the BCS approach

JT effects are correlated with strong electron-phonon coupling. In systems with a strong competition between t_+ and t_- hoppings, possible JT distortions are always large [36]. They reduce the influence of the incoherent t_- moves. To summarize, in JT-active systems there are two ways to attenuate the influence of these incoherent moves, i) spatial distortion of the atoms and ii) the superconducting pairing.

iii) The detailed analysis in [13] has shown that superconductivity is favoured in materials with a small Hubbard U term. As discussed in [36] small two-electron elements are the electronic prerequisite to have a strong competition between t_+ and t_- hoppings. In the present model the superconducting transition has been traced back to the presence of t_- elements. Only if the t_- hoppings have a sizeable energetic influence, pair formation can be expected. Despite the small U terms encountered in superconductors it has been found that the electronic correlations in these materials often are rather strong [1, 2]. Strong correlations in the presence of small U integrals are possible only if the number of t_- hoppings is large. In the framework of a fractional quantum statistics, the electronic correlations would be measured by the ratio $U/\exp(ia_s\pi)t$ with an exponential phase factor < 1. In the absence of PAP effects the correlation strength is mapped by the ratio U/t. In short, for identical values of U and t the PAP leads to an enhanced correlation strength.

iv) We feel that the present interpretation may lead to a microscopical understanding of the Meißner-Ochsenfeld effect [72], i. e. the perfect diamagnetic properties of superconductors. This behaviour has been explained convincingly in previous works by phenomenological or thermodynamical approaches. In the present theory the Meißner-Ochsenfeld effect can be explained as follows. The superconducting state is characterized by an optimum compromise between attenuation of the PAP and restriction in the number of single-particle moves; see Table 2. The spin flippings under the influence of an external magnetic field would lead to a perturbation of this configuration of minimum energy, i. e. the attenuation of the PAP due to pair formation would not correspond to an optimum any longer. In order to conserve the number of $\uparrow$ and $\downarrow$ spins, the external field is expelled from the superconductor.

v) Finally we have to consider the preference of hole pairing in superconductors. Qualitative models to explain this behaviour have been reported in [21, 73]. On the basis of the present considerations we offer the following preliminary explanation: In Sect. 2 we have emphasized that fermion systems become unstable if the ratio q between out-of-phase and in-phase hoppings exceeds a critical boundary. But this implies that the reservoir of incoherent hoppings in the filled one-particle space is somewhat limited. Hole pairing can be expected whenever the reservoir of h_- hoppings in the virtual one-particle space exceeds the reservoir of t_- hoppings in the filled one-particle space. Pair formation of holes does not correspond to an equilibrium process but to a process initiated by an external electrical field. For quantitative calculations it would be necessary to add the current-current correlation function to the electronic Hamiltonian.

At the end of this article we want to reemphasize that our approach should be accepted as a first attempt towards a general first-order pairing interaction for superconductors. On the basis of the theoretical tools employed, it has been neither possible to derive T_c numbers nor to present a theory where all aspects of superconductivity have been treated comprehensively. Future work is required to develop a quantitative microscopical first-order theory of superconductivity. But we are convinced that the elements discussed in the present work are important key parameters of such a theory. Finally we want to mention that we have pointed out physical similarities between the molecular concepts of antiaromaticity and aromaticity, on the one hand, and superconductivity, on the other. We are certain that these phenomena have a common quantum statistical origin.

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[1] R. D. Parks (ed.), Superconductivity, Marcel Dekker, New York 1969.
[2] W. Buckel, Supraleitung, VCH, Weinheim 1990.
[3] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **106**, 162 (1957).
[4] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[5] J. R. Schrieffer, Theory of Superconductivity, Benjamin, New York 1964.
[6] P. B. Allen, Nature London **335**, 396 (1988).
[7] B. T. Matthias, Phys. Rev. **97**, 74 (1955).
[8] B. T. Matthias, Progress in Low Temperature Physics, Vol. II, C. J. Gorter (ed.), Interscience, New York 1957, p. 138.
[9] B. T. Matthias, Helv. Phys. Acta **41**, 1030 (1968).
[10] I. M. Chapnik, Phys. Lett. A **72**, 255 (1979).
[11] I. M. Chapnik, J. Phys. F **13**, 975 (1983).
[12] I. M. Chapnik, phys. stat. sol. b **123**, K123 (1984).
[13] J. E. Hirsch, Phys. Rev. B **55**, 9007 (1997).
[14] P. W. Anderson, Physica C **185-189**, 11 (1991).
[15] D. J. Scalapino, Physica C **235-240**, 107 (1994).
[16] S. Chakravarty and S. Kivelson, Europhys. Lett. **16**, 751 (1991).
[17] W. E. Pickett, Phys. Rev. Lett. **77**, 3185 (1996).
[18] M. C. Böhm and J. Schulte, Physica C **252**, 282 (1995).
[19] A. E. Ruckenstein, P. J. Hirschfeld, and J. Appel, Phys. Rev. B **36**, 857 (1987).
[20] C. Baskaran, Z. Zou, and P. W. Anderson, Solid State Commun. **63**, 973 (1987).
[21] J. E. Hirsch, Phys. Lett. A **134**, 451 (1989).
[22] J. E. Hirsch, Physica C **158**, 326 (1989).
[23] R. B. Laughlin, Phys. Rev. Lett. **60**, 2677 (1988).
[24] X. G. Wen, F. Wilczek, and A. Zee, Phys. Rev. B **39**, 11413 (1989).
[25] G. S. Canright, S. M. Girvin, and A. Brass, Phys. Rev. Lett. **63**, 2295 (1989).
[26] X. G. Wen and A. Zee, Phys. Rev. B **41**, 240 (1990).
[27] F. Wilczek, Spektr. Wissensch., 54 (1991).
[28] G. S. Canright and S.M. Girvin, Science **247**, 1197 (1990).
[29] D.-H. Lee and P. A. Fisher, Phys. Rev. Lett. **63**, 903 (1989).
[30] W. A. Little, Phys. Rev. A **124**, 1416 (1964).
[31] J. Hubbard, Proc. Roy. Soc. A **276**, 238 (1964).
[32] J. Hubbard, Proc. Roy. Soc. A **277**, 237 (1964).
[33] J. Schütt and M. C. Böhm, Phys. Lett. A **219**, 79 (1996).
[34] M. C. Böhm and J. Schütt, Phys. Lett. A **232**, 107 (1997).
[35] M. C. Böhm and J. Schütt, Z. Naturforsch. **52a**, 717 (1997).
[36] M. C. Böhm, J. Schütt, and S. Philipp, Int. J. Quant. Chem. **69**, 727 (1998).
[37] E. Fradkin, Field Theories of Condensed Matter Systems, Addison-Wesley, New York 1991.
[38] P. Jordan and E. Wigner, Z. Physik **47**, 631 (1928).
[39] J. Schütt, J. Schulte, M. C. Böhm, and Z. G. Soos, Mol. Phys. **84**, 1127 (1995).
[40] J. Schütt and M. C. Böhm, Mol. Phys. **85**, 1217 (1995).
[41] L. N. Cooper, Phys. Rev. **104**, 1189 (1956).
[42] P. W. Anderson, Phys. Rev. **112**, 827 (1958).
[43] P. W. Anderson, Phys. Rev. **112**, 1900 (1958).
[44] M. R. Schafroth, Phys. Rev. **100**, 463 (1955).
[45] J. M. Blatt and S. T. Butler, Phys. Rev. **100**, 476 (1955).
[46] M. R. Schafroth, S. T. Butler, and J. M. Blatt, Helv. Phys. Acta **30**, 93 (1957).
[47] P. J. Garratt, Aromaticity, Wiley & Sons, New York 1986.
[48] V. J. Minkin, M. N. Glukhovtsev, and B. Y. Simkin, Aromaticity and Antiaromaticity; Electronic and Structural Aspects, Wiley, New York 1994.
[49] F. London, Phys. Rad. **8**, 397 (1937).
[50] M. C. Böhm, R. Ramírez, and J. Schulte, Chem. Phys. **227**, 271 (1998).
[51] J. Schulte, M. C. Böhm, and R. Ramírez, Mol. Phys. **93**, 80 (1998).
[52] M. C. Böhm, R. Ramírez, and J. Schulte, Z. Naturforsch. **53a**, 38 (1998).
[53] R. Ramírez, E. Hernández, J. Schulte, and M. C. Böhm, Chem. Phys. Lett. **291**, 44 (1998).
[54] R. P. Feynman and A. R. Hibbs, Quantum Mechanics and Path Integrals, McGraw-Hill, New York 1965.
[55] R. P. Feynman, Statistical Mechanics, Benjamin, New York 1972.
[56] W. Heisenberg, Z. Physik **43**, 127 (1927).
[57] Z. G. Soos and S. Ramasesha, Phys. Rev. B **29**, 5410 (1984).
[58] S. Kuwajima and Z. G. Soos, J. Amer. Chem. Soc. **108**, 107 (1987).
[59] M. A. Lee, S. Klemm, and S. Risser, Condensed Matter Theories, Vol. 1, F.B. Malik (ed.), Plenum Press, New York 1986, p. 89.
[60] S. Sorella, S. Baroni, R. Car, and M. Parrinello, Europhys. Lett. **8**, 663 (1989).
[61] E. Y. Loh, Jr., E. Gubernatis, R. T. Scalettar, R. S. White, D. S. Scalapino, and R. L. Sugar, Phys. Rev. B **41**, 9301 (1990).
[62] E. Hückel, Z. Physik **76**, 628 (1932).
[63] C. A. Coulson and G. S. Rushbrooke, Proc. Cambridge Phil. Soc. **36**, 193 (1940).
[64] N. W. Ashcroft and N. D. Mermin, Solid State Physics, Holt, Rinehart, and Winston, New York 1976.
[65] C. Kittel, Introduction to Solid State Physics, Wiley, New York 1976.
[66] M. C. Böhm, J. Schulte, and L. Utrera, Mol. Phys. **79**, 1239 (1993).
[67] J. Lipkin, Quantum Mechanics, North-Holland, Amsterdam 1986.
[68] J. Schütt and M.C. Böhm, J. Phys. Chem. **96**, 604 (1992).
[69] C.A. Coulson and A. Streitwieser, Jr., Dictionary of π-Electron Calculations, Pergamon Press, New York 1965.
[70] E. Heilbronner and H. Bock, Das HMO-Modell und seine Anwendung. Tabellen berechneter und experimenteller Größen, Verlag Chemie, Weinheim 1970.
[71] J. G. Bednorz and A. Müller, Z. Physik B **64**, 188 (1986).
[72] W. Meißner and D. Ochsenfeld, Naturwiss. **21**, 787 (1933).
[73] J. E. Hirsch, Physica C **161**, 185 (1989).