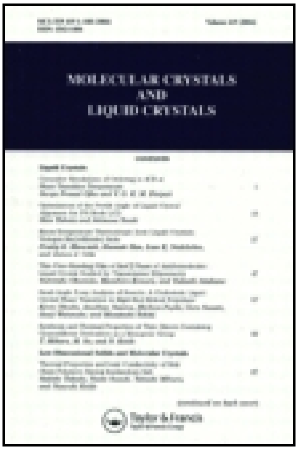

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Timothy Hughbanks [a] & Miklos Kertesz [b]

[a] Department of Chemistry, Texas A & M University, College Station, TX, 77843

[b] Department of Chemistry, Georgetown University, D. C., 20057

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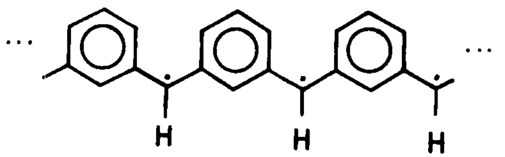
SUPERDEGENERACIES IN EXTENDED SYSTEMS; A PREREQUISITE FOR π FERROMAGNETS?

TIMOTHY HUGHBANKS[a] AND MIKLOS KERTESZ[b]
[a]Department of Chemistry, Texas A & M University, College Station, TX 77843 and [b]Department of Chemistry, Georgetown University, D. C. 20057

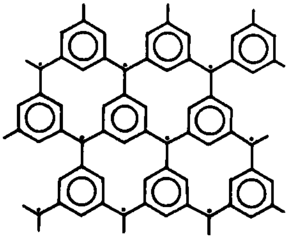
Abstract Using the concept of "superdegenerate" orbitals in extended systems, we examine the feasibility of organic (π) ferromagnetism. A reinvestigation of Mataga's prototype π systems indicates that they would, if synthesized, have ferromagnetic (or ferrimagnetic) insulating ground states. The nonbonding orbitals in these systems are seen to be superdegenerate as we have defined this term in earlier work. Bands in extended systems need not be nonbonding to have superdegenerate character and therefore potential π ferromagnets need not possess half-filled nonbonding bands. This suggests the possibility of synthesizing more stable polymers without radical character but that will be ferromagnetic when heavily doped with donors and/or acceptors. Some tests of these ideas have been carried out using spin-polarized self-consistent field calculations on promising one- and two-dimensional candidates.

INTRODUCTION

Over twenty years ago, Mataga suggested several polycarbenes and polyradicals as potential organic ferromagnets.[1] Of several proposed methods of achieving ferromagnetism in organic systems,[2,3] Mataga's method seems to be the only one which relies on *intra*molecular ferromagnetic coupling in large molecules and polymers. In all cases, the ferromagnetic coupling was considered be mediated by the π electrons of the systems under consideration. Our initial attention here is focused on two prototypes, the one-dimensional polyradical I and the two-dimensional analogue II. I differs from Mataga's originally



I



II

suggested polycarbene (the bridging C-H group was taken to be a carbenoid center), but has the same π orbital topology. We shall see that a more general viewpoint than that offered by alternant MO theory may lead to π ferromagnets that may be more feasibly synthesized.

MATAGA'S PROTOTYPES

The extent of both the practical and theoretical weaknesses of Mataga's prototypes have been overstated. These perceived weaknesses were summarized recently by Miller et al. in a review of this field.[3]

The first problem was envisioned by Mataga in his original paper, where he stated that the band gaps between the nonbonding band and both the filled bonding bands and the vacant antibonding bands would shrink as the size of the system increases. This is not the case. Indeed, the Hückel π band gaps are *exactly the same* as the corresponding gaps between the nonbonding orbital and the closest (anti)bonding orbitals in the benzyl radical! This is true for both the infinite 1-D and 2-D polymers and was pointed out by Tyutyulkov and coworkers several years ago.[4] We show the Hückel π electron density of states (DOS) for II in Figure 1. As we shall discuss below, there are three superdegenerate bands in this system. One is the nonbonding band (at $E = 0$) which is flanked by large band gaps of magnitude $|\beta|$, above and below. The two extra panels in the figure indicate the DOS contributions of the starred atoms in II, with the ring atoms and the trigonal linking centers indicated separately.

A second difficulty is the carbenoid nature of the molecules synthesized by Iwamura and coworkers that are oligomeric models of Mataga's polymers.[5] The practical difficulties of these systems are obvious: one may get spin pairing via distortions and rehybridization at the carbenoid centers and, of course, such carbenes are likely to be quite reactive. But these problems are not as serious as they seem since the *communication* between unpaired spins in these molecules is occurring through the π systems and only the π orbital topology is necessary for magnetic ordering. While Mataga suggested that extended, nonclassical, alternant systems should be ferromagnetic, the *carbenoid* nature of Iwamura's prototypes is not necessary. Mataga's

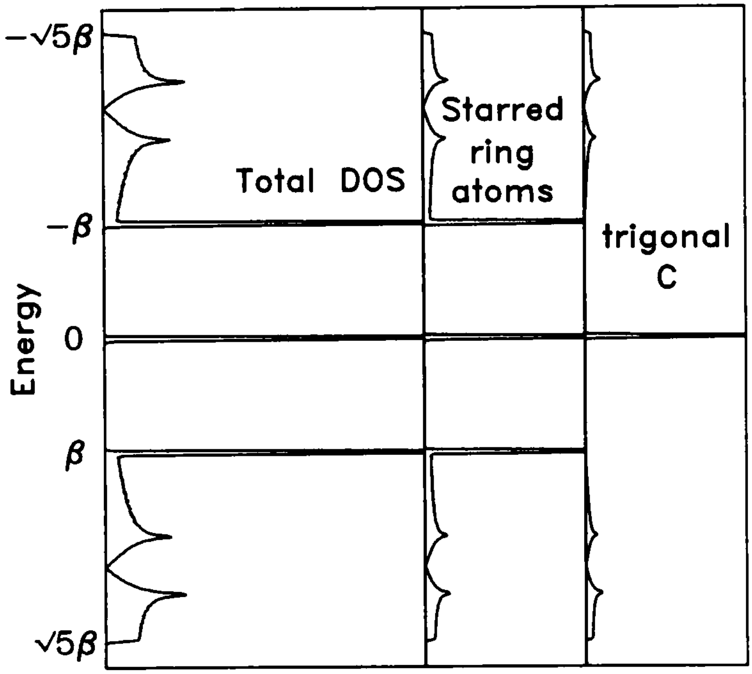


FIGURE 1. Density of states for the π bands of II.

polyradicals may still be subject to spin pairing via bond formation between adjacent polymers, but this problem may be ameliorated by the highly delocalized nature of the unpaired spins, as we discuss below.

SUPERDEGENERACIES

In earlier work, one of us outlined the conditions under which the band structure of an extended system will exhibit "superdegenerate" bands.[6] In the extreme ideal case, such bands have no dispersion (i.e., all the band orbitals are degenerate) and no well localized (Wannier) orbitals can be constructed from the band orbitals. For the sake of brevity, we will not demonstrate how these properties arise in the general case but proceed to examples. First we discuss the nonbonding bands of Mataga's hydrocarbons as a special superdegenerate case and make the connection between *orbital delocalization* and *ferromagnetism*. We then turn to computational results for Mataga's systems and discuss new prospects for stable π ferromagnets.

Nonclassical Alternant Systems as a Special Case

It has been established that an alternant hydrocarbon with N^* starred atoms and N unstarred atoms ($N^* \geq N$) will have at least N^*-N nonbonding π MO's (NBMO's).[7] An understanding of why this result is true lends insight into the form of the NBMO wavefunctions. In simple Hückel theory, in an alternant system starred atoms interact only with unstarred atoms and vice-versa. By taking appropriate linear combinations of the starred atom orbitals one can always construct N^* mutually orthogonal basis orbitals, of which N^*-N can be chosen to have zero interaction with all the unstarred orbitals as well. By construction, these N^*-N basis orbitals are eigenfunctions of the Hückel Hamiltonian and since they do not interact with either each other or any of the remaining orbitals (on starred or unstarred atoms), they are nonbonding. For an extended system (polymer) the band of nonbonding levels is a special kind of superdegenerate band. In general, superdegenerate bands need not be nonbonding, they need not involve the pπ bands of an planar organic system, and they can occur in 1-, 2-, or 3-dimensional systems.

The delocalized nature of superdegenerate band orbitals is characteristic and is the key feature behind the high-spin ground states predicted for systems where these orbitals are half-occupied. Because superdegenerate orbitals are constrained to be orthogonal to all the unstarred atomic orbitals, no combination of these band orbitals can yield a set of (Wannier) functions that are well localized to a few starred centers in each unit cell. This implies that electrons in a half-filled superdegenerate band must reside in orbitals with large intercell overlap densities and therefore will experience large (positive) exchange interactions with their neighbors. By this assertion, we are applying the same qualitative criteria used by Borden and Davidson in explaining why the trimethylenemethane diradical should have a triplet ground state for the planar D_{3h} geometry: the orbitals within the half-occupied degenerate set have a large differential overlap and Hund's rule is operative.[8]

Using a PPP model, we have carried out spin-polarized self-consistent field calculations on several systems. For brevity, let us consider the prototype π electron system in I. In Figure 2, we show the self-consistent PPP band structure for both spin-restricted (paramagnetic) and spin-unrestricted (ferrimagnetic) calculations on this system. In the paramagnetic case, where the the α and β spin density matrices are constrained to be equal, the band structure closely resembles the results of a simple Hückel calculation; there is still a superdegenerate nonbonding band and the two bands flanking it remain almost perfectly flat. The close similarity with the Hückel results for the two-dimensional case is notable (see Figure 1). At right in Figure 2 is the spin-polarized band structure; the α and β spin density matrices are unconstrained except that they are assumed to have the periodicity of the polymer (no translational symmetry breaking). As the figure shows, the superdegenerate band experiences an exchange splitting of 7.5 eV, while the remaining bands are split by 0.62 eV or less. As expected, the starred atoms all have sizable spin densities of like sign (see insert). The unstarred centers show

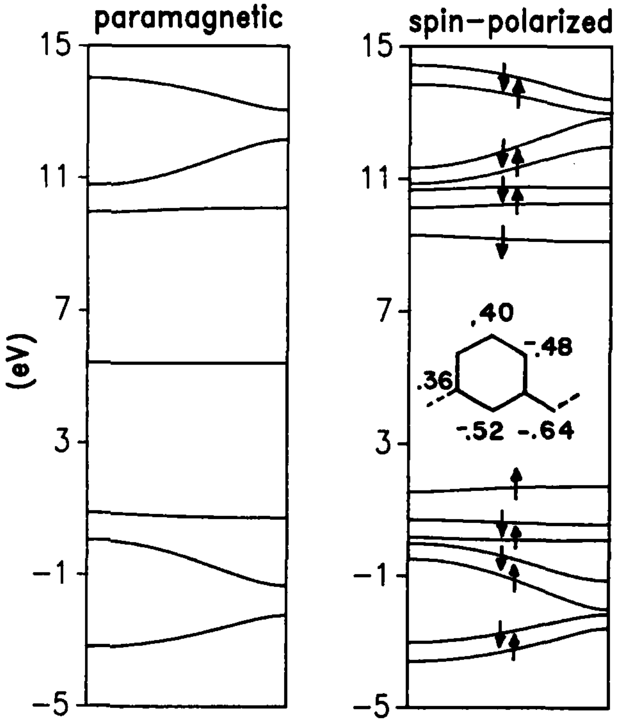


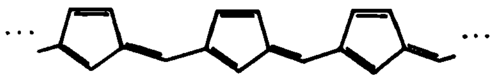
FIGURE 2. Spin-restricted and -unrestricted π bands for I.

effects of considerable spin polarization induced in the subjacent bands. This opposing spin density may lead one to prefer the term 'ferrimagnetic' to describe the wavefunction though the net result is one unpaired spin per unit cell. The ferromagnetic state is calculated to be 1.97 eV (per unit cell) below the paramagnetic state.

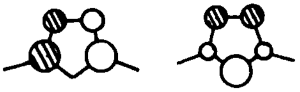
We also investigated the possibility of an antiferromagnetic state by doubling the size of the cell under consideration and beginning our calculation with a trial wavefunction with alternating spin densities. An antiferromagnetic solution emerges in which the alternating spin density is highly localized on the linking atoms and with very little spin polarization of the ring atoms. Despite the seemingly greater variational freedom the period doubling offers, the ferromagnetic wavefunction is calculated to be more stable by 0.52 eV per 7 atom cell. Neither this value nor the energy difference with respect to the paramagnetic state quoted above were computed with the inclusion of configuration interaction.[9] However, these calculated numbers are only one factor contributing to our confidence in reaffirming Mataga's prediction of one- and two-dimensional ferromagnetic ordering in I and II. In particular, we note that the extent of electron correlation should depend on the gaps between the superdegenerate band and the surrounding bands. But these π band gaps are unchanged from the corresponding MO energy gaps for the polycarbene oligomers which are known to have high-spin ground states.[10]

Other Superdegenerate Band Polymers

As we have stated, superdegenerate bands need not involve nonbonding orbitals. The hypothetical polyfulvene (III) is now under study. This system is clearly not alternant, but there is a way to easily diagnose the existence of two superdegenerate bands in the π band structure by simply disecting the system into the constituent rings and linking carbons. As long as the rings are ideal pentagons, there



III



IV

are two sets of doubly degenerate π orbitals per ring. We then have 2N degenerate basis orbitals in an polymer with N unit cells for each degenerate set of ring orbitals. The rings are linked to their neighbors via bonds with the linking carbon centers; *one* per ring and N in a N-membered chain. Thus, despite the fact that each of a set of degenerate ring orbitals overlaps with the adjacent linking atoms (see IV), N combinations of the the ring orbitals can be con-structed that are orthogonal to the linking atoms. In the band structure then, we find two superdegenerate bands appear at the same (Hückel) energies that we find for the doubly degenerate sets of orbitals for a single ring: $(\sqrt{5}\pm1)\beta/2$. The superdegenerate band orbitals are purely ring localized, as can be seen by the conspicuous absence of bridging carbon contributions to the superdegenerate peaks in figure 3.[11]

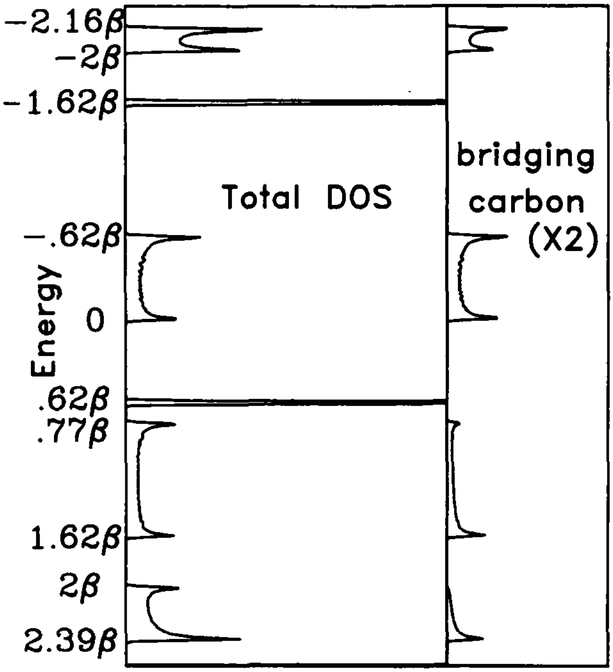


FIGURE 3. Density of states for the π bands of III.

For the six electron neutral polymer, the valence band is superdegenerate. If this system could be heavily doped with an appropriate acceptor, a cationic polymer with a half-filled superdegenerate band might be realizable. In a preliminary PPP calculation on the five electron polymer, the superdegenerate band is split by 5.2 eV by exchange. We are now studying alternative ground states (paramagnetic, antiferromagnetic) and the effects that bond length variations have on the band structure.

Clearly, this route to an organic ferromagnet may pose complications. Nevertheless, there would seem to be considerable advantages in seeking out polymers with superdegenerate valence (conduction) bands which can potentially be oxidized (reduced) to a ferromagnetic state. Not the least of these advantages is the possibility of formulating more tractable synthetic targets that need not have radical character when undoped. We are evaluating polyfulvene and several other systems as to their "theoretical" viability as ferromagnetic precursors. The general recognition of the properties of superdegenerate bands should open up more possibilities than offered by nonclassical alternant hydrocarbons alone.

Acknowledgments

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