Pure Appl. Chem., Vol. 80, No. 7, pp. 1399–1414, 2008.
doi:10.1351/pac200880071399

Defected/decorated benzenoid/graphitic nanostructures*

D. J. Klein

Texas A&M University at Galveston, Galveston, TX 77553, USA

Abstract: Various decorations, functionalizations, or defects of conjugated benzenoid or graphitic networks are considered, with special attention to the case that the structures are possibly extended in one or two dimensions. This includes various polymers, their end structures, and defects of side groups or vacancies along the chain, strip, or nanotube. This approach further includes various boundary (or edge) structures on semi-infinite graphite, as well as various "quasi-local" defects in what is otherwise two-dimensionally infinite graphite, such defects encompassing vacancy defects, selected substitutional defects, and perhaps even dislocations and disclinations. There are many possible such nanostructures, but property characterization is ultimately desired. Attention is paid to consequent occurrences of defect-localized unpaired (or weakly paired) electrons, as formulated within a resonating valence bond (RVB) framework, especially as regards simple classically appealing theorems or rules. But a further molecular orbital (MO) view is developed. Note is made of associated modifications in the local density of states near the Fermi energy. Consonance of predictions from RVB and MO viewpoints is taken as an indicator of reliable prediction.

Keywords: defects; benzenoids; graphite; valence bond theory; unpaired electrons; bond order; free valence.

INTRODUCTION

Conjugated carbon networks and the behavior of the π-electrons therein have long been of interest. They have proved a testing ground for ideas about delocalized bonding patterns as regards "aromaticity". And in the last three decades, several novel conjugated networks have emerged: conjugated polymers, exemplified by poly-*para*-phenylene; buckminsterfullerene and other fullerenes; carbon nanotubes; and various decorations of various extended conjugated networks. Especially with the advent of interest in nanotechnology, the associated nanostructures typically involve rather large molecular networks, with different possible decorations, so that this, coupled with the delocalized bonding in such systems, then engenders a desire (if not a need) for nice ways to understand these systems in a simple fashion. As is well known, there are two complementary simple approaches—via resonating valence bond (RVB) theory and via simple (tight-binding) molecular orbital (MO) theory. Although MO theory is the basis for most ab initio work, RVB theory connects rather directly to classical ideas, and is here argued to manifest a remarkable ability to make predictions which are both simple to make and qualitatively (or even semiquantitatively) correct. Simple interlocking pictures in both the MO and RVB theoretic frameworks would really be best.

---

*Paper based on a presentation at the International Conference on Modern Physical Chemistry for Advanced Materials (MPC '07), 26–30 June 2007, Kharkiv, Ukraine. Other presentations are published in this issue, pp. 1365–1630.

Before three decades ago, smaller benzenoids (of, say, <40 carbons) or extended graphite were the focus of theoretical treatments, including conceptual developments. On the MO side, early on, Hückel [1] announced his $4n+2$ rule for aromaticity. Coulson and Rushbrooke [2] clearly identified special characteristics of *alternants*, which are systems with separate sets of *starred* and *unstarred* sites such that a site in one set has neighbors solely within the other set. Coulson [3] introduced his bond order. Longuet-Higgins [4] put forward simple techniques to deal with radicaloid aspects, and he also later treated what has since come to be called the "Peirels distortion" in polymers [5], while Pople and Walmsley [6] identified what have come to be called "solitons". Indeed, the British school established a number of conceptual ideas [7–9]. The important role of "frontier orbitals" was (constructively) emphasized, especially by Fukui [10,11]. Woodward and Hoffmann [12,13] introduced simple techniques to address reactivities. Borden and Davidson [14–16] developed qualifications to Longuet-Higgins techniques for radicaloid species. In the 1980s and 1990s, various simple ideas to characterize translationally symmetric extended systems were extensively pursued by Hoffmann [17] and colleagues [18].

There also were VB-theoretic conceptual developments. First, Rumer [19] and then Pauling and Wheland [20] auspiciously advocated RVB theory as a natural quantum mechanical extension of classical chemical-bonding ideas. Pauling [21] widely popularized the ideas in a qualitative format. Hartmann [21] derived a (little-known but nice) substructural expansion for the ground-state energy, such as was later emphasized and extended by Malreiu and coworkers [23–25]. Ovchinnikov [23] enunciated a simple VB-based rule for the ground-state spin-multiplicity of conjugated alternants—and some further related (theorematic) extensions were made [27–30]. Still, MO theory dominated, and ultimately this dominance and especially related criticisms of VB theory were (soundly) critiqued [31]. Developments on through the 1990s are discussed more elaborately in later sections here.

Moreover, there were extensive formal graph-theoretic developments [32–37], which form a precise basis for formulation and characterization of molecular structure. Though sometimes there was emphasis on Hückel MO theory (as with refs. [36,37]), much of the work (e.g., in refs. [33,34,37]) encompassed RVB approaches and more.

On the computational side, there was incredible development, most successfully based on the MO framework (and typically applicable well beyond conjugated networks). But there is no attempt to describe the computational efforts here.

Yet this diversity of work did not for the most part address conjugated-network "nanostructures" before the last two or three decades. This attitude predominated despite the fact that real graphite has boundaries or edges, and often markedly so, in the sense that most graphite is rather impure, consisting of smaller pieces, or having rather many imperfections which may often be viewed to introduce additional (internal) boundary edges. Experimentally occurring graphites seem typically to be ill characterized as to the nature of the edges or of the imperfections, and instead often seem to be characterized [38–42] as to a few bulk properties and methods of preparation. One attempt to forego ideal translational symmetry was made by Coulson and coworkers, first with just one dimension of symmetry [43,44] (for a special case of graphitic strips), and then with no translational symmetry, for the special case [45,46] of a single vacancy in graphite. But overall, decorated graphite was little treated via either MO or RVB, either computationally or conceptually. And even perfect graphite was little treated by VB theory in any mode (e.g., until the 1980s) first primarily in a computational mode [47,48], though in fact some initial conceptual ideas for defects at ends of polymer strips [47] or for selected edges [49] were intimated. In fact, some numerical work in the 1980s [50,51] was interpreted to indicate that MO and RVB theories were at odds with one another as concerns edge effects in large benzenoid flakes. Defect (or decoration) illuminating work starting in the 1990s is discussed in later sections here.

Interest and work on π-network polymers took off dramatically around 1980 with seminal experiments [52,53] and MO theoretical developments [54,55] involving Peirels distortions and solitonic excitations. Indeed, this theoretical work [5,6] was anticipated more than a decade earlier, but the later treatment was independent and more complete. Numerous chemically oriented reviews and books appeared, framed entirely in the MO picture. Still, some RVB computational and conceptual developments were occasionally made.

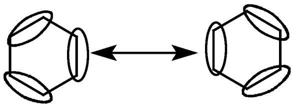
As to fullerenes, theoretical work [56–58] predating the seminal experimental discovery of Kroto et al. [59] was largely of a qualitative nature. But immediately after, progress was made not only in an MO framework, but also in a resonance-theoretic framework [60–62], which included the initial announcement of the "isolated-pentagon rule". Much was also made of the relevance of "leap-frog" structures, with motivation from a combination of structural [63,64], MO-theoretic [65,66], and VB-theoretic [67,68] arguments.

And finally, another major development concerned carbon nanotubes [69,70] (or buckytubes), with much of the general initial work [71,72] in an MO-theoretic framework. Here there is a widespread view that these very strong and often electrically conducting tubes may be the centerpiece of different nanodevices. And it has further been generally understood that decorations of the tubes are likely fundamental. Indeed, numerous computational studies have been made, almost all entirely in an MO- or band-theoretic framework.

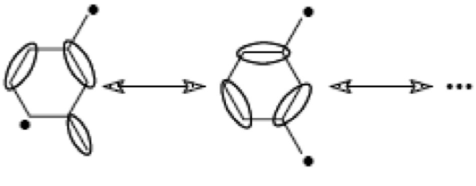
Here attention is directed to conceptual approaches to conjugated network nanostructures, especially those which are extended in one or two directions of meso- or macroscopic lengths, though with the allowance of decorations or defects. Both RVB and MO concepts are noted, with special attention to their coincidences of prediction, and the consequent extension of classical chemical ideas into the realm of extended decorated (or functionalized) nanostructures.

A SIMPLE RESONATING VALENCE BOND APPROACH

The RVB development is conveniently phrased pictorially, in consonance with traditional resonance theory. A single π-electron of spin up or down is viewed to occur on each π-center, with the resonance structures being *pairing* patterns between these spins. Such electron-pairing patterns are long well-known in the case of benzene



following Pauling and Wheland [20,21], and many organic texts. But also radicals have resonance structures, as for *m*-xylylene:



manifesting unpaired spins. Both radicaloid and non-radicaloid resonance structures are of interest in polymers and large extended systems, as are relevant for materials science and nanotechnology. If allowance of a very few but non-minimal number of unpaired electrons gives many additional resonance structures, then these (often called "excited") structures might significantly contribute to the (ground-state) description—and if the unpaired electrons are very delocalized, they need not be so reactive, in the sense that the "free valence" on any given site can then be very small. That is, more than the highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) gap or net free valence, a "better" reactivity indicator is free-valence "density" (or spin density).

It is convenient especially for larger systems to use an "averaged" representation of resonance structures, to bypass detailed consideration of the possibly hugely immense numbers or resonance structures, even with limitation to the fully paired Kekulé structures. For example, for buckminsterfullerene C_{60}, there are 12 500 Kekulé structures [60], and for the icosahedral-symmetry C_{180} fullerene, there are over 10^{12} (i.e., 1 389 029 765 625) Kekulé structures [73]. For a buckytube with a 6-ring cyclic polyacene unit repeated L times along the length, there are (asymptotically) $\approx A{\cdot}6^L$ Kekulé structures [73], with A an L-independent constant depending on the terminal cap structure, so that for a relatively short length $L = 100$ buckytube, one finds an astronomical number $\sim 10^{78}$ of Kekulé structures. Thence again, it seems desirable to avoid a traditional generation of explicit resonance patterns.

The presently considered simplified formulation [75–79] is most readily made to *alternant* systems in which the conjugated centers are partitioned into *starred* (*) and *unstarred* (o) subsets such that neighbors of a site in one of these sets are always in the other set. Then, in consonance with classical chemical-bonding ideas, stability is to be enhanced in accordance with three *stability criteria*:

($\mathbf{0_{RVB}}$) **alternancy pairing:** Lower-energy states entail pairings solely between sites of different *types* (starred and unstarred).

($\mathbf{I_{RVB}}$) **pairing locality:** Stability is enhanced by more pairings of neighbor spins, and the stabilization rapidly falls toward 0 as the distance between spins increases.

($\mathbf{II_{RVB}}$) **resonance:** Stability is enhanced by greater extents of spin-pairing delocalization (or resonance) amongst different pairs of atoms.

The alternancy criterion ($\mathbf{0_{RVB}}$) is suggested [75] from quantum mechanical VB-theoretic considerations [19,24,80–82], but it was arguably complicit in early classical ideas of Thiele [83], and more marginally back to Claus [84], Armstrong [85], and Bamberger [86]. Criterion ($\mathbf{0_{RVB}}$) is not exactly a "stability" criterion in that in addition to the low-energy states, many high-energy states are also encompassed. A quantification of the pairing-locality criterion ($\mathbf{I_{RVB}}$) simply counts the number of nearest-neighbor pairings (and at a finer level of detail one could attend to the number of non-neighbor pairings). A quantification of the resonance criterion ($\mathbf{II_{RVB}}$) is more delicate, but it is noted that the last two criteria can act either in concert or in opposition, depending on the structural circumstances. That is, non-neighbor pairing may enhance resonance at the expense of neighbor pairings.

To understand better the balance between local pairing and resonance, consider some average or "mean-field" quantities. Let p_{ij} be a resonance-theoretic (π) *bond order* between sites i and j (of opposite types) as the fraction of resonance structures in the considered ground state having a pairing between sites i and j. Then

$$v_i = 1 - \Sigma_j\, p_{ij} \tag{1}$$

is a resonance-theoretic *free valence*, where it is understood that the p_{ij} are non-negative with a sum at each site ≤ 1, so that each free valence v_i satisfies $0 \leq v_i \leq 1$, and is viewable as the unsatisfied portion of the π-valence at site i. Stability enhancement via local pairing, as in ($\mathbf{I_{RVB}}$), entails larger values of p_{ij} for nearer spins. Stability enhancement via resonance, as in ($\mathbf{II_{RVB}}$), entails comparable p_{ij} for different j adjacent to i, i.e., $p_{ij} \approx 1/d$ if site i is of degree d (with $d = 3$ in graphite and buckytubes, while $d = 2$ in annulenes). With i and j restricted to neighbors, Pauling [87] took p_{ij} to be the fraction of maximally paired resonance structures with a π-bond between sites i and j. And such a 0-order p_{ij} has been demonstrated [35,88–90] to correlate nicely with experimental bond lengths, of closed shell (non-radicaloid) species. Sometimes it is appropriate to relax this (0-order) neighbor restriction, and consider the p_{ij} for non-neighbor i and j (perhaps without recourse to a detailed consideration of the resonance structures).

A simple approach [75–78] previously used for defected graphite takes the $p_{ij} \approx 1/3$ for nearest neighbors in the bulk of the material. Then the v_i can (effectively) be non-zero solely in the region of the defect. This result is strengthened on noting that if v_i is restricted so that only sites j within a certain distance are summed upon, then this is really an effective free-valence in that any pairing between distant sites generally should contribute little to stability (i.e., the unpairing of spins paired only at a great distance in an exact ground-state should cost little energy, and thereby give rise to low-lying excited states). In particular, neglect of pairing over bulk distances is surely reasonable for a meaningful free valence, if it is to indicate an unsatisfied propensity for the formation of local strong bonds. On the other hand, attention to long-distance pairing is appropriate if global ground-state (finite-molecule) spin is addressed.

These ideas now outlined are in reasonable consonance with standard presentations in organic textbooks of 40 years or so ago, though subtly differing in an emphasis on (Pauling) bond orders p_{ij} and free valences v_i. The utilization of p_{ij} and v_i without explicit reference to individual resonance structures leaves some ambiguities for small molecules—though for extended systems there arise some unambiguous results, which in fact are typically not readily obtained otherwise in a general form. The application to small-molecule systems is perhaps less interesting, but there are a couple points which may be made, using primarily just the "stability" criteria ($\mathbf{0_{RVB}}$), ($\mathbf{I_{RVB}}$), and ($\mathbf{II_{RVB}}$). First, from ($\mathbf{0_{RVB}}$) and ($\mathbf{I_{RVB}}$), it is seen that if pairing to all distances is taken into account in an alternant molecule B, then the ultimate remaining number of unpaired electrons is simply

$$u(B) = |\#_*(B) - \#_o(B)| \tag{2}$$

where $\#_*(B)$ and $\#_o(B)$ are the respective numbers of starred and unstarred sites in B. That is, the RVB-predicted ground-state spin is $S = |\#_*(B) - \#_o(B)|/2$. But this is in precise agreement with the surmise of Ovchinnikov [26] as well as with rigorous theorems both for the full covalent-space Pauling–Wheland VB model [91–93] and for the Hubbard model [94], these theorems considering exact solutions rather than say SCF approximations. And yet further there are [95] systematic computed tests for the PPP model yielding uniform agreement (for most all systems exactly treatable via brute force configuration interaction). And also there are occasional high-quality ab initio computations or experimental data for different individual molecules (typically also in agreement). Besides the ground-state spin, more details of the p_{ij} and v_i indicate where the ground-state unpaired spin-density tends to be localized and whether there might be low-lying excited states (if the paring is weak, being between very distant sites). But large (e.g., infinitely extended) systems are also of interest.

SIMPLE RESONATING VALENCE BOND APPROACH APPLIED TO DEFECTED GRAPHITE

For extended conjugated networks, the three stability criteria often provide surprisingly strong results. A further general long-held idea is often also used, namely:

saturation principle: Many (size-extensive) properties saturate, in that they manifest (near linear) dependencies only on local (or nearby) substructures.

Indeed, this is often implicit in much chemical reasoning, e.g., including the idea of functional groups in organic (and even inorganic) chemistry. That is, if the behavior of functional groups were to depend strongly on distant structural features, then they would not be so extremely important.

An informative example is that of *semi-infinite* graphite with a single long "globally straight" boundary, for which there are many possibilities, including the so-called "zig-zag" boundary of alternating degree-2 and degree-3 atoms. See Fig. 1. For this zig-zag boundary, traditional fully paired Kekulé structures are possible, though then the interior does not appear as in bulk graphite with bonds in each of the three directions equivalent. But attending instead directly to bond orders and free valences, the competition between resonance (criterion ($\mathbf{II_{RVB}}$)) and local pairing ($\mathbf{I_{RVB}}$) implies that the bulk interior manifests full resonance, with bond-orders of 1/3 in each direction from an atom up to or near the boundary. As a consequence, one finds a plausible pattern for free valence gives a net of 1/3 of an unpaired electron on each aceneic point of the zig-zag boundary—and all being sites of the same type, the "alternancy pairing" criterion ($\mathbf{0_{RVB}}$) implies that they do not pair to one another. But this is an extreme approximation as to spin-density location, with the plausibility that some delocalization of

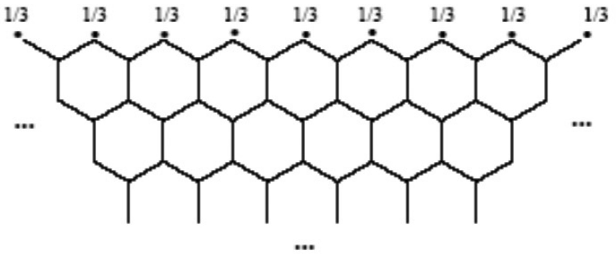


Fig. 1 A portion of zig-zag boundary, with free valences following from the RVB arguments.

the unpaired electrons occurs a little into the region near the boundary (but remaining primarily though not necessarily only on the same type of sites), with the net unpaired spin density being 1/3 of an electron per unit cell of edge.

Another example of a graphitic boundary is that which looks like a corrugated "arm-chair" boundary, and has a repeating pattern of two degree-2 sites followed by two degree-3 sites. Here one still imagines that the bulk of the interior is like bulk boundary-less graphite, though now this does not imply any unpaired spin density near the boundary, as is summarized in the pairing-pattern data of Fig. 2, where the bulk of the bonds with bond orders of 1/3 have not been explicitly so labelled, so as to keep the figure "cleaner", and show values only for the modified bond orders. Again, these "0-order" bond orders near the boundary are not necessarily exactly correct but should take modified non-1/3 (and non-2/3) values with associated partial "bond localization" extending a short distance away from the boundary, while still approaching the uniform-1/3 values of bulk graphite in the interior. Here there remain no unpaired electrons.

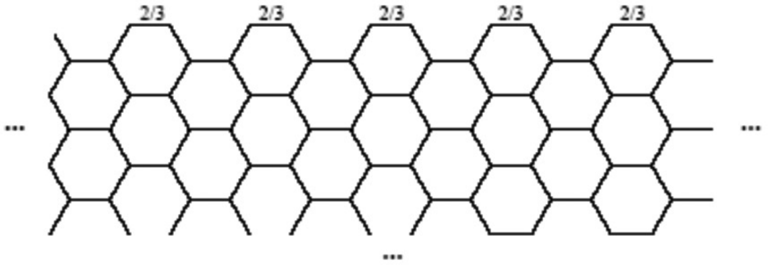


Fig. 2 A portion of semi-inifinite graphite with "arm-chair" edge. So-called "non-normal" bond orders of other than 1/3 are shown.

Such results for general translationally symmetric graphitic boundaries are really fairly easily established within the simple RVB scheme outlined, and in fact through it one may make [75–77] a general formula. If $\#_{n*}$ and $\#_{no}$ denote the numbers of degree-n starred and unstarred sites per repeat unit along the boundary, then the number of unpaired electrons per unit cell is

$$u_{\text{cell}} = \left|(2\#_{1*} + \#_{2*}) - (2\#_{1o} + \#_{2o})\right|/3 \tag{3}$$

Of course, it is realized that the degree-1 and -2 sites occur exclusively at the boundary.

A rather general result is also possible for vacancy defects in graphite. That is, one or more nearby sites are imagined missing from an extended graphitic structure leaving a hole of some shape. For instance, with a single-atom hole and the bulk of the bond orders being 1/3, most simply all the way up to the defect, this leaves 1/3 of an unpaired electron on each of the 3 adjacent sites, as in Fig. 3, where the exceptional sites are marked with dots. Again, one expects some delocalization of the unpaired electron away from the defect, though there remains a net of 1 unpaired electron.

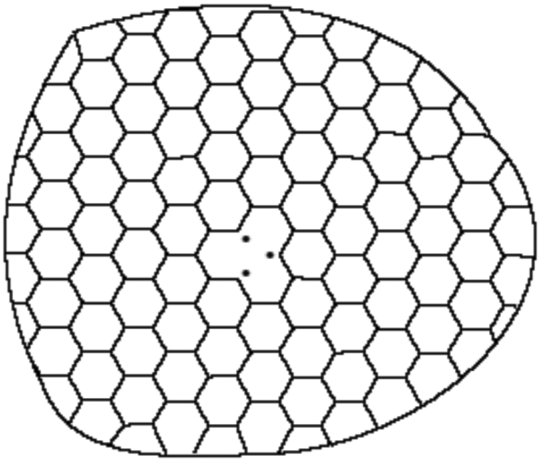


Fig. 3 A portion of doubly infinite graphite with a single vacancy defect, and consequent "0-order" unpaired spin densities (of 1/3) on the sites adjacent to the vacancy.

Rather generally, a hole may be viewed to arise from deletion of some benzenoid molecular network R, so that one might denote the so defected graphite by Я. Then the general prediction [76,77] for the number u(Я) of unpaired electrons localized in the area of the defect Я is

$$u(\text{Я}) = |n_*(\mathrm{R}) - n_o(\mathrm{R})| \tag{4}$$

where the right-hand side is just what was earlier identified as the number of unpaired electrons in a molecule R. Really, this just says that the local pairing of the deleted molecule being incomplete would, when inserted in the graphitic vacancy Я, be such that there would be pairing between R and Я such as to precisely accommodate one another and leave perfect graphite. That is, Я is sort of an *anti-molecule* to R. Further R need not be connected—or equivalently R could represent a pair of molecules, though one then needs [77] to take care in assigning * and o sites of R to coincide with that for the underlying parent graphite net.

Elsewhere, such general related RVB predictions have been elaborated for

- different "locally neighbor paired" polymers with various types of ends terminating the polymer to give different predicted spin densities at these ends [76,78];
- different "locally neighbor paired" polymers with various types of vacancy or add-on defects along the otherwise very long polymer to give different predicted spin densities at these defects [78];
- different defects along otherwise perfect edges in graphite [78]; and
- a few more speculative related applications to heteroatomic and even inorganic systems [78].

Further predictions for carbon nanotubes are readily implemented with various types of ends leading to different spin densities at these ends—or alternatively with different defects along the length of the tube—or yet further at junctions or joinings of different such tubes.

A SIMPLE MOLECULAR ORBITAL APPROACH

Though these general results of the preceding two sections were made here (and originally) in the RVB framework, it would be nice to have a parallel simple tight-binding or Hückel-theoretic development. Thence, in consonance with traditional MO-theoretic ideas, three *stability criteria* are here formulated:

($\mathbf{0_{MO}}$) **alternancy pairing:** Orbital energy levels are paired about the 0 of energy (or Fermi level), and bonding is to occur only between sites of different types.

($\mathbf{I_{MO}}$) **bonding locality:** Stability is enhanced by stronger interaction energies (or bonding propensities) between neighbor sites, and these propensities rapidly fall toward 0 as the distance between sites increases.

($\mathbf{II_{MO}}$) **delocalization:** Stability is enhanced by greater uniformity of interaction energies amongst different pairs of neighbor sites.

The alternancy criterion ($\mathbf{0_{MO}}$) is simply that proved for alternants by Coulson and Rushbrooke [2], and also (in parallel to the RVB case) ($\mathbf{0_{MO}}$) is not exactly a "stability" criterion in that it allows many (symmetric) distributions of the levels about 0. A quantification of the bonding-locality criterion ($\mathbf{I_{MO}}$) might be sought in terms of standard Coulson bond orders. A quantification of the delocalization (or resonance) criterion ($\mathbf{II_{MO}}$) is more delicate, but as in the RVB picture the last two criteria can act either in concert or in opposition, depending on the structural circumstances. That is, non-neighbor interaction energies may enhance resonance at the expense of neighbor interaction energies.

Quantification might reasonably be approached via Coulson bond orders and free valences, which, however, only approximately comport with both the corresponding RVB and classical ideas. For instance, the Coulson bond order [3,96] between sites i and j is rather generally taken as $\langle h_{ij} \rangle$ where the Hückel interaction between sites i and j is just $\beta_{ij} h_{ij}$, with β_{ij} the intersite electron-hopping integral, and the expectation is with respect to the ground-state wave-function. Though clearly Coulson designed this MO concept to correspond to classical bond-order ideas, the π-bond orders can be greater than 1, as for benzene, which has 4/3. The complementary Coulson free valence has been defined [75–77] slightly differently at different times, but generally taking it to be of the form $A - \Sigma_j^{\sim i} \langle h_{ij} \rangle$ with different choices for the reference value of A.

Granted, the proportionality of the bond order to the $\langle h_{ij} \rangle$, the MO criteria ($\mathbf{0_{MO}}$), ($\mathbf{I_{MO}}$), and ($\mathbf{II_{MO}}$) may be rationalized in more detail, with the utilization of the expression

$$\langle h_{ij} \rangle = \sum_{\xi}^{occ} (c_{\xi i}^{*} c_{\xi j} + c_{\xi j}^{*} c_{\xi i}) \tag{5}$$

where the sum is over occupied MOs ψ_ξ with an amplitude $c_{\xi i}$ on site i. From the Coulson–Rushbrooke result [2] that the MO $\psi_{\bar{\xi}}$ correspondent to ψ_ξ has amplitudes $c_{\bar{\xi} i} = \pm c_{\xi i}$ as site i is starred (*) or unstarred (o), it follows that if i and $j \neq i$ are of the same type (* or o), then the sum Σ_ξ^{occ} of eq. 6 may be replaced by $\frac{1}{2}\Sigma_\xi^{all}$ and give $\langle h_{ij} \rangle = \langle i, j \rangle = \delta_{i,j} = 0$. That is, just as for the RVB case "pairing" between sites of the same type is avoided. Also, eq. 6 is useful when one understands that the $c_{\xi i}$ are essentially wave amplitudes with the longer wavelengths corresponding to lower energies and greater stability. Thence, when i and j are far apart, there are more sign changes for $c_{\xi i}^{*} c_{\xi i}$ as ξ ranges over the occupied orbitals, so that then there is more cancellation in the ξ-sum, thereby yielding a smaller $\langle h_{ij} \rangle$, at larger i,j-distance, as claimed in ($\mathbf{I_{MO}}$). The justification for ($\mathbf{II_{MO}}$) is similar, in that it essentially demands little such cancellation from one neighbor of a site i to another neighbor—such cancellation needs to happen if there were very different (i.e., non-uniform) $\langle h_{ij} \rangle$ for site i to its different neighbors.

Discrepancies of these bond orders and free valences from classical expectations often are viewed simply as naught but an imperfection of the classical ideas, with the quantum formulation the proper one. But there is also an "opposite" argument, that the Hückel model is naively simple, with an expectation (or at least a possibility) that improved quantum mechanical modeling may bring behavior more closely in consonance with classical ideas. In fact, it seems reasonable to expect that both the Hückel model and the classical ideas will have shortcomings, very likely to different extents in different circumstances in describing different properties and molecules. It is especially clear (for perhaps the last half-century) that the classical ideas, even when the simplest RVB modifications are casually invoked, are rather poor in application to "anti-Hückel" systems, with rings of size 4n. But this does not mean that classical ideas as moderated by RVB are poorer for benzenoid systems. And, for example, RVB ideas have here been noted to give rise to the simple ground-state spin formula for which a range of rather sound evidence has accumulated, as mentioned earlier. But also for benzenoids, there is [100] rather precise agreement between the restricted form of RVB theory with focus exclusively on neighbor pairing, and Hückel MO theory. Indeed, this agreement has been noted [101,102] at least a couple times around 1980, though ref. [100] in 2005 seems to be the first proof of this. But, again, as already complicit in the discussion preceding the formula 2, the RVB argument for this generally goes beyond the nearest-neighbor limitation. Thus, this bit of evidence suggests that at least as far as ground-state spin density goes, the refined RVB theory described here is superior to simple Hückel theory, while at the same time there is a degree of agreement for benzenoids between the nearest-neighbor restricted RVB picture and Hückel theory. This in turn suggests that some slight modification of Hückel theory may do very well for benzenoids and perhaps beyond, in light of the great success of Hückel's $4n+2$ rule.

Overall, it might be reasonable to make slight modifications of the ordinary (Coulson) bond order and free valence. As already noted, the $\langle h_{ij}\rangle$ are often >1, though there is little evidence to indicate that the π-bond is so much more stabilizing than a σ-bond, which is assigned a bond order of 1. Also, the A in the free-valence definition as $A - \Sigma_j^{\sim i} \langle h_{ij}\rangle$ is usually assigned a value so that this free valence (at least often) remains >0. But one common choice of $A = \sqrt{3}$ (to keep the free valence at the center carbon of trimethylene methyl ≥0) gives other free valences rather high (e.g., ≅ 1.732 for the methyl radical and ≅ 0.732 for ethylene). At the same time, if one interprets the free valence as a spin density, then it should in fact occasionally be <0 (indeed for trimethylene methyl). Here, it is proposed to use a different reference benzenoid in defining these quantities (i.e., the "perfect" defectless benzenoid) that is, the benzenoid without external or internal defect (i.e., without outer boundary or inner vacancies)—that is, graphite is used as a reference. Thus, a *Coulson bond propensity* (or *ideal* Coulson bond order) is defined as

$$p_{ij} = \langle h_{ij}\rangle / \langle h\rangle_{\mathrm{ref}} \tag{6}$$

where $\langle h\rangle_{\mathrm{ref}}$ is the nearest-neighbor Coulson bond order for graphite, i.e., $\langle h\rangle_{\mathrm{ref}} \cong 1.04973$. Moreover, the *ideal* Coulson free valence is defined as

$$v_i = 1 - \Sigma_j^{\sim i}\, p_{ij} \tag{7}$$

This then is in rather precise consonance with both classical and RVB ideas (so that the same notation has been used for p_{ij} and v_i).

It is imagined that these "ideal" MO quantities correlate to molecular reality in the same way as anticipated classically. This really is just to say that classical ideas being based on chemical reality have some degree of correctness, and that Coulson got his correspondent nomenclature right. Then, for graphite with a boundary, it is imagined that in the bulk, the (ideal) free valences are 0 with the (ideal) bond orders each 1/3, any deviations arising at or near the edges, with the condition (eq. 7) then holding. As a consequence, exactly the same overall formulas follow for the MO-based approach as for the RVB approach.

In conclusion, eqs. 2–4, and others [79] are obtained in an MO framework. Notably, the applications are simpler to make than the size of the present section might suggest, because here background justifications and derivations have been addressed, and these need not be used in applications. The point is that the earlier RVB-based tools are also justifiable from an MO viewpoint. A question remains as to whether our "massaged" Hückel theory (or RVB theory) really does comport with the apparent chemical reality in the way postulated, when more empirical tests are made.

TIGHT-BINDING MOLECULAR ORBITAL COMPUTATIONAL TESTS

Computational MO-based tests of these predictions (as in eqs. 2–4) have indeed been made, though there is some trickiness in dealing computationally with defected graphitic structures. Thus, in place of semi-infinite graphite, with a nice translationally symmetric boundary, one may deal with a strip with two parallel edges cut from graphite, and investigate the behavior as the width *w* of the strip becomes ever wider. Thus, for the polyacene-like zig-zag edge of Fig. 1, computations have been made [103–106], though only the last of these computations identifies the relevant band-theoretic feature described below. This important feature entails many band states which are localized near the edges (primarily on the polyaceneic degee-2 points) and these states have very nearly 0 energy (i.e., are essentially nonbonding). Indeed, these band states are exponentially localized near the strip edges, and are exponentially (in strip width) close to nonbonding. Moreover, these exceptional localized nonbonding band states are easy to recognize in the band structure, as they occur in regions outside of that appropriate to extended graphite. And yet further, the number of such nonbonding band states is precisely such as to give the same number of unpaired electrons per unit of strip length as predicted by the simplified schemes of the preceding two sections. For the polyacenic example, this number is 1/3 of an unpaired electron per unit of length and is reflected in terms of a nonbonding 1/3-portion of an otherwise binding band—as in Fig. 4 for strips of width *w* = 1, 2, 3, and 4 hexagons. Following an earlier type of presentation [107], this figure has [77] a shaded area locating the great portion of the bands where for any strip width the orbitals are delocalized across the strip, and only the portions of the band penetrating out of this "normal" region are detailed. The exceptional band portions for the widths *w* = 1, 2, 3, and 4 strips are respectively shown in the 1st, 2nd, 3rd, and 4th quadrants, whence it is seen that these band portions close in ever more tightly on the nonbonding energy 0 as *w* increases. For *w* > 10, these exceptional 1/3-portions are (on the scale shown) essentially identical to 0 where the wave-vector *k* is either in the region 2π/3 → π or in the region –π → –2π/3.

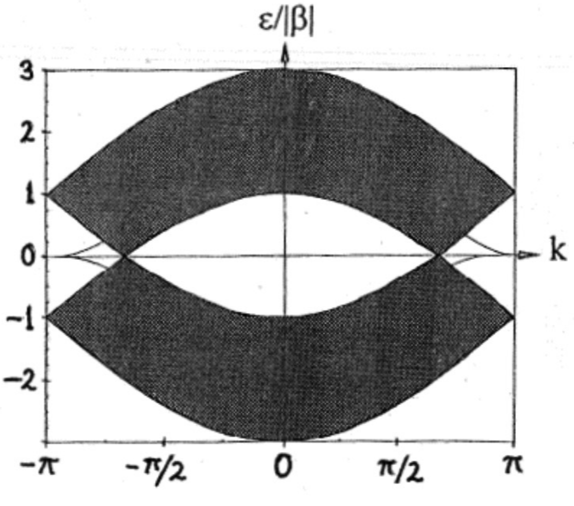


Fig. 4 Zig-zag strip band structure, with the delocalized band region shaded, while the band portions for edge-localized orbitals penetrate outside into the unshaded area. The exceptional band at width *w* appears in the *w*th quadrant, near the *k*-axis.

Looking at the argument in greater detail, first note that the Coulson–Rushbrooke alternancy theorem [2] implies that to each (provisionally bonding, but very nearly nonbonding) band there corresponds a mirror provisionally anti-bonding band which similarly manifests a similar 1/3-portion which approaches 0, also as seen in the figure. Second, one notes that in proceeding just a little beyond the simple tight-binding model, as to an SCF solution of the Hubbard model, it becomes energetically favorable to make an unrestricted Hartree–Fock (UHF) solution, where such Coulson–Rushbrooke pairs of near-0-energy MOs are combined in + and – combinations to give nonsymmetric UHF orbitals localized on the two different band edges, whereafter these new UHF orbitals are singly occupied. This single occupancy reduces electron–electron repulsion within these orbitals, while at the same time costing just the barest promotional orbital energy, since the splitting between these paired bonding and antibonding orbitals is exponentially small. This single occupancy then places electrons of one spin (say up) along one edge and those of the other spin (down) along the other edge. Thus, the amount of spin density precisely comports with the simple predictions, and the location also comports roughly with the simple predictions. Interestingly, there are now in the last decade perhaps a dozen more computations (e.g., [108–112]) on this particular sort of polyacene edge, all incorporating these same points, short of mentioning the RVB view, though it was first [49] in 1985 that RVB theory (in an earlier Kekulé-structure attentive form) that predicted extensive unpaired electron density at this boundary edge.

This general picture of portions of essentially nonbonding band states localized near an edge has been tested, first for a few edges [106,107,113,114] and then more completely [75–78,115], now for roughly two dozen choices of edge. In the different cases, the simple RVB prediction varies over values 0, 1/3, 2/3, 1, 4/3, … of an unpaired electron per unit cell of edge. And in all cases examined, the UHF picture outlined in the preceding paragraph applies to accommodate exactly the same number of unpaired electrons per unit cell of edge, with the unpaired electrons always localized in the region indicated by the simple argument. Moreover, the results qualitatively corroborate different observations [50,51] of nonbonding edge-localized orbitals on large benzenoids.

But in addition to defects consisting of edges, one might reasonably test predictions made for vacancy defects (e.g., predictions via formula 4). To make such computational tests, one works not with (defected) infinite graphite but rather with large fragments of 1000 or more sites with the defect localized near the center of the fragment. But it is then of value to understand the effects of edges, and choose an edge that does not lead to nonbonding orbitals which could in such a finite fragment interfere (i.e., mix) to some extent with the defect-localized orbitals, and complicate the results—indeed, it is even of value to try to avoid corners (where two edges meet) leading to unpaired electron density in these regions. Indeed, all this has been done [76,77], with the orbital density for the HOMO (or LUMO) indicated as a function of the distance from the defect indicated in Fig. 5 for three example defects. There, the logarithm of the net density at a given number n of hexagons away from the defect is plotted as a function of n. It is seen, for the first case consisting of a single-site vacancy defect, that this orbital is fairly strongly localized near the vacancy. In the second case with two adjacent sites vacant, our simple argument predicts no defect-localized orbitals and again agreement is obtained. The third case is for a vacancy of three adjacent sites, giving one singly occupied defect-localized nonbonding orbital. The ~5 orders of magnitude drop of the defect-localized orbital density is quite dramatic—but also the energies of the localized and next-higher HOMO energy delocalized orbital are larger by a factor ~10. For a sampling of about two dozen different choices of defects, one finds defect-localized nonbonding MOs processable into UHF orbitals to precisely match the number of unpaired electrons predicted by formula 4. And again this corroborates some other qualitative observations which were previously made [45,46] on a selected few vacancy defects. Evidently, a point of utility of the simple predictions is as a guide of what to look for, such as in some cases was not originally imagined, or checked.

Yet further similar MO-based tests have been made [76,77] for predictions of unpaired spin density at the ends of polymer chains. Though tests here are perhaps for no more than a dozen cases, the agreement again is perfect (so far as tested). In addition to MO tests, there have been some qualitative tests [47,49] via more computationally related VB-based arguments.

A number of RVB predictions [78] for defected edges, corner defects, and internally defected polymers have been made. Though these have not yet been well tested via computational MO work, the success with the edges and vacancy defects bodes well for these other predictions.

A not unrelated comparison [116] has been made of predictions concerning Peirels distortions and solitonic excitations. Here, simple (but more conventional Kekulé-structure-attentive) RVB predictions appear to be in perfect agreement with simple Hückel-theoretic computations for about a dozen cases.

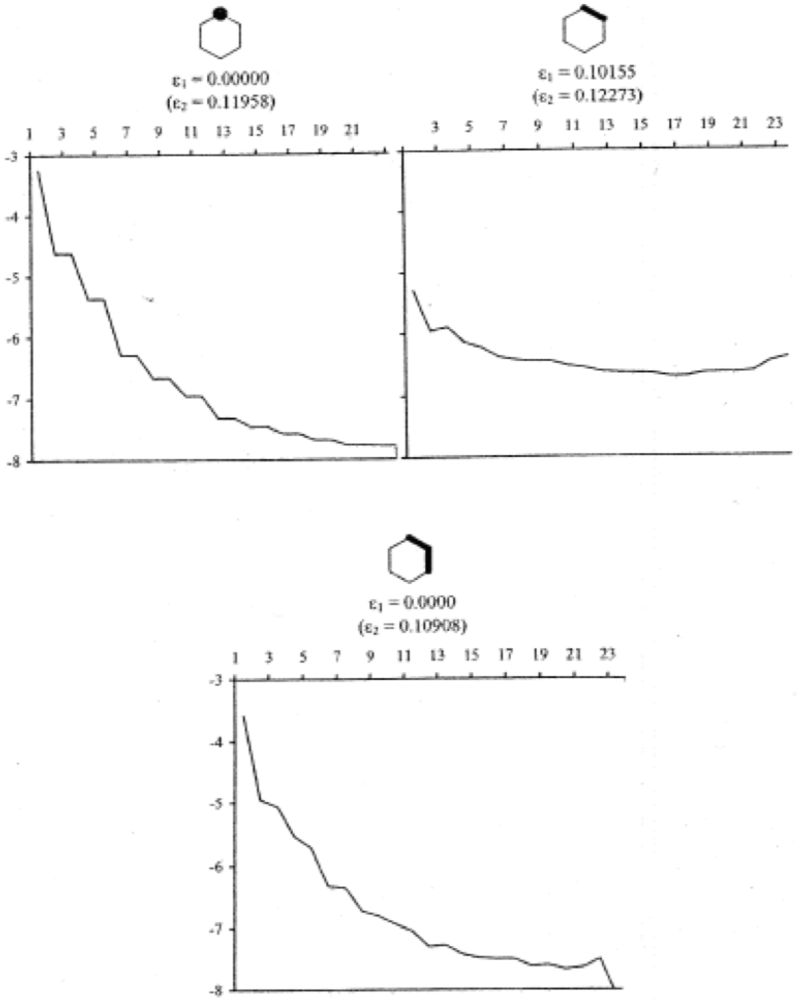


Fig. 5 Log-density plotted as a function of the distance from the defect for three different types of vacancy defects. Here, ε_1 is the HOMO energy (in units of $|\beta|$), and ε_2 is the next higher orbital energy.

DISCUSSION AND PROGNOSIS

Finally, there is the question of comparison to experimental data. Such experiments unambiguously testing such predictions appear to be a challenging matter. But, e.g., for polyaceneic zig-zag edges [117] (with $u = 1/3$) and arm-chair edges [118] (with $u = 0$), there are electron-tunnelling microscopy results. These data do not give very precise values for the extent u of unpairing, but the data appear in at least qualitative concert with the RVB predictions: the emission of electrons occurs more readily from the acenic edges (just where the prediction indicates that the more weakly bound electrons reside). Much the same can be said for the cases [119–121] of a single vacancy and a neighbor vacancy pair [122] of sites.

Overall, it seems that there is a close correspondence between our simple RVB predictions and UHF-modified Hückel-theoretic predictions, at least for benzenoid (or graphitic) π-networks, and yet this agreement seems to carry over to chemical reality. This then recommends the general bond-order and free-valence ideas, at least in this benzenoid context. The ideas are easy to apply in extended systems, even when defected, with nontrivial predictions for a suite of prospective novel nanostructures.

The consonance with classical chemical-bonding ideas is notable and encouraging. The once-questioned idea that the RVB approach is reasonable is further [31] supported. It seems that extended conjugated networks can be quite profitably viewed in a simple extension of classical chemical-bonding ideas. The simple formulas 2–4 seem to work—and then presumably also a couple of further related formulas in ref. [79].

Certainly these ideas should be further used to guide conventional quantitative computations. Such guidance is useful as an indication of what to look for, and the relevance in this regard appears in that relevant aspects were sometimes missed in a few earlier studies (often MO-based, but sometimes also resonance-theoretically based). The relevance of UHF ideas, and associated orbital localization, and further associated "unpairing" is evidently important to keep in mind.

Some additional MO-based computational tests are plausible, for some predictions not yet so well tested. In particular, such work on carbon nanotubes should be of value—say, as concerns their end structures, and also as concerns internal defects, decorations, or functionalizations.

Application to dislocations and disclinations is of great promise since these are in general rather difficult to treat because of the loss of translational symmetry. The extension to these cases is to be made with some care, as this proceeds outside of the seemingly safe realm of strict benzenoids, which are alternant and largely Hückeloid with a preponderance of $4n+2$-sized conjugated circuits. Such defects may be involved [123] in possible brittle-ductile transitions, and melting of graphite. Disclinations in graphite are naturally composed from 5- or fewer-membered rings, and lead to bucky-cones (e.g., as discussed elsewhere [124]), and if the Gaussian curvature is imagined to be increased (through the additional small rings) so that such a cone closes on itself, fullerenes are obtained. Thus, a refined view of fullerenes might emerge. Indeed, more traditional RVB work (e.g., in refs. [60–62,67]) for fullerenes holds some promise for the present ideas (perhaps somewhat modified) to apply to non-alternants.

It would be desirable to extend the RVB ideas to describe electrical conduction. In this regard, Anderson's [125] ideas about RVB theory to describe high-temperature superconduction indicates that the approach is quantum mechanically sound. See also reviews [126–129]. And in the context of benzenoids, there is some indication [60,130] of the success of RVB theory in dealing with conduction.

Finally, more quantitative development of the "mean-field" RVB ideas outlined here certainly seems promising.

ACKNOWLEDGMENT

Support via grant BD-0894 from the Welch Foundation of Houston, Texas, is acknowledged.

REFERENCES

1. (a) E. Hückel. *Z. Phys.* **72**, 310 (1932); (b) E. Hückel. *Z. Phys.* **76**, 628 (1932).
2. C. A. Coulson, G. S. Rushbrooke. *Proc. Cambridge Philos. Soc.* **36**, 193 (1940).
3. C. A. Coulson. *Proc. R. Soc. London, A* **169**, 413 (1939).
4. C. H. Longuet-Higgins. *J. Chem. Phys.* **18**, 265 (1950).
5. H. C. Longuet-Higgins. *Proc. R. Soc. London, A* 251 (1959).
6. J. A. Pople, S. J. Walmsley. *Mol. Phys.* **5**, 15 (1962).
7. (a) C. A. Coulson, C. H. Longuet-Higgins. *Proc. R. Soc. London, A* **191**, 39 (1947); (b) C. A. Coulson, C. H. Longuet-Higgins. *Proc. R. Soc. London, A* **192**, 16 (1947); (c) C. A. Coulson, C. H. Longuet-Higgins. *Proc. R. Soc. London, A* **193**, 447 (1948); (d) C. A. Coulson, C. H. Longuet-Higgins. *Proc. R. Soc. London, A* **193**, 456 (1948); (e) C. A. Coulson, C. H. Longuet-Higgins. *Proc. R. Soc. London, A* **195**, 188 (1948).
8. M. J. S. Dewar, H. C. Longuet-Higgins. *Proc. R. Soc., A* **214**, 482 (1952).

9. (a) M. J. S. Dewar. *J. Am. Chem. Soc.* **74**, 3341 (1952); (b) M. J. S. Dewar. *J. Am. Chem. Soc.* **74**, 3345 (1952); (c) M. J. S. Dewar. *J. Am. Chem. Soc.* **74**, 3350 (1952); (d) M. J. S. Dewar. *J. Am. Chem. Soc.* **74**, 3353 (1952); (e) M. J. S. Dewar. *J. Am. Chem. Soc.* **74**, 3355 (1952); (f) M. J. S. Dewar. *J. Am. Chem. Soc.* **74**, 3357 (1952).
10. K. Fukui, T. Yonezawa, C. Nagata. *Bull. Chem. Soc. Jpn.* **27**, 423 (1954).
11. K. Fukui, T. Yonezawa, C. Nagata. *J. Chem. Phys.* **27**, 1247 (1957).
12. (a) R. B. Woodward, R. Hoffmann. *J. Am. Chem. Soc.* **87**, 395 (1965); (b) R. B. Woodward, R. Hoffmann. *J. Am. Chem. Soc.* **87**, 2511 (1965).
13. R. B. Woodward, R. Hoffmann. *Angew. Chem., Intl. Ed. Engl.* **8**, 781 (1969).
14. W. T. Borden. *J. Am. Chem. Soc.* **97**, 5968 (1975).
15. W. T. Borden, E. R. Davidson. *Acc. Chem. Res.* **14**, 69 (1981).
16. D. Feller, E. R. Davidson, W. T. Borden. *Isr. J. Chem.* **23**, 105 (1982).
17. R. Hoffmann. *Rev. Mod. Phys.* **60**, 601 (1988).
18. J. K. Burdett. *Chemical Bonds in Solids*, Oxford University Press, Oxford (1995).
19. G. Rumer. *Nach. Gesselschaft Wissen. Gottingen, Math.-Phys. Klasse* 337 (1931).
20. L. Pauling, G. W. Wheland. *J. Chem. Phys.* **1**, 362 (1933).
21. L. Pauling. *The Nature of the Chemical Bond*, Cornell University Press, Ithaca (1939) and later editions.
22. H. Hartmann, *Z. Naturforsch., A* **2**, 259 (1947).
23. (a) J. P. Malrieu, D. Maynau. *J. Am. Chem. Soc.* **104**, 3021 (1982); (b) J. P. Malrieu, D. Maynau. *J. Am. Chem. Soc.* **104**, 3029 (1982).
24. D. Maynau, M. Said, J. P. Malrieu. *J. Am. Chem. Soc.* **105**, 5244 (1983).
25. M. Said, D. Maynau, J. P. Malrieu. *J. Am. Chem. Soc.* **106**, 580 (1984).
26. A. A. Ovchinnikov. *Theor. Chim. Acta* **47**, 297 (1978).
27. A. A. Ovchinnikov, V. O. Cheranovski. *Teor. Eksp. Khim.* **16**, 147 (1980).
28. D. J. Klein. *J. Chem. Phys.* **77**, 3098 (1982).
29. D. J. Klein, C. J. Nelin, S. A. Alexander, F. A. Matsen. *J. Chem. Phys.* **77**, 3101 (1982).
30. S. A. Alexander, D. J. Klein. *J. Am. Chem. Soc.* **110**, 3401 (1988).
31. D. J. Klein. *Pure Appl. Chem.* **55**, 299 (1982).
32. A. Graovac, I. Gutman, N. Trinajstic. *Topological Approach to the Chemistry of Conjugated Molecules*, Springer Verlag, Berlin (1977).
33. A. T. Balaban (Ed.). *Chemical Applications of Graph Theory*, Academic Press, New York (1975).
34. N. Trinajstic. *Chemical Graph Theory*, CRC Press, Boca Raton (1983).
35. I. S. Dmitriev. *Molecules without Chemical Bonds*, Mir, Moscow (1980).
36. A.-C. Tang, Y.-S. Kiang, G.-S. Yan, S.-S. Tai. *Graph Theoretical Molecular Orbitals*, Science Press, Beijing (1986).
37. S. J. Cyvin, I. Gutman. *Kekule Structures in Benzenoid Hydrocarbons*, Springer Verlag, Berlin (1986).
38. J. B. Donnet. *Carbon* **20**, 267 (1982).
39. I. C. Lewis. *Carbon* **20**, 519 (1982).
40. T. Wigmans, A. Hoogland, P. Tromp, J. A. Moulijn. *Carbon* **21**, 13 (1983).
41. J. Ayache, A. Oberlin, M. Inagaki. *Carbon* **28**, 337 (1990).
42. M. Mose-Yacaman, H. Terrones, L. Rendon, J. M. Dominguez. *Carbon* **33**, 669 (1995).
43. M. Bradburn, C. A. Coulson, G. S. Rushbrooke. *Proc. R. Soc. Edinburgh, A* **62**, 336 (1948).
44. C. A. Coulson, G. S. Rushbrooke. *Proc. R. Soc. Edinburgh, A* **62**, 350 (1948).
45. C. A. Coulson, M. A. Herraez, M. Leal, E. Santos, S. Senet. *Proc. R. Soc. London, A* **274**, 461 (1963).
46. C. A. Coulson, M. D. Poole. *Carbon* **3**, 275 (1964).
47. G. E. Hite, A. Metropoulos, D. J. Klein, T. G. Schmalz, W. A. Seitz. *Theor. Chim. Acta* **69**, 369 (1986).

48. G. E. Hite, T. P. Źivković, D. J. Klein. *Theor. Chim. Acta* **74**, 349 (1988).
49. W. A. Seitz, D. J. Klein, T. G. Schmalz, M. A. Garcia-Bach. *Chem. Phys. Lett.* **115**, 139 (1985).
50. S. E. Stein, R. L. Brown. *Carbon* **23**, 105 (1985).
51. S. E. Stein, R. L. Brown. *J. Am. Chem. Soc.* **109**, 3721 (1987).
52. H. Shirakawa, I. J. Louuis, A. G. MacDiarmid, C. Chiang, A. J. Heeger. *J. Chem. Soc., Chem. Commun.* 578 (1977).
53. C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, I. J. Louuis, S. C. Gau, A. G. MacDiarmid. *Phys. Rev. Lett.* **39**, 1098 (1977).
54. W. P. Su, J. R. Schreiffer, A. J. Heeger. *Phys. Rev. Lett.* **42**, 1698 (1979).
55. W. P. Su, J. R. Schreiffer, A. J. Heeger. *Phys. Rev. B* **22**, 2099 (1980).
56. Z. Yoshida, E. Osawa. *Aromatic Compounds*, Section 5.6.2, Kagakudojin, Kyoto (1971).
57. D. A. Bochvar, E. G. Galpern. *Dokl. Akad. Nauk SSS*R **209**, 610 (1973).
58. R. A. Davidson. *Theor. Chim. Acta* **58**, 193 (1981).
59. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley. *Nature* **318**, 162 (1985).
60. D. J. Klein, T. G. Schmalz, G. E. Hite, W. A. Seitz. *J. Am. Chem. Soc.* **108**, 1301 (1986).
61. T. G. Schmalz, W. A. Seitz, D. J. Klein, G. E. Hite. *Chem. Phys. Lett.* **130**, 203 (1986).
62. T. G. Schmalz, W. A. Seitz, D. J. Klein, G. E. Hite. *J. Am. Chem. Soc.* **110**, 1113 (1988).
63. D. E. Manolopoulos, D. R. Woodall, P. W. Fowler. *J. Chem. Soc., Faraday Trans.* **88**, 2427 (1992).
64. P. W. Fowler, T. Pisanski. *J. Chem. Soc., Faraday Trans.* **90**, 2865 (1994).
65. P. W. Fowler. *Chem. Phys. Lett.* **131**, 444 (1986).
66. P. W. Fowler, J. I. Steer. *J. Chem. Soc., Chem. Commun.* 1403 (1987).
67. P. W. Fowler. *J. Chem. Soc., Perkin Trans. 2* 145 (1992).
68. X. Liu, D. J. Klein, T. G. Schmalz. *Fuller. Sci. Tech.* **2**, 405 (1994).
69. S. Iijima. *Nature* **354**, 56 (1991).
70. T. W. Ebbesen, P. M. Ajayan. *Nature* **358**, 220 (1992).
71. D. J. Klein, W. A. Seitz, T. G. Schmalz. *J. Phys. Chem.* **97**, 1231 (1993).
72. B. I. Dunlap. *Phys. Rev. B* **49**, 5643 (1994).
73. D. J. Klein, W. A. Seitz, T. G. Schmalz. *Nature* **323**, 703 (1986).
74. D. J. Klein, H.-Y. Zhu. *Disc. Appl. Math.* **67**, 157 (1996).
75. D. J. Klein, L. Bytautas. *J. Phys. Chem.* **103**, 5196 (1999).
76. O. Ivanciuc, L. Bytautas, D. J. Klein. *J. Chem. Phys.* **116**, 4735 (2002).
77. O. Ivanciuc, D. J. Klein, L. Bytautas. *Carbon* **40**, 2063 (2002).
78. D. J. Klein, N. H. March. *Int. J. Quantum Chem.* **85**, 327 (2001).
79. D. J. Klein, T. Ivanciuc. *Arkovic* **x**, 292 (2005).
80. G. Rumer, E. Teller, H. Weyl. *Nach. Gesselschaft Wissen. Gottingen, Math.-Phys. Klasse* 499 (1931).
81. M. Simonetta, E. Gianinetti, I. Vandoni. *J. Chem. Phys.* **48**, 1579 (1968).
82. W. Marshall. *Proc. R. Soc. London, A* **232**, 48 (1955).
83. J. Thiele. *Ann. Chemie* **306**, 125 (1898).
84. A. Claus. *Theoretische Betrachtungen und deren Anwendung zur Systemik der Organischen Chemie*, Frieburg (1866).
85. H. E. Armstrong. *J. Chem. Soc.* **51**, 258 (1887).
86. E. Bamberger. *Ber. Deutsch. Chem. Ges.* **24**, 1758 (1891).
87. L. Pauling. *The Nature of the Chemical Bond*, 3rd ed., pp. 232–238 and 239–240, Cornell University Press, Ithaca (1939).
88. N. S. Ham, K. Ruedenberg. *J. Chem. Phys.* **29**, 1215 (1958).
89. L. Pauling. *Acta Crystallogr., Sect. B* **36**, 1898 (1980).
90. W. C. Herndon, M. L. Ellzey. *J. Am. Chem. Soc.* **16**, 6631 (1974).
91. E. H. Lieb, D. C. Mattis. *J. Math. Phys.* **3**, 749 (1962).
92. D. J. Klein. *J. Chem. Phys.* **77**, 3098 (1982).

93. D. J. Klein, C. J. Nelin, S. A. Alexander, F. A. Matsen. *J. Chem. Phys.* **77**, 3101 (1982).
94. E. H. Lieb. *Phys. Rev. Lett.* **62**, 1201 (1989).
95. D. J. Klein, S. A. Alexander, M. Randić. *Mol. Cryst. Liq. Cryst.* **176**, 109 (1989).
96. C. A. Coulson. *Proc. R. Soc. London, A* **207**, 91 (1951).
97. R. Daudel, A. Pullman. *Compt. Rend.* **220**, 888 (1945).
98. C. A. Coulson. *Trans. Faraday Soc.* **42**, 265 (1946).
99. W. E. Moffit. *Trans. Faraday Soc.* **45**, 373 (1949).
100. S. Fajtlowicz, P. E. John, H. Sachs. *Croat. Chem. Acta* **78**, 195 (2005).
101. I. S. Dmitriev. *Molecules without Chemical Bonds*, p. 57, Mir, Moscow (1980).
102. I. Gutman. *J. Chem. Soc., Faraday Trans. 2* **79**, 337 (1983).
103. M.-H. Whangbo, R. Hoffmann, R. B. Woodward. *Proc. R. Soc., A* **366**, 23 (1979).
104. T. Yamabe, K. Tanaka, K. Ohzeki, S. Yata. *Solid-State Commun.* **44**, 823 (1982).
105. M. Kertesz, R. Hoffmann. *Solid-State Commun.* **47**, 97 (1983).
106. K. Wakabayashi, M. Fujita, K. Kusakabe, K. Nakada. *Czech. J. Phys. S4* **46**, 1865 (1996).
107. D. J. Klein. *Chem. Phys. Lett.* **217**, 261 (1994).
108. A. Yamashiro, Y. Shimoi, K. Harigaya, K. Wakabayashi. *Phys. Rev. B* **68**, 193410 (2003).
109. K. Wakabayashi, K. Harigaya. *J. Phys. Soc. Jpn.* **72**, 998 (2003).
110. K. Harigaya, A. Yamashiro, Y. Shimoi, K. Wakabayashi. *Curr. Appl. Phys.* **4**, 587 (2004).
111. L. R. Radovic, B. Bockrath. *J. Am. Chem. Soc.* **127**, 5917 (2005).
112. D. Jiang, B. G. Sumpter, S. Dai. *J. Chem. Phys.* **126**, 134701 (2007).
113. M. Fujita, K. Wakabayashi, K. Nakada, K. Kusakabe. *J. Phys. Soc. Jpn.* **65**, 1920 (1996).
114. K. Nakada, M. Fujita, K. Wakabayashi, K. Kusakabe. *Czech. J. Phys. S4* **46**, 2429 (1996).
115. M. Nakada, M. Fujita, G. Dresselhaus, M. S. Dresselhaus. *Phys. Rev. B* **54**, 17954 (1996).
116. D. J. Klein, T. G. Schmalz, W. A. Seitz, G. E. Hite. *Int. J. Quantum Chem.* **S19**, 707 (1986).
117. M. Hjort, S. Stafström. *Phys. Rev. B* **61**, 14089 (2000).
118. P. L. Giunta, S. P. Kelty. *J. Chem. Phys.* **114**, 1807 (2001).
119. Z. Y. Rong. *Phys. Rev. B* **50**, 1839 (1994).
120. J. R. Hahn, H. Kang, S. Song, I. C. Jeon. *Phys. Rev. B* **53**, R1725 (1996).
121. F. Atamny, O. Spillecke, R. Schlögl. *Phys. Chem. Chem. Phys.* **1**, 4113 (1999).
122. S. M. Lee, Y. H. Lee, Y. G. Hwang, J. R. Hahn, H. Kang. *Phys. Rev. Lett.* **82**, 217 (1999).
123. D. J. Klein, N. H. March. *Phys. Chem. Liq.* **45**, 609 (2007).
124. D. J. Klein. *Phys. Chem. Chem. Phys.* **4**, 2099 (2002).
125. P. W. Anderson. *Science* **287**, 1196 (1987).
126. E. Mansosakis. *Rev. Mod. Phys.* **63**, 1 (1991).
127. G. Senatore, N. H. March. *Rev. Mod. Phys.* **66**, 445 (1994).
128. E. Dagotto. *Rev. Mod. Phys.* **66**, 763 (1994).
129. P. W. Anderson. *The Theory of Superconductivity in the High-T_c Cuprates*, Princeton University Press, Princeton (1997).
130. T. Morikawa, S. Narita, D. J. Klein. *Chem. Phys. Lett.* **402**, 554 (2005).