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Radicals, Metals and Magnetism

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Radicals, metals and magnetism

DAVID J. R. BROOK

The interaction between unpaired electrons governs many physical properties of materials. Although in a fundamental sense the interaction is simple, a full understanding of the interaction in molecular systems is complicated by the presence of other bonding and non-bonding electrons. The resulting many body problem is very challenging. Nevertheless, much qualitative understanding can be obtained from applying simple molecular orbital theory and considering only the partly filled orbitals. The resulting model can be used to describe existing diradical and metal-radical systems and also has predictive value in the search for molecular magnets and the design of nanoscale devices.

Introduction

The interaction between electrons controls a significant portion of chemistry and solid state physics. Although, in principle, the interaction between two electrons is simple and is dominated by electrostatic repulsion, understanding these interactions is severely complicated by the interaction with further electrons and atomic nuclei, such that obtaining useful understanding of even the simple two electron systems is challenging. Significant understanding of chemistry can be achieved through complete ignorance of the electronic repulsion, or its introduction as an averaged field, however, understanding the properties of molecules and atoms with partly filled shells (free radicals) and bulk physical properties such as magnetism requires its specific inclusion. While the problem is a long standing one, its importance has become increasingly significant in chemistry with the new experimental fields of molecular magnetism and molecular conductors. The problem of interacting unpaired electrons has been

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extensively discussed in the context of transition metal chemistry, particularly because transition metal ions and ion clusters with partly filled shells are frequently stable and thus more easily probed. Recently there has been considerably more focus on organic free radicals, with the discovery of new types of stable free radical and new techniques for the characterization of reactive systems. This review provides a brief introduction to the theory behind electronic interactions and application to some recent problems of interest.

Theory

Even within a single atom, understanding the interactions between electrons is complicated. Just two electrons interacting with each other and a nucleus results in several possible configurations of varying energy. Calculating these energies accurately requires elaborate computation on high speed computers but, fortunately, consideration of a few simple rules allows at least a qualitative prediction of the configuration energies. Within atoms and molecules, electrons can only occupy certain specific regions of space known as orbitals. Each orbital is associated with a specific energy which can be the same, or different from the energies of other orbitals. Orbitals with the same energy are known as degenerate. Ignoring electronic repulsion, the most stable configuration will be obtained when electrons occupy only the lowest energy orbitals; however, because of a property of electrons known as *spin* there is a restriction on the number of electrons per orbital. The Pauli principle states that if electrons are to occupy the same orbital, they must have different spins. Since each electron can be spinning in only one of two directions (variously labelled 'up' and 'down' or α and β) each orbital can only hold a maximum of two electrons with their spins in opposite directions. Hund's rules state that in a set of orbitals of the same energy, the configuration with the most electron spins aligned in the same direction (the configuration with the greatest spin angular momentum) is the most stable. If we have a set of orbital energies calculated by ignoring electronic repulsion, these principles, for the most part, successfully predict the effects of electronic interactions in atoms. The question is: how do they pertain to molecules? To begin to answer this we must first understand the basis of Hund's rule.

We have already encountered the spin of electrons which gives rise to their magnetic properties but the interaction between magnetic dipoles is very weak compared to the electrostatic repulsion between like charges. The Pauli principle actually provides a link

between charge and spin that allows the much stronger electrostatic force to control the spins of electrons. Two electrons with opposite spins can reside in the same orbital and thus the same region of space. Consequently they repel each other strongly. Conversely, if two electrons have the same spin they must reside in different orbitals and thus different regions of space reducing electrostatic repulsion. This is the basis for Hund's rule. It also gives rise to the concept of a spin pairing energy: the repulsion energy that results from putting two electrons in the same orbital. Because of the spin pairing energy, the electronic configuration with all the electrons in the lowest energy orbitals is not necessarily the state with the lowest overall energy. If the energy difference between successive orbitals is small, it can cost less energy to put an electron in a higher energy orbital than to pair the electron with another in a lower energy orbital.

We can apply these ideas to molecular systems, but because molecules have many nuclei, it is convenient to make some simplifications. Molecules can be described with molecular orbitals in the same way that atoms can be described by atomic orbitals. Molecular orbitals are conveniently divided into two groups by their shape. Those that lie on a line between the two bonded atoms are labelled σ orbitals, and those with lobes either side of the line between the atoms are labelled π orbitals (Figure 1). Because even simple molecules have many molecular orbitals, we will assume that energies of the lowest electronic states are only dependent upon the highest energy occupied molecular orbitals (HOMO) and lowest energy unoccupied molecular orbitals (LUMO). This is known as the "active electron approximation". Secondly, we will consider initially the case with only two interacting electrons.

Two approaches are possible. Following the atomic model we can compare the energy gap between HOMO and LUMO and compare it with the spin pairing energy. If the HOMO-LUMO gap is greater than the spin pairing energy, then the spin paired configuration is favored and vice-versa. Though construction of molecular orbitals is straightforward, the spin pairing energy, because it is essentially an



Fig. 1. Shapes of σ (left) and π (right) orbitals.

electronic repulsion, will be highly dependent upon the size and shape of the orbitals and thus hard to estimate. Consequently, as an alternative approach that is easier to visualize, in certain circumstances it is easier to divide the molecule into two fragments, each with its own singly occupied molecular orbital (SOMO). These singly occupied orbitals are referred to as 'magnetic orbitals' in the description of Kahn. The overlap of these two orbitals results in formation of a lower energy orbital (the bonding orbital) and a higher energy orbital (the antibonding orbital). Increasing overlap between the orbitals produces more widely separated bonding and antibonding orbitals and thus favors a spin paired ground state with the bonding orbital doubly occupied. The proximity of the two orbitals tends to increase electron-electron repulsion and thus favors the triplet (spins parallel) ground state with each orbital singly occupied.

The energy difference between the spin paired state (the singlet state) and the spin unpaired state (the triplet state) is often referred to as the exchange interaction and given the symbol J . (Depending upon the author, negative J is taken to mean either the singlet or the triplet state is lower in energy; in some cases the singlet-triplet energy gap is designated $2J$. Care must be taken to understand which convention is being used. In this paper I will designate the singlet-triplet energy gap as J , and assume negative J implies that the singlet state is lower in energy). Depending upon the magnitude of the overlap and repulsion terms, or pairing energy and HOMO-LUMO gap, several extreme situations can be envisaged (Figure 2).

(1) When the spatial separation between the magnetic orbitals is large, both the bonding interaction and electronic repulsion is small and there is no significant difference in energy between the singlet and triplet states ($J = 0$). Alternatively this can be described as the case where both the spin pairing energy and HOMO-LUMO gap are very small. This is the case for two radical centers (unpaired electrons) at opposite ends of a large, saturated molecule. Each radical behaves independently of the other.

(2) When there is significant overlap between the magnetic orbitals, the bonding interaction generally outweighs the electronic repulsion; the ground state is a spin paired singlet and J is negative. The alternative picture is that the HOMO-LUMO gap is larger than the spin pairing energy. This is known as antiferromagnetic exchange. In the extreme case, this is typified by a normal covalent bond.

(3) When the overlap between magnetic orbitals is small, perhaps due differing symmetry, but the orbitals are close together and thus the electronic repulsion is large, the triplet state is the ground state

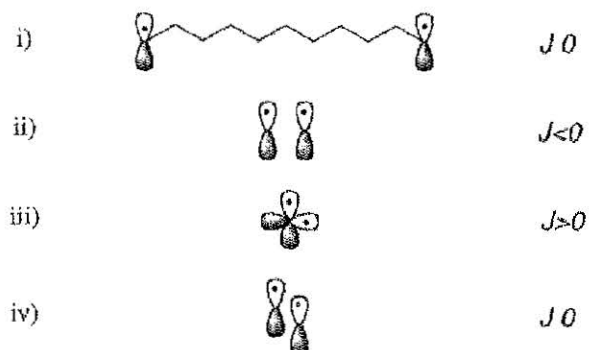


Fig. 2. Possible interactions of free radicals. i) Weak exchange, ii) Strong overlap; antiferromagnetic exchange, iii) Orthogonal orbitals (zero overlap); ferromagnetic exchange, iv) fortuitously degenerate singlet and triplet.

and J is positive. (The HOMO-LUMO gap is smaller than the spin pairing energy). This is known as ferromagnetic exchange. High spin transition metal ions show ferromagnetic exchange between electrons, though it is not normally labelled as such since the electrons reside on the same atom. Similarly, highly symmetric molecules such as dioxygen, where the occupied orbitals do not overlap yet the electrons occupy close regions of space, show triplet ground states.

(4) It is possible to have a fourth situation; that where the effects of overlap and electronic repulsion cancel resulting in almost degenerate singlet and triplet states, though the unpaired electrons are interacting relatively strongly. (The HOMO-LUMO gap is approximately equal to the pairing energy). This case can be distinguished from case (1) above through ESR spectroscopy which allows probing of the magnetic dipole interactions between the electrons.

It must be pointed out that in this description we have completely neglected the effect of the other electrons within the molecule, the magnetic dipole interaction, orbital angular momentum and spin-orbit coupling. Despite these simplifications, the above analysis provides a useful basis upon which to build our understanding. When we discuss transition metals we will see where these approximations begin to break down.

Measurement

Two techniques: electron spin resonance (ESR) spectroscopy and magnetic susceptibility are typically used to investigate the interaction between electrons in a diradical. Since both techniques require the presence of unpaired spins for detection, these methods require that the triplet state be thermally populated at accessible temperatures. (Although ESR can be used to investigate photo-physically populated triplet states, this does not give the energy of the state, just structural information). Both techniques depend upon the magnetic dipole resulting from the spin of unpaired electrons. In an external magnetic field, electrons will tend to align with the magnetic field but thermal motion will 'jostle' some of them into pointing against the field. The lower the temperature, the more the electrons will align with the magnetic field. The proportion of electrons aligned with the magnetic field is given by a mathematical function called the Boltzmann distribution.

Magnetic susceptibility measurements measure the population difference between the electrons pointing in each direction by measuring the enhancement of the magnetic field within the sample; susceptibility (χ) being defined as $\chi = \partial M / \partial H$ as $H \rightarrow 0$ where H is the applied field and M is the magnetization (The magnetization is the difference between the applied field and the field within the sample; it can be positive or negative). Since M is often linearly dependant upon H for small H , this is often represented as $\chi = M/H$. The contributions to

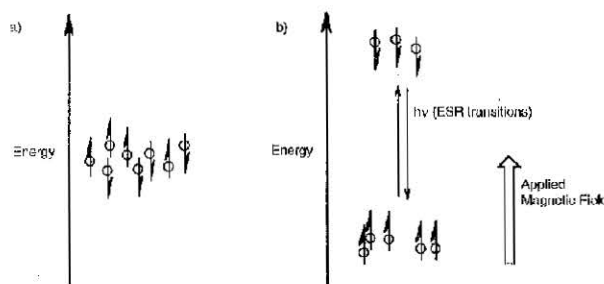


Fig. 3. Effect of magnetic fields on partly filled orbitals. *a*, Paramagnetic molecules in zero field have random spins. *b*, Spins can align with or against an applied field. Spins aligned with the field have lower energy, and consequently this state is more populated. The population difference results in sample magnetization, and transitions between the two levels gives electron spin resonance spectra.

magnetic susceptibility come from several sources. The tendency of unpaired electrons to align with the magnetic field enhances the magnetization within the sample and gives a positive contribution, the paramagnetic susceptibility (χ_{para}). Electron pairs give rise to a temperature independent, negative contribution as a result of their orbital motion. This is the diamagnetic susceptibility (χ_{dia}). Because of the temperature dependence of the Boltzmann distribution, χ_{para} is found to be inversely proportional to temperature (the Curie law), however, the product $\chi_{\text{para}} T$, when measured per mole, provides a direct measure of the number of unpaired electrons in a mole of sample.

Electron spin resonance spectroscopy also probes the differing populations of the electron spin states by using microwave radiation to excite electrons to the higher energy spin state. The amount of energy absorbed is proportional to the paramagnetic portion of magnetic susceptibility. Although absolute susceptibilities can be measured using ESR, instrument calibration is hard, and consequently, typically only relative susceptibilities are measured. This inability to determine absolute susceptibilities can result in ambiguity in determining the nature of the ground state of a diradical with ESR. For instance, a molecule with a triplet ground state and no other thermally populated states cannot be distinguished from a molecule with degenerate singlet and triplet states. The power of ESR resides in its sensitivity, which allows the investigation of low concentrations of reactive radicals, and its ability to probe the interaction of the electron spin with other magnetic species. ESR signals are split by atomic nuclei, to give information about the location of the electron within the molecules (hyperfine coupling) and by other unpaired electrons through the dipole-dipole interaction which gives information about the average distance between the two unpaired electrons. ESR is thus complementary to magnetic susceptibility.

Exchange interactions provide additional forces affecting the alignment of spins in a magnetic field. If the interaction stabilizes the singlet state (case (2) above), the exchange interaction tends to cancel out the population difference between the spin up and spin down states and the susceptibility is reduced. If the spins tend to align parallel (triplet state, case (3) above), then the exchange interactions enhance the effect of the magnetic field, and susceptibility is increased. Application of the Boltzmann distribution to the case of a molecule with closely separated singlet and triplet states gives rise to the Bleaney-Bowers equation:¹

$$\chi = \frac{Ng^2\mu_B^2}{3T} \left(\frac{1}{3 + e^{-J/kT}} \right)$$

Measuring the temperature dependence of the susceptibility and fitting the results to this equation allows determination of the singlet-triplet separation.

When more than one interaction is involved (as in the case of a crystalline material composed of radicals), the relationship between exchange parameters and paramagnetic susceptibility becomes considerably more complicated. There is no longer a simple interpretation of the exchange parameter, and many problems do not have an analytical solution. Furthermore, though multiple exchange parameters may seem necessary from a consideration of the crystal structure, statistical problems are often found in curve fitting with the exchange parameters being strongly correlated². Consequently, it is generally easier to investigate isolated diradical systems, though in certain cases the analysis of exchange in extended arrays is possible.

Organic systems

A review of high spin organic polyradicals was provided by Iwamura³. Although organic diradicals are relatively simple, predicting the ground state of even these systems can be remarkably complex. One only needs to read the history of attempts to determine the ground state of carbene (:CH₂) to appreciate the myriad pitfalls in determination of ground states from first principles⁴. Nevertheless, with the exception of carbenes, which exhibit complexity from having both σ and π contributions to the singly occupied orbitals, most organic radicals are π delocalized systems, and can be reasonably well described by only considering π orbitals. Application of the method described above for determining exchange is qualitatively easy. In fact, the extreme cases of covalent bonding (case 2 above) are generally, readily identified by drawing chemical structures. Other molecules require a greater degree of sophistication. Though any π system may be drawn as a diradical, it requires an analysis of molecular orbitals to begin to make ground state predictions. Fortunately there are some very simple methods derived from molecular orbital analysis that can be applied to obtain useful information. Alternant, conjugated hydrocarbons are those in which the carbon atoms are all planar with at least partial multiple bonds, and in which alternate carbon atoms can be labeled with stars such that no starred (or unstarred) carbon atoms are next to each other. For such molecules it can be demonstrated that if the number of starred carbon atoms is equal to the number of unstarred carbon atoms, two singly occupied molecular orbitals can be localized on

separate groups of carbon atoms. This reduces electronic repulsion and a singlet ground state is expected. The result was summarized by Ovchinnikov⁵ (who used a different strategy to achieve the same result) as:

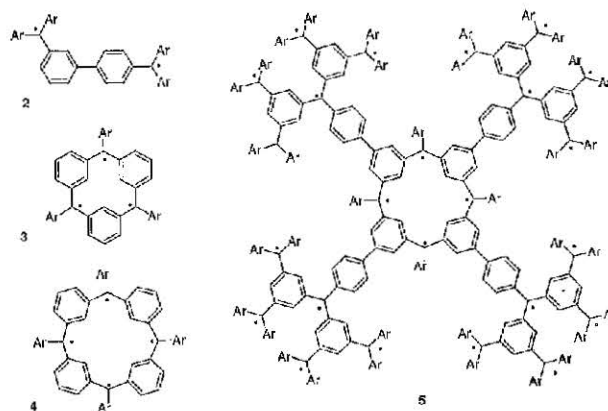
$$S = (n^* - n)/2$$

where S is the ground state spin multiplicity of the molecules (*i.e.* the number of unpaired electrons + 1), n^* is the number of starred carbon atoms and n is the number of unstarred carbon atoms. For example, application of the rule to cyclobutadiene (**1**) gives



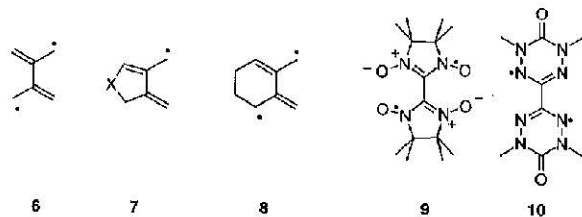
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i.e. a singlet ground state (no unpaired electrons). Because of its relative simplicity, Ovchinnikov's rule has been extensively tested and used to construct a variety of triplet and higher spin diradicals. Recently the power of this simple approach has been demonstrated by the synthesis of some extremely high spin hydrocarbon polyradicals (**2-5**)⁶⁻⁸.

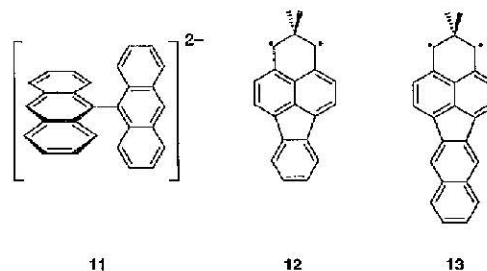


Though useful, Ovchinnikov's rule does have limitations. It has been successfully applied to some systems that contain oxygen and

nitrogen in addition to carbon and hydrogen, but it fails with others. It does not apply to non-alternant or non-planar systems and provides no information about exchange through single bonds, all of which can complicate the interpretation of data. For instance tetramethylenecyclohexane (TME, **6**) is predicted by Ovchinnikov's rule to have a singlet ground state, yet measurements in frozen matrices tend to suggest that the ground state is a triplet or at least the triplet and singlet are almost degenerate⁹. Although this appears to be a possible violation of Ovchinnikov's rule, further consideration reveals that the ground state of TME is expected to be non-planar and Ovchinnikov's rule does not apply. The conformationally restricted diradicals **7** and **8** also gave ambiguous results, but exchange through the σ system may be significant in **7**¹⁰ and **8** actually deviates significantly from planarity¹¹. Conversely, the two heterocyclic TME analogs, bis nitronyl nitroxide (**9**) and the bis oxoverdazyl (**10**) both have singlet ground states (by 311 cm^{-1} and 760 cm^{-1} respectively) yet the former is non planar¹², and calculations suggest the latter is non planar in solution¹³.



Overlap considerations suggest that identical π radicals arranged perpendicular to each other should possess triplet ground states because the π orbitals for each radical do not overlap (they are orthogonal). Few organic examples have been characterized, because the twist angle is either unknown or deviates from 90° , but inorganic examples are relatively common (*vide infra*). One organic example is the dianion of 9,9'-bianthryl (**11**) which has a triplet ground state¹⁴. As previously mentioned, non-alternant hydrocarbons are also not covered by Ovchinnikov's rule. Interesting examples are the recently described hydrocarbons, **12** and **13**¹⁵. These molecules have perfectly acceptable, fully bonded resonance structures, yet molecule **12** has a low lying, thermally populated triplet state, and molecule **13** has a triplet ground state.



The stabilization of the triplet state in these molecules can be accounted for in two ways. Hückel molecular orbital calculations indicate that the HOMO-LUMO gap for these molecules is very low. Consequently, the triplet state can be favorable in energy when the spin pairing energy is accounted for. An alternative viewpoint is that the triplet diradical structure is stabilized by increased aromatic resonance not available to the bonded singlet state¹⁵. Prediction of ground states in these more complex systems can be extremely challenging. In the more subtle cases, the active electron approximation must be abandoned and the interaction of molecular orbital configurations must be included. Though prediction of ground states is possible, unfortunately the elegance of Ovchinnikov's rule is lost.

In the design of magnetic systems, and prediction of other bulk properties, interactions between molecules are potentially as important as interactions within them. Unfortunately, understanding such interactions is considerably more challenging, partly because the three dimensional structure of molecular crystals is very hard to control. The same factors that control intramolecular exchange should be at work, but the regions of the molecular orbitals involved are considerably less well characterized. Experimentally, interactions between paramagnetic molecules are largely antiferromagnetic (aligning spins antiparallel) but under certain circumstances ferromagnetic interactions are observed. Few authors have dealt with intermolecular interactions specifically, notable is the model for predicting the sign of exchange proposed by McConnell⁶. This model uses the concept of spin density to predict interactions. Spin density is a mathematical function that describes the distribution of the unpaired electron through a free radical. For the most part the spin density is positive and follows the shape of the singly occupied molecular orbital, but where the singly occupied molecular orbital has a zero point (or node), the spin density can actually be negative. The

McConnell model suggests that if regions with positive spin density in one molecule interact with regions with negative spin density in a neighboring molecule, ferromagnetic exchange will result. The McConnell model was experimentally confirmed using cyclophane bis(carbenes) as probe molecules⁷. In the pseudortho- and pseudopara-cyclophane diradicals **14** and **15**, regions of positive spin density on each ring (shaded) overlap with regions of negative spin density on the opposite ring. These molecules are expected to have, and indeed are observed to have, ferromagnetically coupled quintet ($S = 2$, four unpaired electrons) ground states. Conversely the pseudometa-cyclophane **16** has regions of positive spin density overlapping with similar regions of positive spin density and giving an experimentally observed singlet ground state. Though this demonstration is reasonably conclusive, demonstrating the effect in a molecular crystal is challenging because of the lack of general control over three dimensional crystal structure. A fortuitous example is the TCNQ complex of the donor 4a,8a-diaza-2,6-dioxo-3,4,7,8-tetrahydro-4,4,8,8-tetramethylantracene-1,5-dione (DDTTA)¹⁸. The donor radical cation is arranged in extended chains within the crystal held together by weak hydrogen bonds. These hydrogen bonds also hold the carbonyl oxygen atoms (positive spin density) close to the vinylic hydrogen (negative spin density) on a neighboring molecule. Though interpretation of the magnetic data is complicated by antiferromagnetic interactions in the accompanying [TCNQ]₂ stacks, sufficient evidence exists to indicate the presence of ferromagnetic interactions between cations.

Metal-radical systems

An increasing number of studies describe systems where organic free radicals interact with a metal centre. This produces many potential complications, since more varied interaction geometries can be obtained, the metal itself may have unpaired electrons, and may also introduce complications such as orbital angular momentum. Nevertheless, there are many systems where qualitative predictions can be made using the analysis described above, especially in systems where two radical ligands are linked by a diamagnetic metal center. Care must be taken, however, since the utility of the magnetic orbital method depends upon correct selection of the magnetic orbitals; something that is not always straightforward.

When the metal is acting as a link between radicals, the geometry of the coordination is of fundamental importance. The pyridinyl-

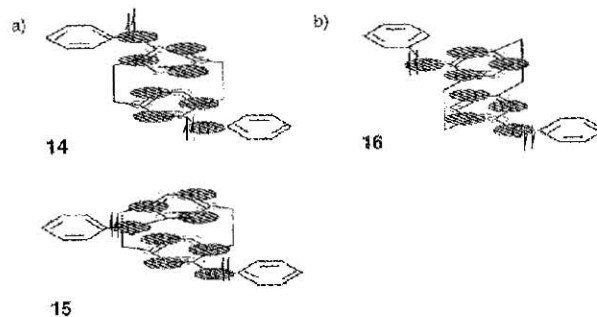
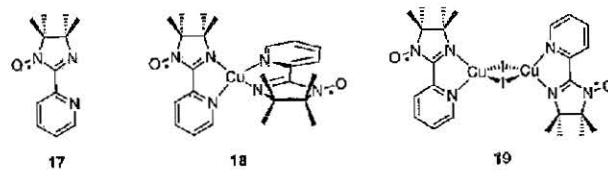
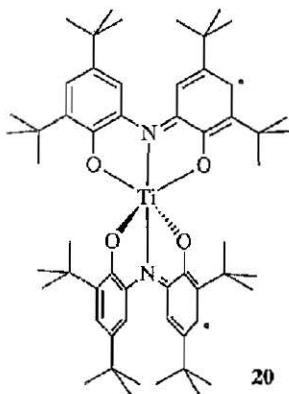


Fig. 4. Interaction between regions of positive and negative spin density in cyclophane bis(phenylcarbenes). *a.* In the pseudopara and pseudortho isomers regions of positive spin density (shaded ellipses) overlap with regions of negative spin density (open ellipses) giving ferromagnetic exchange and a quintet ($S = 4$) ground state. *b.* In the pseudometa isomer regions of positive spin density (shaded) overlap giving antiferromagnetic exchange and a singlet ground state.

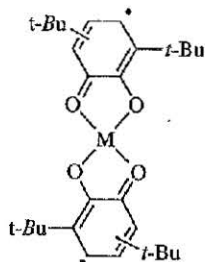
iminonitroxide radical **17** is a chelating radical ligand for which two contrasting copper(I) complexes have been studied. With two radicals directly coordinated to the copper atom, (**18**), the molecule has a triplet ground state with $J = 200 \text{ cm}^{-1}$ (ref. 19). This can be attributed to the perpendicular arrangement of the two radicals, which results in zero overlap between the two singly occupied ligand orbitals. This compares with the copper (I) iodide complex, (**19**) where the two radicals are linked through a metal-bromide-metal bridge²⁰. In the latter case, the exchange is weak ($\sim -2 \text{ cm}^{-1}$) as a result of the increased radical-radical distance and antiferromagnetic as a result of the coplanar arrangement of the two radicals which allows overlap between the SOMOs.



Similar structure property relations have been made for other metal complexes containing several paramagnetic ligands. With quinones, the titanium(IV) semiquinone-schiff base complex (**20**) shows a triplet ground state as a result of the perpendicular ligand orientation²¹. Again, this geometry prevents overlap between the ligand π orbitals. Square planar semiquinone complexes of Ni(II), Pd(II) and Pt(II) have been reported (**21**)^{2,22}. Within these complexes, two chelating radical ligands coordinate a central metal in a square planar geometry. In this configuration, the d electrons of the metal center are spin paired and do not contribute to the paramagnetism, though they contribute to the exchange pathway between radicals. The π orbitals containing the unpaired electrons overlap through delocalization onto the metal, resulting in strong antiferromagnetic exchange and a diamagnetic ground state. Evidence for the participation of d orbitals is provided by comparison of the three metal complexes. Exchange in the Pt complex, where $5d$ orbitals participate, is considerably stronger than in the Ni complex².



20



21 M=Ni, Pd, Pt

In these cases, the delocalization of radical spin onto the metal center changes the magnetic orbitals, but does not change the overall result of the analysis; however, care must be taken before we extend this principle too far. The coincidence of coplanar radical ligands and antiferromagnetic exchange does not necessarily indicate the true role of the metal in the exchange interaction and the geometry of both ligand and metal orbitals must be analysed to reach a valid conclusion. The copper(I) complexes of the bis verdazyl radical **10** show

antiferromagnetic exchange between the two halves of the verdazyl system; however, this exchange is considerably reduced compared with the free ligand²³. Although the two radicals are constrained to be coplanar, the two verdazyl magnetic orbitals overlap with different d orbitals on the copper(I) atom, providing a ferromagnetic exchange pathway (Figure 5). This pathway is not enough to counteract the direct exchange between the radicals but it does significantly reduce the overall exchange magnitude.

Other metal semiquinone complexes provide further examples of the geometric dependence of radical-radical exchange; however, electronic configuration of the metal also becomes significant. Considering the case of octahedral (or pseudo octahedral) geometry, the main group metal tris(semiquinone) complexes Ga^{III}(3,6-DBSQ)₃ and Al^{III}(3,6-DBSQ)₃ (3,6-DBSQ=3,6-di-*tert*-butylbenzosemiquinone) both have high spin ($S=3/2$) ground states because each semiquinone π orbital overlaps only with the p orbitals on the metal center. Since each metal p orbital is orthogonal to the other two, the SOMOs do not overlap and ferromagnetic exchange is observed.²⁴ With these two systems, the d orbitals are lower in energy and do not play a role. Conversely, for the complexes Zn^{II}(3,6-DBSQ)₂(TMEDA) and Co^{II}(3,6-DBSQ)₂, overlap with the metal d orbitals produces an effective overlap between the unpaired electrons and thus low spin ground states ($S=0$ for Zn^{II}(3,6-DBSQ)₂(TMEDA), $S=1/2$ for Co^{II}(3,6-DBSQ)₂)²⁴. At this point in our analysis we are beginning to see the breakdown of some of our earlier approximations. In particular, we see that though the magnetic orbital approach is intuitively easy, determination of the individual atomic contributions to the magnetic orbitals is crucial for meaningful results.

The complexity of these systems illustrates the effects of interaction with a partly occupied d sublevel on the metal atom. In order to study explicitly the interaction of ligand and metal unpaired electrons, copper(II)-nitroxide complexes have been extensively investigated, partly because of their relative simplicity and the ease of investigation by both magnetic susceptibility and ESR. Because of their stability, the electronic structure of nitroxide free radicals is well known. The unpaired electron is located in a π type molecular orbital with most of the spin density on the nitrogen atom. Using the same analysis as above, coordination modes in which this orbital overlaps with other singly occupied metal orbitals would be expected to provide singlet, or low spin ground states and geometries where this orbital is orthogonal to singly occupied orbitals on the metal would be expected to provide high spin ground states.

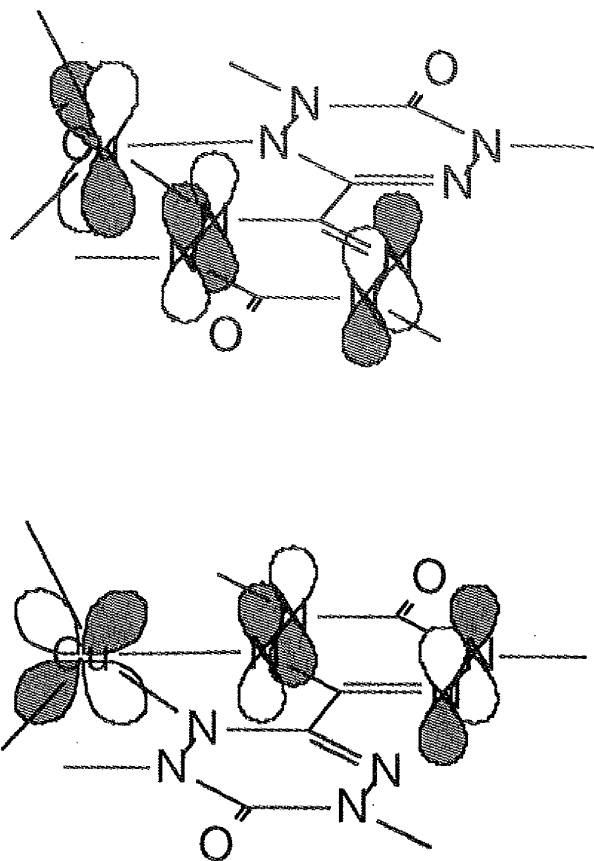


Fig. 5. Ferromagnetic exchange between coplanar verdazyl radicals mediated by copper(I). Each copper d orbital can only overlap with one of the two verdazyl radicals.

Copper(II) in an octahedral environment typically undergoes Jahn-Teller distortion, giving four tightly bound equatorial ligands in a square plane, and two less tightly bound axial ligands. The unpaired electron resides in the $d_{x^2-y^2}$ orbital in the equatorial plane. Consequently an axially bound nitroxide is expected to be ferromag-

netically coupled to the copper, whereas for an equatorially bound nitroxide, with overlap between the d and π orbitals, antiferromagnetic exchange is expected (Figure 6). Examples of both coordination modes are known, and in general the sign of exchange corresponds to that expected from overlap considerations. Detailed calculations indicate that in certain cases the magnitude of the ferromagnetic exchange is larger than expected. This was explained by invoking an exchange mechanism that delocalizes spin from the nitroxide onto the copper d_{z^2} orbital, increasing the coulombic repulsion between electrons and stabilizing the high spin state²⁵. Similar effects were observed for nickel(II) nitroxide complexes²⁶. Such delocalization introduces additional complexity in interpreting and predicting electronic interactions, partly because some of the approximations made in our initial discussion begin to break down with asymmetric systems.

The combination of d orbitals, variable coordination geometries and the possibility of variable oxidation state of both the metal and ligand, while severely complicating the analysis can lead to extremely novel properties such as photochromism, and photo-mechanical effects in addition to new magnetic properties²⁷. These effects are best illustrated with metal complexes of quinone ligands. The quinone ligand can support three oxidation states; diamagnetic

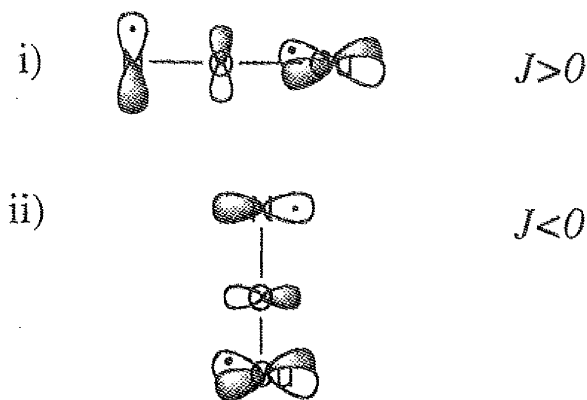


Fig. 6. Exchange between nitroxide and Cu(II). i) In plane coordination; ferromagnetic exchange, ii) perpendicular coordination; antiferromagnetic exchange.

quinone and catecholate and the free radical semiquinone. In the semiquinone radical the unpaired electron occupies a π^* orbital that is of similar energy to transition metal d orbitals; however, the properties of the complexes are best described by assuming the ligand and metal orbitals remain localized. The localization of metal and quinone orbitals produces unusual effects involving electron transfer between metal and ligand. For instance cobalt(II) bis(semiquinone) bipyridine complexes have an isomer written as cobalt(III) (semiquinone)(catecholate) bipyridine²⁷. At high temperatures, the Co(III) form is more stable, but upon cooling a transition occurs to the Co(II) form. Under certain circumstances the transition between the two forms can be induced by light (Figure 7). The changes in geometry of the molecule upon irradiation results in bending of the crystals. Such remarkable light induced changes may have important applications in molecular electronics applications and information storage.

Conclusions

From our brief survey of radical-radical and metal-radical interactions, we can see that such interactions can give rise to very novel properties, and that a qualitative understanding of the interactions can often be obtained by simply considering the orbitals occupied by the unpaired electrons. However, we have only considered systems with two or three interacting radical centers and even for these, rationalization of properties is possible, but accurate prediction is much harder. Synthesis of systems with far greater complexity is quite possible, but a theoretical understanding of their properties

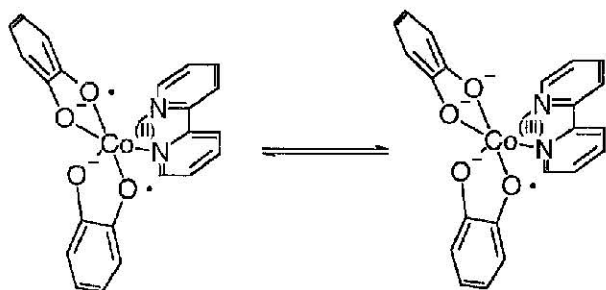


Fig. 7. Spin isomerism of cobalt bis(semiquinone)bipyridine.

may be a long way off. Nevertheless, as a result of increasing interest in magnetic materials for information storage, many research groups are currently devoting considerable effort towards complex magnetic systems. This research will expand the empirical data currently available and provide a basis for confirmation (or refutation) of current theory. Furthermore with increasing complexity, many new and unusual properties of metal-radical complexes remain to be discovered.

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