



Theory and practice of uncommon molecular electronic configurations

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The electronic configuration of the molecule is the foundation of its structure and reactivity. The spin state is one of the key characteristics arising from the ordering of electrons within the molecule's set of orbitals. Organic molecules that have open-shell ground states and interesting physicochemical properties, particularly those influencing their spin alignment, are of immense interest within the up-and-coming field of molecular electronics. In this advanced review, we scrutinize various qualitative rules of orbital occupation and spin alignment, viz., the aufbau principle, Hund's multiplicity rule, and dynamic spin polarization concept, through the prism of quantum mechanics. While such rules hold in selected simple cases, in general the spin state of a system depends on a combination of electronic factors that include Coulomb and Pauli repulsion, nuclear attraction, kinetic energy, orbital relaxation, and static correlation. A number of fascinating chemical systems with spin states that fluctuate between triplet and open-shell singlet, and are responsive to irradiation, pH, and other external stimuli, are highlighted. In addition, we outline a range of organic molecules with intriguing non-aufbau orbital configurations. In such quasi-closed-shell systems, the singly occupied molecular orbital (SOMO) is energetically lower than one or more doubly occupied orbitals. As a result, the SOMO is not affected by electron attachment to or removal from the molecule, and the products of such redox processes are polyradicals. These peculiar species possess attractive conductive and magnetic properties, and a number of them that have already been developed into molecular electronics applications are highlighted in this review. © 2015 The Authors. *WIREs Computational Molecular Science* published by John Wiley & Sons, Ltd.

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INTRODUCTION

The electronic configuration and state of a molecule characterize the distribution of electrons

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across the corresponding one-electron wavefunctions, i.e., orbitals.¹ This model description, albeit approximate, is nonetheless indispensable in explaining and predicting molecular geometry and various chemical and physical properties. As orbitals comprise not only the spatial component, but also the spin, they also give rise to such key features as the nature of configuration shell—open or closed—and the multiplicity of the electronic state. While the majority of stable organic molecules have a closed-shell singlet ground state, species with unpaired electrons display unique chemical reactivity and are capable of carrying magnetism and conductivity functionalities.

Although historically the latter have been the domain of metals and, in particular, transition metal complexes, in the recent years the focus has shifted toward fully organic functional materials as promising sustainable alternatives for applications ranging from information storage to environmental sensors.² The state-of-the-art research in the field of organic molecular electronics, including photovoltaics, spin valves, nano switches, field effect transistors, and logic circuits, is targeted at species with a predetermined spin state that can be affected *via* well defined stimuli. The main difficulty is that of the huge pool of organic radicals only very few are stable against dimerization (persistent),^{3,4} can be crystallized, are not Mott insulators, and provide a clear preference for the desired spin alignment.⁵ Development of such materials requires not only an in-depth understanding of the factors that control molecular electronic configuration and state, but also thinking outside the box of conventional physical organic chemistry rules. In the present review, we discuss these factors with a particular focus on unconventional orbital occupations and orderings, which lead to unexpected, practically useful or simply interesting chemical entities and behaviors.

FLUCTUATING GROUND-STATE MULTIPLICITY

According to the *Pauli exclusion principle*, the wavefunction for a system of fermions must be antisymmetric with respect to the interchange of any two particles. When applied to a molecule, this means that all of the occupied orbitals describe all electrons simultaneously, and, while the electrons are indistinguishable, orbitals, by definition, are not. Thus, within the framework of modern quantum mechanics assigning individual electrons to individual orbitals and individual sets of quantum numbers is erroneous; only the system (atom, molecule) as a whole possesses well-defined (sharp) stationary states.^{6,7} Furthermore, in the case of systems with unpaired electrons approximating true zeroth-order wavefunction with just one state/configuration, i.e., a single Slater determinant in the Hartree–Fock theory, is often just as erroneous. Let us consider an active space of two electrons, 1 and 2, in two spatial orbitals φ_a and φ_b with corresponding spin eigenfunctions α and β (Figure 1). The components of a triplet state wavefunction ${}^3\Psi$ are

$${}^3\Psi_{(M_s = +1)} = \frac{1}{\sqrt{2}}[\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)][\alpha_1\alpha_2]$$

	<i>i</i>	<i>ii</i>	<i>iii</i>	<i>iv</i>	<i>v</i>	<i>vi</i>
φ_b	—	$\uparrow\downarrow$	\downarrow	\uparrow	\uparrow	\downarrow
φ_a	$\uparrow\downarrow$	—	\uparrow	\downarrow	\uparrow	\downarrow
M_S	0	0	0	0	+1	-1

FIGURE 1 | Various arrangements (determinants) of two electrons in two molecular orbitals and the corresponding values of the secondary spin quantum number.

and

$${}^3\Psi_{(M_s = -1)} = \frac{1}{\sqrt{2}}[\varphi_a(1)\varphi_b(2) - \varphi_b(1)\varphi_a(2)][\beta_1\beta_2]$$

i.e., they can be represented as single determinants *v* and *vi* (Figure 1). However, the description of both the closed- and open-shell singlet wavefunctions requires multiple configurations. For example, the open-shell singlet wavefunction

$${}^1\Psi_{(M_s = 0)} = \frac{1}{\sqrt{2}}[\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)] \frac{1}{\sqrt{2}}[\beta_1\alpha_2 - \alpha_1\beta_2]$$

is a combination of two determinants, *iii* and *iv*:

$${}^1\Psi_{(M_s = 0)} = \frac{1}{\sqrt{2}} \left[\frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_a(1)\alpha_1 & \varphi_b(1)\beta_1 \\ \varphi_a(2)\alpha_2 & \varphi_b(2)\beta_2 \end{vmatrix} + \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_a(1)\beta_1 & \varphi_b(1)\alpha_1 \\ \varphi_a(2)\beta_2 & \varphi_b(2)\alpha_2 \end{vmatrix} \right]$$

In relation to diradicals,⁸ which are the species of interest in molecular electronics, their triplet state is therefore accurately described by a single reference determinant, however open-shell singlets require multiconfigurational (multireference) treatment.

Typically, in systems with significant energy difference between φ_a and φ_b , the ground state is the closed-shell singlet, and the two electrons are paired on one of the orbitals (highest occupied molecular orbital, HOMO), leaving the other one empty (lowest unoccupied molecular orbital, LUMO). However, if φ_a and φ_b are degenerate or nearly degenerate, diradical character becomes pronounced, raising the question of whether the ground state configuration is a triplet or an open-shell singlet.⁸ This question is of particular importance to molecular electronics applications since magnetic behavior of the molecule is defined by whether the coupling of its unpaired electrons is ferromagnetic (triplet) or antiferromagnetic (open-shell singlet).

The simplest spin alignment rule is the *Hund's multiplicity rule*, derived empirically from atomic spectra in 1925.⁹ It states that of the different multiplets resulting from different configurations of electrons in degenerate orbitals of an atom those with greatest multiplicity have the lowest energy.¹ The rule was originally explained by Slater in terms of the interelectronic repulsion. Specifically, two electrons, x and y , both carrying a negative charge, experience *Coulomb repulsion* J_{xy} . The magnitude of J_{xy} does not depend on their spins, but increases as these electrons get closer to each other. Correspondingly, the Coulomb hole is the region around one electron that is avoided by the second electron so as to minimize this electrostatic repulsion. At the same time, in accordance with the Pauli exclusion principle, two electrons of the same spin cannot occupy the same space, i.e., they tend to avoid each other. Pauli repulsion originates in the kinetic energy increase upon orthogonalization of two same-spin one-electron wavefunctions, which in turn stems from the Heisenberg uncertainty principle.¹⁰ This ensures that the configurations with high Coulomb repulsion are avoided and is reflected in the *exchange interaction* K_{xy} . The corresponding shortage of the electron of a certain spin in the vicinity of another electron of the same spin is known as the Fermi hole. Two opposite-spin electrons, on the other hand, are not subject to the exclusion principle. Slater's original explanation of the Hund's rule preference for the high-spin state was therefore based upon less electron–electron Coulomb repulsion in the triplet state due to opposing (stabilizing) exchange, which is absent in the low-spin state.⁹ However, it has been later shown that the electron–electron repulsion is actually greater in

the high-spin state, and an alternative explanation—the so-called *less screening rule*—has been offered. According to this rule, Fermi holes in the triplet state lead to decreased screening of the nucleus and larger electron–nucleus attraction. While this in turn causes the electron clouds to contract and partially restores the electron–electron repulsion, the system overall is nonetheless stabilized.^{11–14}

Most importantly, the aforementioned arguments invoke exchange and electrostatic interactions to correlate electron motion within a single configuration. This so-called dynamic correlation is weak compared to *static correlation* effects, i.e., correlation between configurations in the multireference wavefunction, particularly important in open-shell singlet state.¹⁵ Indeed, the absolute value of the correlation energy is approximately an order of magnitude lower for a pair of two same-spin electrons compared to that of opposite-spin electrons.¹⁶ The weaker the interaction between the two nonbonding molecular orbitals (MOs), the stronger the static correlation (Figure 2). This is clearly illustrated by such well-known examples, as the H_2 homolytic dissociation curve¹⁷ or the singlet ground state of square cyclobutadiene (CBD),¹⁸ which are described correctly only when multireference nature of the problem is accounted for. The *kinetic exchange picture* based on the Hubbard model is a related, yet also simplistic (and not satisfying virial theorem) spin alignment rule. It attributes stability of a singlet state in the case of orthogonal atomic orbitals (AOs) to the fact that perturbation yielding ionic configuration is allowed only from this state, and not from the triplet.¹⁹ An alternative theoretical interpretation of the Hund's multiplicity rule has been proposed on the basis of

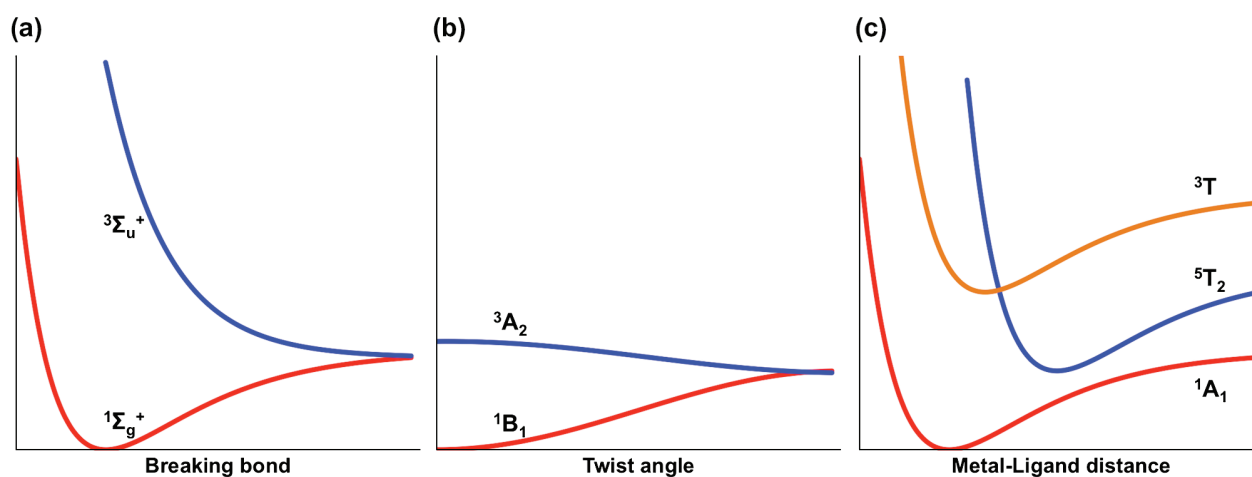
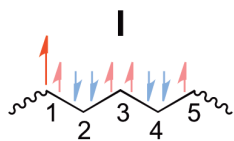


FIGURE 2 | Energies of ground and excited states of different multiplicities as a function of (a) H–H distance in H_2 homolytic dissociation, (b) twist angle around C–C bond in ethylene, and (c) metal–ligand separation in a transition metal complex.

Janak theorem (or extended Koopmans' theorem) in excited state density functional theory (DFT) for multiplets: at the Hartree–Fock level, the singlet-triplet gap (STG) is equal to the difference between the energies of the triplet's and open-shell singlet's HOMOs. This explanation echoes Pearson's maximum hardness principle, but lacks dynamic electron correlation.²⁰

Naïve qualitative rules of thumb for identifying the diradical ground state multiplicity emerged over the years within both MO and valence-bond theories. Borden and Davidson proposed to classify the non-bonding molecular orbitals (NBMOs) φ_a and φ_b as either *disjoint* or *nondisjoint*. If the two orbitals do not have common atoms and the probability of two electrons occupying the same space is nil independent of their spins, they are termed disjoint.²¹ Under such circumstances, the energy of an open-shell singlet can become comparable to or even lower than that of a triplet. Moreover, Coulomb interactions of the unpaired electrons with the paired (bonding) ones are generally weaker in open-shell singlets compared to triplets and are ascribed qualitatively to instantaneous correlation effects, in particular the *dynamic spin polarization* (Scheme 1). A damped spin wave so formed generates ferromagnetic coupling between the spins separated by an odd number of sites, and anti-ferromagnetic between those separated by an even number of sites,²² thus yielding the *topology* rules of spin coupling.^{23,24} Within the spin-Hamiltonian VB theory, Ovchinnikov's qualitative rule dictates that the most spin-alternant determinant is expected to have the lowest energy and the highest contribution.²⁵ Crucially, all of these rules are not the direct consequences of quantum mechanics and only mimic the dynamic and static correlation effects with the help of simplifying assumptions, thus inevitably having limited scope.

Therefore, it is evident that the ground state multiplicity in a given diradical is not due to one single term in a reference determinant, but rather is a complex interplay of exchange, kinetic, nuclear attraction, electron repulsion, and orbital relaxation contributions in both the single-reference triplet and multireference open shell-singlet states.^{19,20} Experimentally, discrimination between the two is fairly



SCHEME 1 | Dynamic spin polarization.

straightforward by the measurement of the electron spin resonance (ESR) signal splitting. Other experimental methods—measuring the linearity of the Curie plot of the ESR signal or the magnetic susceptibility *via* NMR, UV–Vis and IR spectroscopy—also allow one to distinguish between the high- and low-spin states, or in the least indicate when the energy gap between them is very small. If, however, the studied diradical is not stable or isolatable, theoretical and computational chemistry can offer a number of methods to assess the energies of the two states. However, the abundance of various qualitative rules of thumb is often symptomatic of their presumptuous nature and limited applicability. In terms of computations, relatively ‘cheap’ methods such as unrestricted or broken symmetry formalisms suffer from a number of serious drawbacks, while rigorous methods—configuration interaction (CI), multiconfigurational self-consistent field (MCSCF), complete active space (CAS), multireference and spin-flip equation-of-motion coupled clusters (MR-CC and SF-EOM-CC)—are generally not feasible for systems large enough to be practically valuable. A number of promising accurate AND affordable methods to treat strongly correlated systems, including Quantum Monte Carlo with the Jastrow ansatz,²⁶ DFT with fractional occupations,²⁷ delta self-consistent field (Δ SCF) approximation in DFT,²⁸ fractional-spin DFT,^{29,30} density matrix renormalization group (DMRG) theory,³¹ constraint-pairing mean-field theory,³² particle–particle random phase approximation³³—have been in development in recent years.^{34,35} Despite these challenges, a range of species have already been extensively studied and characterized with either an open-shell singlet ground state, or nearly degenerate singlet and triplet states. Of particular interest are the systems, in which the ground state multiplicity can be manipulated externally, and in the next section we discuss some illustrative simple and then more exotic and/or practically valuable organic diradicals.

Prototypical Cases

Among the most famous examples of low-spin diradicals are many $[4n]$ -annulenes, such as the square planar CBD, and non-Kekule hydrocarbons, e.g., the planar tetramethyleneethane (TME). Both species have disjoint sets of NBMOs and an open-shell singlet ground state (Figure 3). In the singlet state of D_{4h} CBD, the bonding π -electrons can partially localize on the same pair of atoms as the same-spin unpaired electrons; however, in the triplet state such advantageous spin polarization is not possible. In the

planar TME, which essentially consists of two allylic radicals, the long-range bonding between their termini and the interaction between the $p-\pi$ AOs of their central carbons stabilizes the singlet compared to the triplet. However, neither of these geometries are equilibria for the corresponding species, and thus the theoretical predictions of the ground state's multiplicity are nearly impossible to test experimentally.³⁶ Experimentally, a diradical with a singlet ground state was eventually obtained for the equilibrium planar geometry of 1,2,4,5-tetramethylenebenzene (TetraMB, see Figure 3). However, in TetraMB the long-range interactions between the $p-\pi$ AOs of non-ring carbons lift the degeneracy of the NBMOs.³⁷ The breakdown of the preference for the high-spin ground state of truly degenerate orbitals was shown to be viable in systems with a fourfold symmetry,³⁸ e.g., the singlet state with a C_4 symmetry axis has indeed been detected as lying well below the D_{8h} triplet by transition-state spectroscopy in another $[4n]$ -annulene, planar cyclooctatetraene (COT).^{37,39}

In some polyradicals, the spin state can be qualitatively predicted by the *topology* and nature (σ or π) of the NBMOs.⁴⁰ For example, such π_n polyradicals as *m*-xylylene (MX) and 1,3,5-trimethylenebenzene (TriMB) have nondisjoint NBMOs with strong ferromagnetic spin coupling and resulting triplet ground states (Figure 3). Among the α,n -didehydrotoluenes (DHT), ortho- ($n=2$) and para- ($n=4$) isomers have triplet ground states (due to large coefficients of the benzylic π -SOMO in these

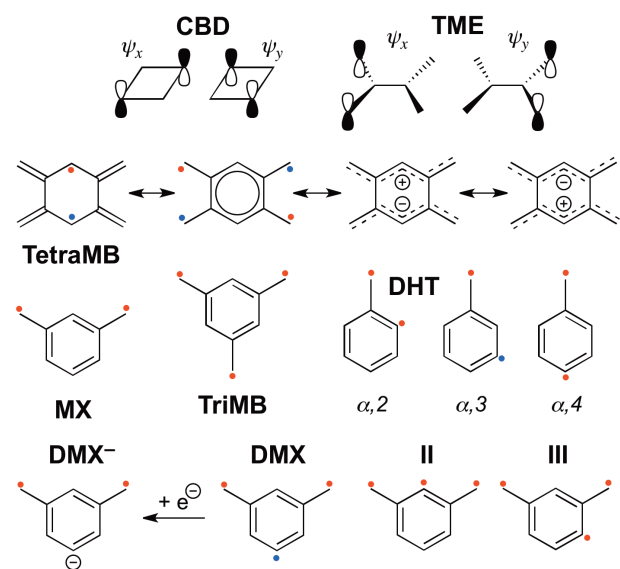


FIGURE 3 | High- and low-spin polyradicals. Red dots denote spin-up (α) electrons and blue dots represent spin-down (β) electrons.

positions and the consequential preference for ferromagnetic coupling with the orthogonal σ -SOMO), while the meta-isomer ($n=3$) is an open-shell singlet (Figure 3).²³ Similarly, 5-dehydro-1,3-quinodimethane (DMX) is a triradical with an open-shell doublet ground state because it combines parallel spin alignment between two benzylic π -SOMOs of MX with their antiparallel coupling to a ring σ -SOMO of $\alpha,3$ -DHT.^{41,42} The dominant product of electron attachment to DMX is a rare triplet carbanion.⁴³ Topologically different isomers of DMX **II** and **III** with nondisjoint NBMOs have high-spin (quartet) ground states (Figure 3).^{23,24} These simple polyradicals can also be thought of as *coupling units* that sustain certain spin alignment depending on topology, as seen in Schlenk's and Chichibabin's hydrocarbons, or in isomers of dinitroxide **IV** (Figure 4).⁴⁴

Cycloheptatrienyliene (tropyliene, see Figure 5) is another interesting example of a ground state open-shell singlet. An unpaired electron in a $2a_2$ π -orbital polarizes the spins of the bonding π -electrons in $2b_1$. As a result, spin opposite to that in $2a_2$ is accumulated on carbenic C-atom. It interacts with p -electron in orthogonal a_1 NBMO, centered on the same atom, with the preference for the ferromagnetic coupling, making the overall singlet state lower in energy.⁴⁵

As noted above, one of the qualitative spin alignment rules—the kinetic exchange—highlights the importance of resonance between open-shell singlet and closed-shell zwitterionic configurations (see resonance descriptors of TetraMB in Figure 3). In the pyridinium analog of MX (**V** in Figure 6) this contribution exceeds the exchange and Coulomb terms, which formally favor the triplet state of this system

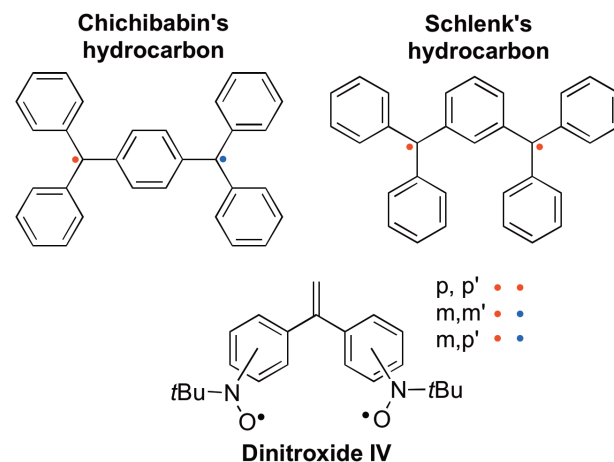


FIGURE 4 | Topology-driven ground state multiplicity. Red dots denote spin-up (α) electrons and blue dots represent spin-down (β) electrons.

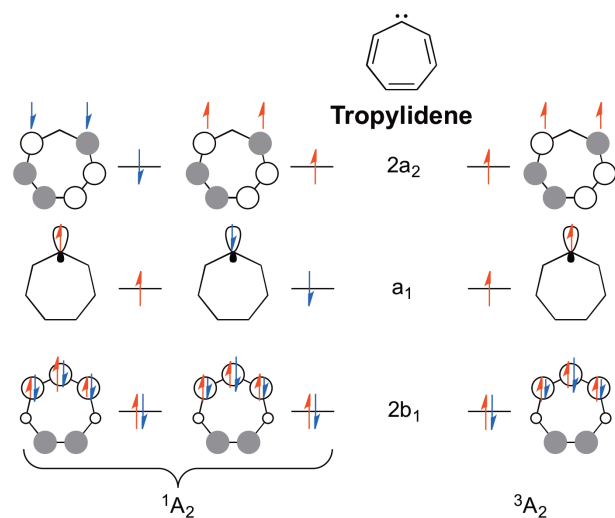


FIGURE 5 | Schematic orbital diagram of singlet and triplet tropyliene.

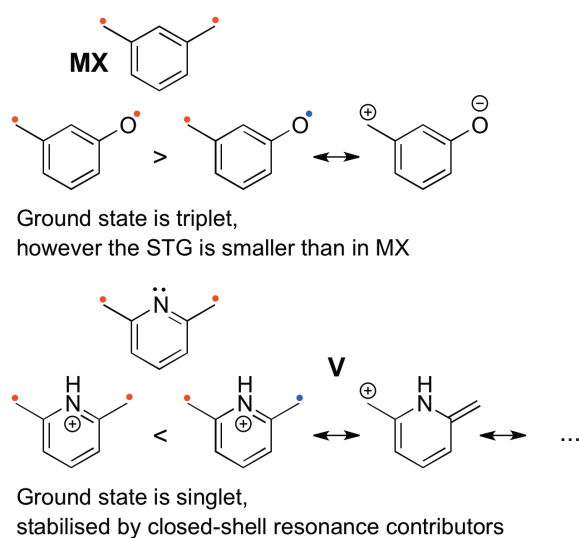


FIGURE 6 | Spin-state reversal by ionic resonance contributors. Red dots denote spin-up (α) electrons and blue dots represent spin-down (β) electrons.

with nondisjoint NBMOs.⁴⁶ This example again illustrates the narrow scope of Hund's and other simplified spin alignment rules.

Exciting Cases

The prototypical examples, described above, lay the groundwork for some exciting—and practically useful—physics and chemistry. For example, ability to switch the spin state of the system—and thus reverse the *magnetization vector*—by external stimuli is extremely attractive for data storage

applications. Redox switching between ferro- and antiferromagnetic coupling of two nitroxide radicals has been achieved *via* quinone coupling unit (Figure 7(a)).^{47,48} The photo-induced magnetic crossover between triplet and singlet states of diradical azobenzene (Figure 7(b)) due to the loss of planarity in the *cis*-isomer has been predicted computationally.⁴⁹ The concept was later embodied experimentally (Figure 7(c)): switching from the *trans*- to *cis*-isomer of a crowded alkene bearing two distant TEMPO moieties brings them in close proximity, sufficient for spin-spin antiferromagnetic coupling, as a result of intramolecular H-bonding.⁵⁰ Photo-induced bonding in the system, shown in Figure 7(d), switches ground state multiplicity by altering orbital topology.⁵¹ Coordination to Zn^{2+} brings about O–Zn–O superexchange and O···O through-space exchange, which favor antiferromagnetic coupling and override the preference for the triplet ground state, predicted on the basis of disjoint NBMOs in parent dinitroxide ligand (Figure 7(e)).⁵² A fascinating example of switching spin state by external stimuli is that of 1,4-phenylenedinitrene. Crossover from an open-shell singlet into a higher-energy triplet state has been observed under increased temperature, which promotes electrons to populate the triplet state, and also under external magnetic field that splits the triplet into microstates, one of which approaches the energy of the ground-state singlet (Figure 7(f)).⁵³

Systems with *borderline open/closed-shell states* deserve special attention, because they afford switching between dia- and paramagnetic properties. 1,3-Dinitrophenyls carrying anionic substituents were shown both computationally and experimentally to undergo intramolecular electron transfer and form anionic diradicals. Depending on the system, the open-shell triplet state was found to be either the ground state, or to be negligibly higher in energy than the closed-shell singlet. The diradical state is stabilized by cation binding to the nitro group (Figure 8).^{54,55}

The change from the closed-shell singlet into a triplet ground state, and hence *magnetization*, has been shown to occur as a result of *protonation* and/or *oxidation* in a number of systems. For instance, a diradical was formed by double protonation and subsequent intramolecular electron transfer from donor to acceptor unit, as shown in Figure 9(a).⁵⁶ A singlet biradical was generated by protonation, coupled with oxidation, of a modified sapphyrin analog (Figure 9(b)).⁵⁷ A paramagnetic diradical dipyrilium salt in equilibrium with the corresponding closed-shell dication was formed by protonation-induced cyclization in a

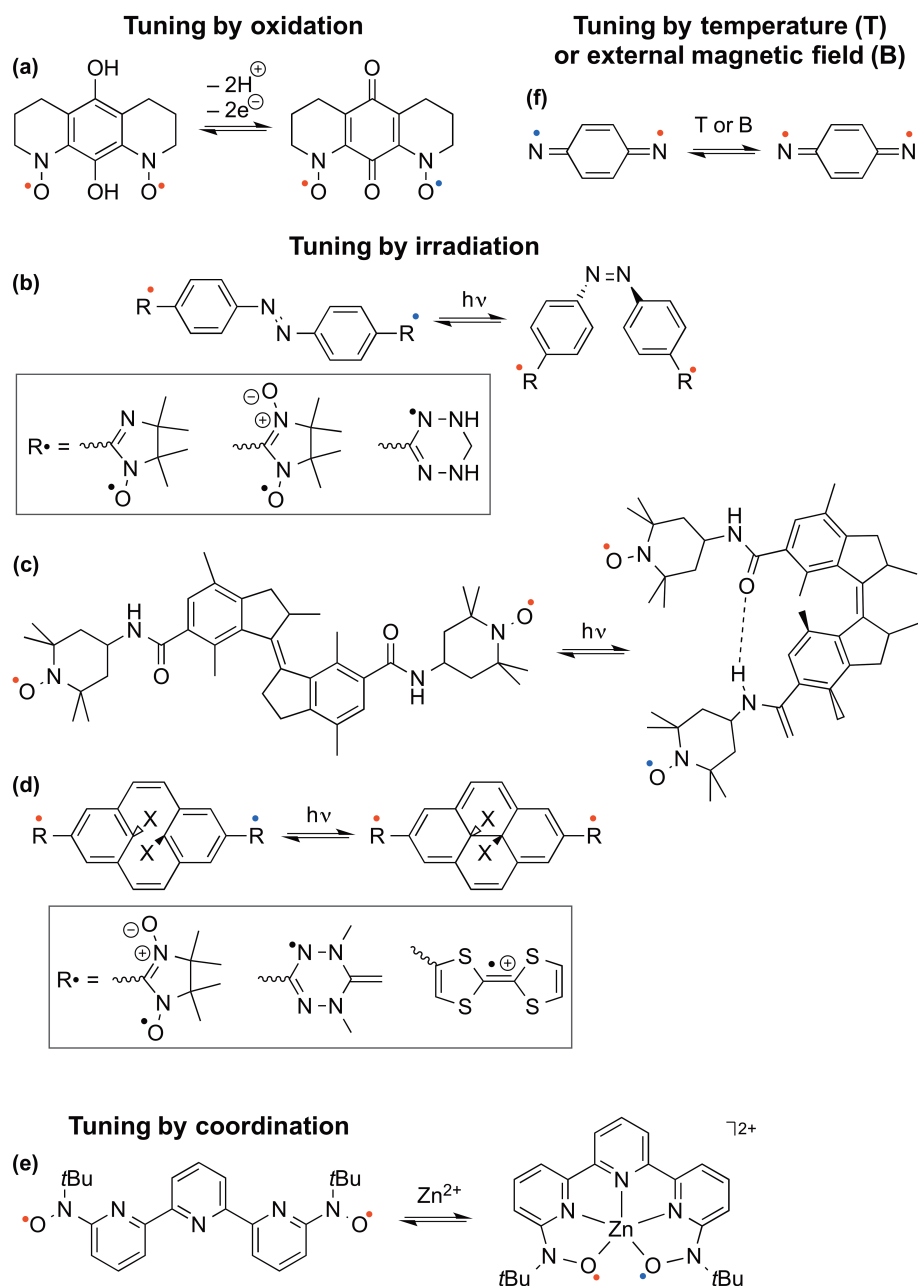


FIGURE 7 | Spin-state crossover by external stimuli. Red dots denote spin-up (α) electrons and blue dots represent spin-down (β) electrons.

donor–acceptor–donor triad molecule, as shown in Figure 9(c).⁵⁸ The preference for high-spin state can also be employed as a synthetic strategy, for example to obtain building blocks for polaronic ferromagnetic polymer chains (Figure 9(d)).⁵⁹ Finally, singlet-to-triplet transition can occur *via* singlet fission in, e.g., molecular crystals of organic chromophores, when one molecule is excited from the ground state closed-shell singlet to an excited open-shell singlet and ‘shares’ its excitation with a neighboring

chromophore. As a result, the two species end up in a low-lying triplet excited state.⁶⁰

AUFBAU PRINCIPLE

The orbital model might be a floating one (see Box 1), but it is unarguably an extremely useful and conveniently intuitive concept. The shapes and energies of the orbitals and the ordering of their

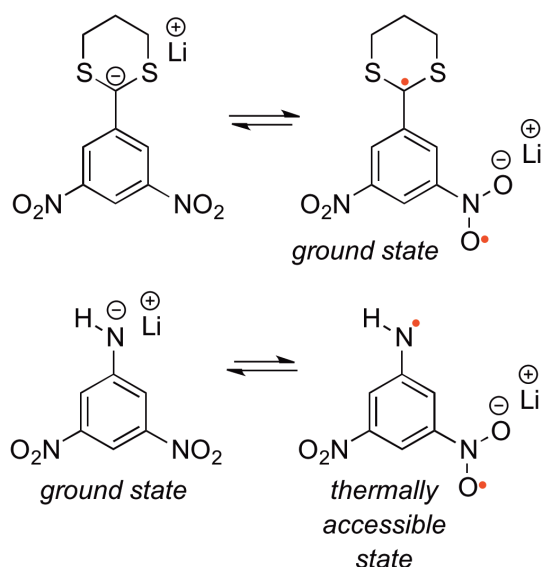


FIGURE 8 | Systems with borderline triplet/closed-shell singlet preference. Red dots denote spin-up (α) electrons.

occupation with electrons in a molecule facilitate the explanation and prediction of its chemical reactivity. As has already been emphasized, within modern quantum mechanics the orbital energies should not be equated to the electron energy levels, and should be considered only within the investigated electronic configuration of the many-electron system. Within the configuration itself the ordering of orbitals by energies affects their occupation, which in turn determines properties of the reactive, frontier orbitals.⁷ The orbital configuration is colloquially thought to conform to the *aufbau principle*: a maximum of two electrons are put into orbitals in the order of increasing orbital energy, i.e., the lowest-energy orbitals are filled before electrons are placed in higher-energy orbitals,¹—leading to a low-spin state.²³ The *aufbau* (from German for ‘building up’) principle was formulated by Niels Bohr in 1923 on the basis of an empirical *Madelung’s rule*.^{75,76} In order to establish the physical grounds for his building up principle, Bohr

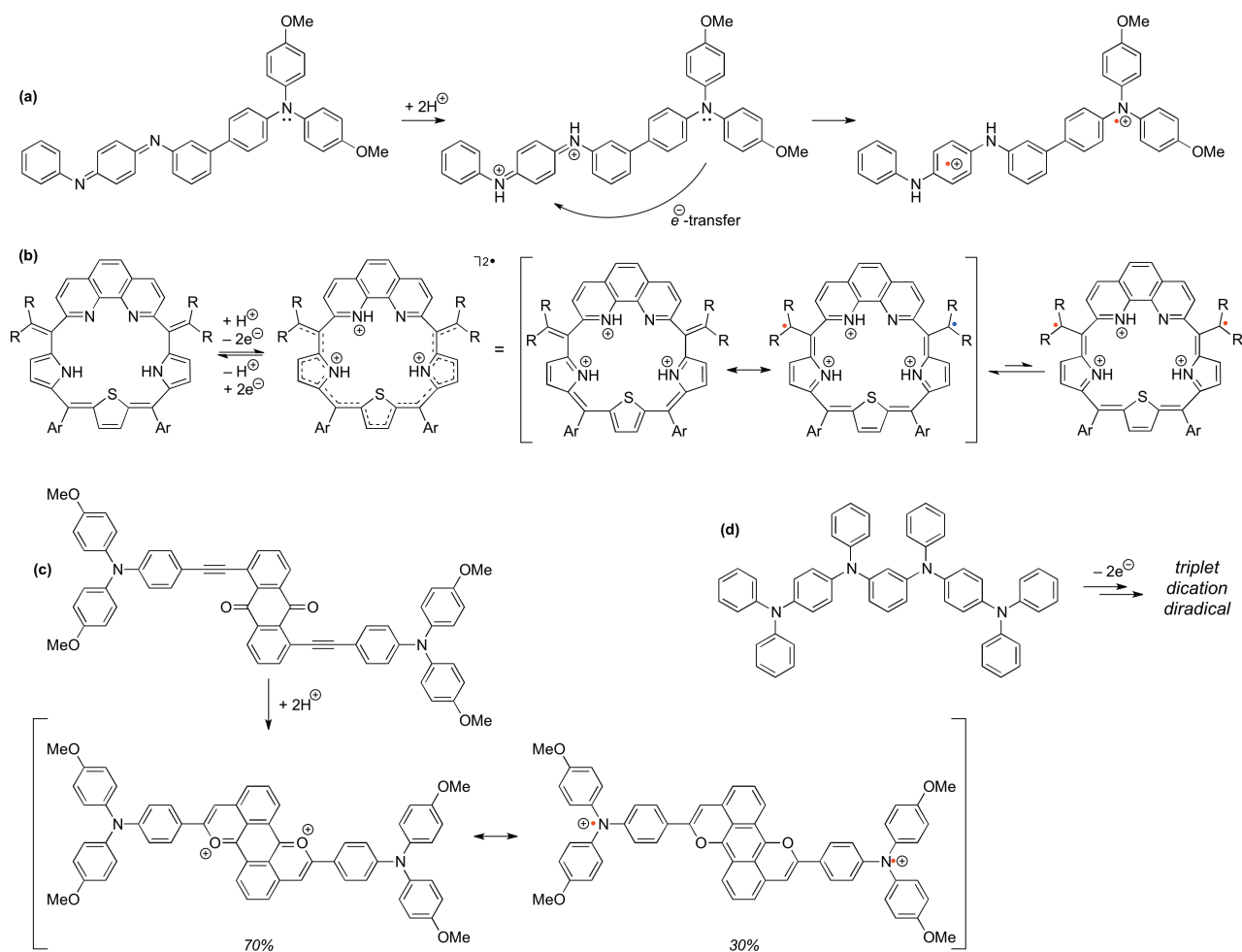


FIGURE 9 | Protonation-induced magnetization. Red dots denote spin-up (α) electrons and blue dots represent spin-down (β) electrons.

BOX 1

MUCH ADO ABOUT ORBITALS

Orbitals provide a natural language for an Aufbau of the complex reality of the molecules of the inorganic and organic world.

Roald Hoffmann⁶¹

An orbital is a one-electron wavefunction that describes the behavior of an electron in an atom (AO), or a molecule (MO). The orbital concept is arguably one of the cornerstones of the physical chemistry, familiar to all and appreciated by most chemists, and routinely utilized to rationalize chemical stability and reactivity. Yet, just like many other chemistry cornerstones—partial charges, aromaticity, the chemical bond itself—this concept is a rather ‘fuzzy’ one.^{62,63} The reality is that an orbital is a mathematical construct, an approximate, non-unique solution to the Schrödinger equation. It is then not surprising that a report⁶⁴ and an associated editorial⁶⁵ on the direct observation of copper’s d-orbitals in Nature in 1999 caused a stir within the chemistry community and ignited a chain reaction of both critical and supportive comments and replies.⁶⁶ Aside from some concerns regarding the methodology and data analysis,^{67,68} the key question that arose was whether an orbital could be observed. The answer depends on how the orbital is defined – as a mathematical function or as a region of space where an electron is likely to be observed.⁶⁹ The two notions are closely connected. The nondistinguishability of the electrons does not imply the inexistence of orbitals as the spatial regions with high probability of finding electrons in the same way, as the three body problem in classic mechanics does not deem the planetary orbits nonexistent.⁷⁰ In quantum mechanics, orbital (wavefunction) ψ is a state of the system in the Hilbert space, square of which, ψ^2 , yields an expectation value of the corresponding observable of this given system—the electron density.⁷ Thus, in the strictest sense, the descriptive and interpretative power is contained not in an orbital itself, but in its occupation, which describes how often a certain one-electron function is used in the construction of a many-electron wavefunction of the system. Indirect observation of an orbital can be justified, i.e., an orbital can be reconstructed from direct measurement, provided this orbital is a good approximation of the investigated system.^{71–74}

made the following *assumptions*: that electrons exist in sharp stationary states, and that these states are preserved upon addition of an electron and a proton to the system.⁷⁷ These assumptions in turn originate from the *Ehrenfest’s adiabatic principle*: ‘if a system be affected in a reversible adiabatic way, the allowed motions are transformed into allowed motions.’⁷⁸ However, this principle does not apply to aperiodic systems, i.e., all systems other than a hydrogen atom. Nonetheless, Pauli in his attempt to derive an independent electron model while preserving the quantum numbers still erroneously adopted the adiabatic principle. In 1925, he postulated his famous principle as: ‘it should be forbidden for more than one electron with the same value of the main quantum number n to have the same value for the other three quantum numbers k , j and m .’ Yet, according to modern quantum mechanics, in the stationary states the quantum numbers of individual electrons do not commute with the Hamiltonian, only the total angular momentum does. For this reason in the framework of the modern quantum mechanics, the Pauli exclusion principle has been reformulated to reflect the antisymmetry of the wavefunction upon the interchange of two particles.⁷⁷

In other words, the aufbau principle, by assuming the existence of unchanging stationary individual electronic states, violates the Pauli exclusion principle. Only the many-electron system as a whole possesses stationary states. This mirrors the discussion of the spin alignment rules above—as the electrons are indistinguishable, each one-electron wavefunction (orbital) in the system depends on all other one-electron wavefunctions, and the change in system’s overall configuration (by, e.g., electron addition or removal) will cause all of the orbitals to change. With this notion in mind it is fairly easy to rationalize many formal aufbau principle violations, e.g., the infamous *3d–4s crossover*. In neutral atoms, the energy of a 4s orbital is slightly above that of a 3d orbital (when both orbitals are populated), therefore, 4s electrons are first ionized. However, 4s orbital is also populated first, because it offers less repulsion with a 3d electron than that between two 3d electrons, once the orbital energies are re-evaluated in the new configurations.^{79–81}

Quasi Closed-Shell Molecules

In molecular systems with unpaired electrons, the violation of the aufbau principle in electron configuration is reflected in the *conversion* of the SOMO and HOMO orbital energies, yielding a so-called *quasi-closed-shell state* (Figure 10). Its main

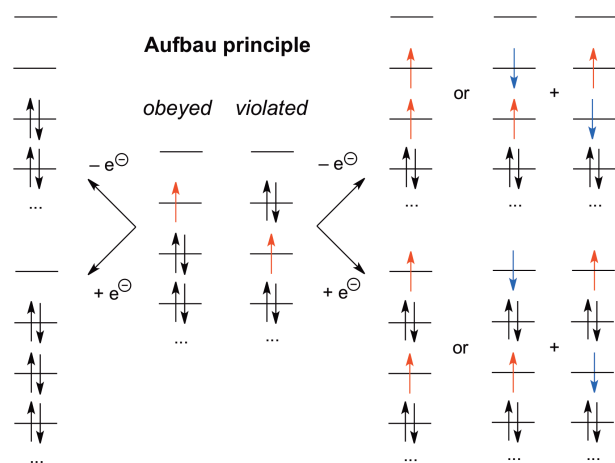
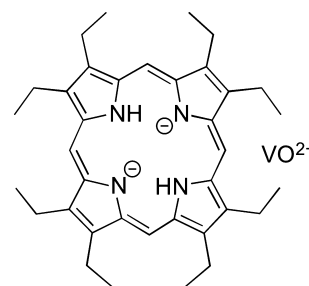


FIGURE 10 | aufbau principle of orbital occupation.

fingerprint is the electron attachment or removal pattern: upon ionization an electron is removed from the higher energy doubly occupied MO, leaving another unpaired electron behind, while upon addition new electron enters the former LUMO; essentially, SOMO does not participate in these processes. Subsequent orbital relaxation can further rearrange orbital energy levels. Since, as noted above, the orbitals themselves are neither observable, nor unique (in fact, erroneous *non-aufbau* occupations can be observed with restricted open-shell methods depending on the canonicalization parameters of the α and β electrons in Fock matrix, see Ref 82), a rigorous support for the non-aufbau occupation can be obtained *a posteriori* from the ionization potentials and electron affinities (or redox potentials in solution), measured using, e.g., cyclic voltammetry (CV), as well as from the determination of the spin state and magnetic properties of the corresponding open-shell oxidation/reduction products. Conservation of the initial unpaired electron and preferential formation of poly-radical species upon electron(s) removal from or addition to such non-aufbau molecules is an intriguing feature on its own, and, moreover, leads to the fascinating diradical chemistry. The applications and implications of such behavior in various molecular systems are discussed below.

The aufbau principle is frequently violated in inorganic molecules, such as the octaethylporphyrinate VO(oep) (Scheme 2), in which the unpaired electron is localized on vanadium, while one-electron oxidation and reduction involves respective occupied and unoccupied orbitals of the porphyrin ligand.⁸³ Non-aufbau occupation has also been observed in various quantum dots,^{84–86} and along the dissociation curve of LiF.⁸⁷



SCHEME 2 | VO(oep).

Upon one-electron oxidation of a (tempodt)Pt (^tBubpy) complex an electron is removed from HOMO on the dithiolate ligand, suggesting the presence of a SOMO–HOMO conversion in the ground state of an initial compound (Figure 11(a)). This suggestion has been confirmed by UV–Vis and ESR spectra, CV measurements and DFT calculations, as well as characterization of the subsequently formed dimerization product. Interestingly, isolated tempodt has a spin structure of a regular radical, i.e., SOMO is the highest α HOMO. SOMO–HOMO conversion in a Pt complex was thus attributed to an antibonding interaction of a highest doubly occupied MO of tempodt (NHOMO) and HOMO of Pt(^tBubpy)²⁺.⁸⁸ Non-aufbau orbital ordering was also elegantly confirmed in a related ditempo metalladithiolene triplet diradical by detecting and characterizing the bicyclic product that forms by coupling of the pairs of singlet biradicals on each terminus, produced by one-electron oxidation of the HOMO (Figure 11(b)).⁸⁹

A large class of molecules with non-aufbau orbital configurations consists of *nitronyl nitroxide radicals with spin-polarized donors* (Figure 12). Their story began with the TTF-CN-TEMPO radical—its first two one-electron oxidation waves correspond to the tetrathiafulvalene moiety (TTF) rather than the nitroxide, and the product of its first oxidation has a biradical character in ESR.⁹⁰ Reports of various nitronyl nitroxide (NN) radicals, bonded (either directly or *via* a conjugated bridge) to various donor moieties, e.g the aforementioned TTF and its derivatives, benzoquinone (BQ), *N,N*-dimethylamines, among others, followed.^{91–94}

All these species were shown to undergo one-electron oxidation producing triplet cation diradicals with nondegenerate SOMOs. The spin polarization of α and β electrons of the donor's HOMO by the unpaired spin has been proposed to potentially stabilize the electronic structure of the photo-excited triplet state into the ground state (Scheme 3).⁹⁵ The qualitative disjoint/non-disjoint classification of

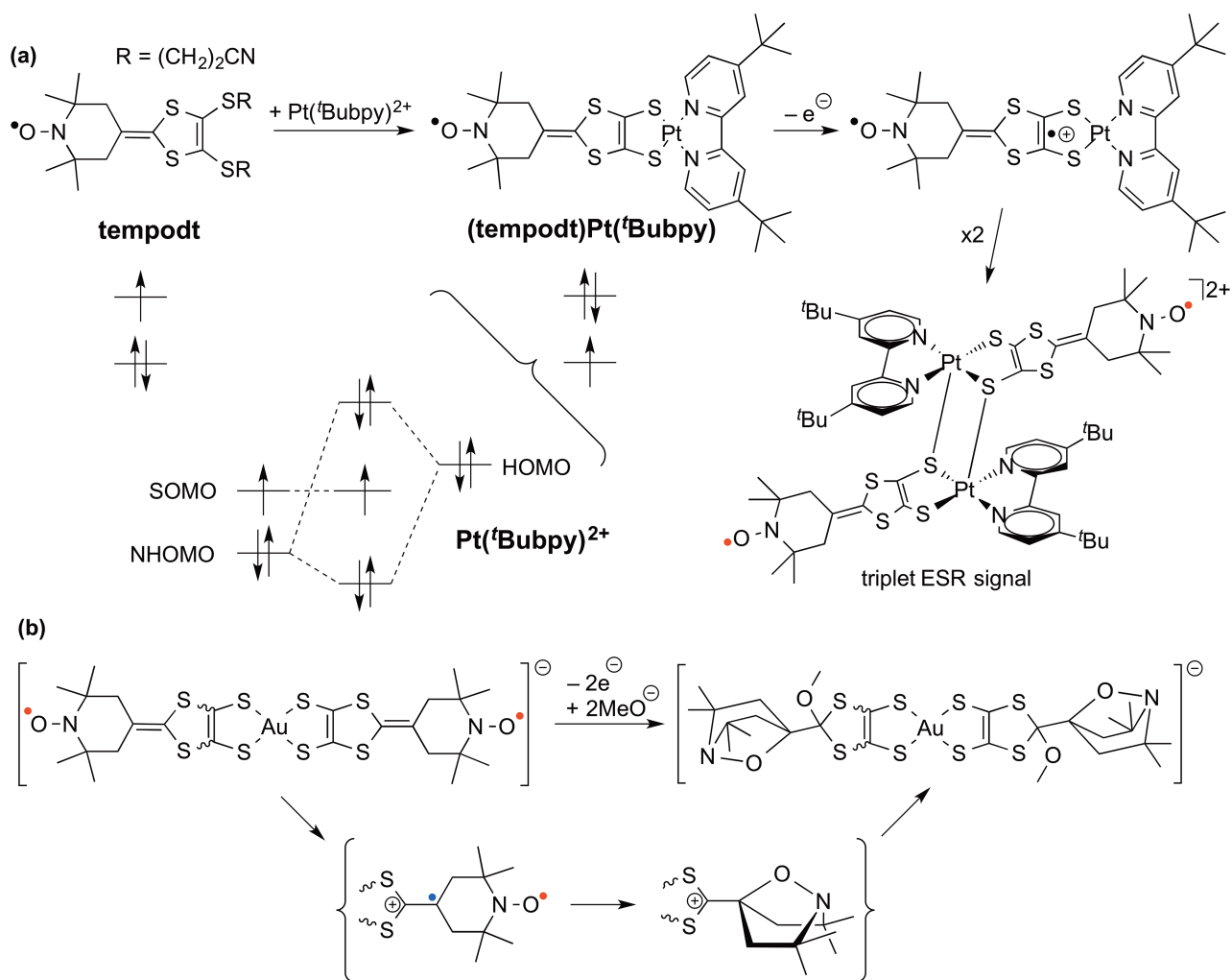


FIGURE 11 | Non-aufbau occupations in tempo dithiolate complexes. Red dots denote spin-up (α) electrons and blue dots represent spin-down (β) electrons.

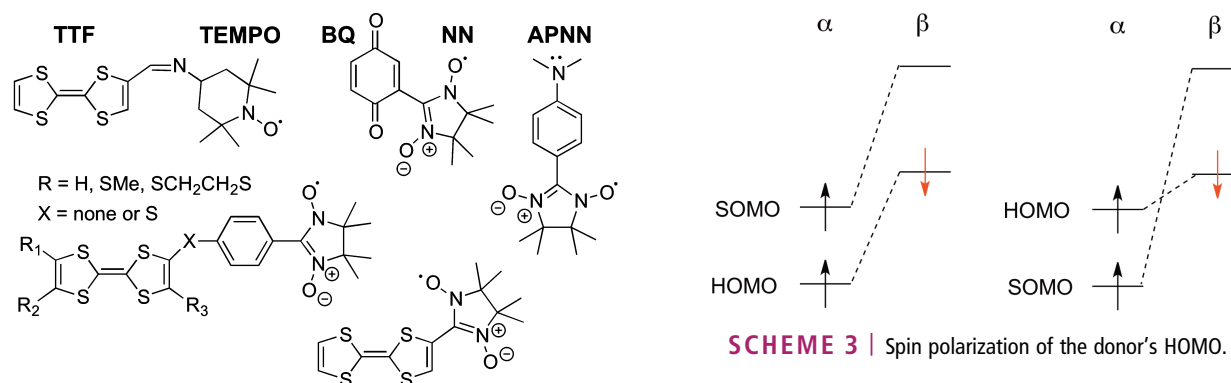


FIGURE 12 | Various (nitroxyl) nitroxide spin-polarized donors.

diradicals' NBMOs has been applied to these compounds in order to explain their SOMO-HOMO orbital energy level conversion in terms of the

symmetries and topologies of the radical's and donor's frontier orbitals.⁹⁶ As shown in Figure 13, in 1-pyrrolyl NN (NNN) the connectivity pattern *via* nodal atoms deems the donor's HOMO disjoint with respect to the radical's SOMO and NHOMO. However, in 3-pyrrolyl NN (β NN) its alternative topology

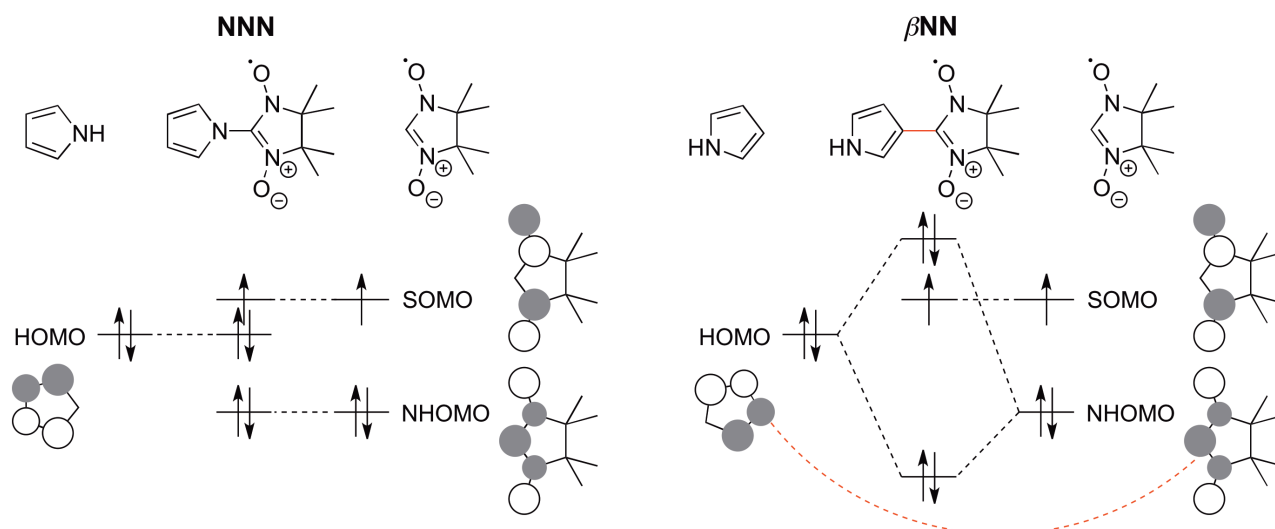


FIGURE 13 | Rationalization of orbital energy level conversion on the basis of the disjoint and nondisjoint character of the frontier orbitals.

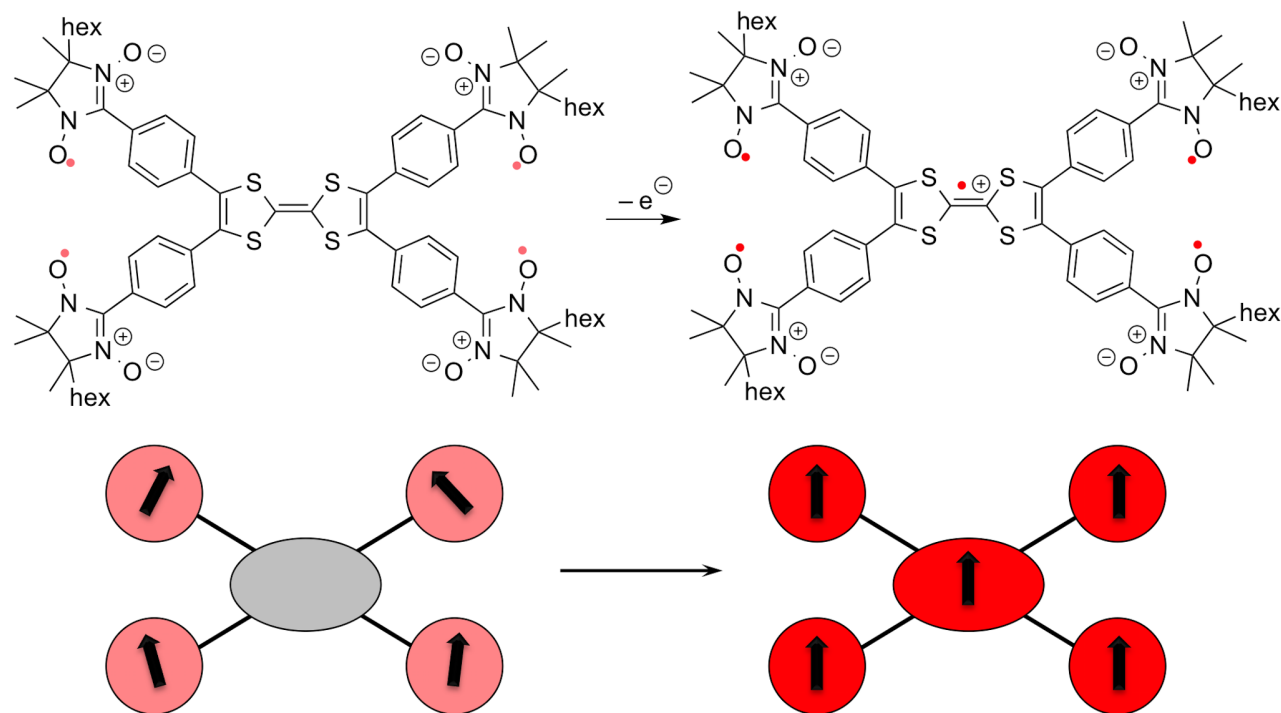


FIGURE 14 | Oxidation-induced ferromagnetic coupling in high-spin polyradical product. Red dots denote spin-up (α) electrons.

turns the donor's HOMO and radical's NHOMO into nondisjoint, leaving SOMO energy below that of their resulting nonbonding combination. Consequently, upon electron removal a nondisjoint triplet diradical is formed.

If several radical moieties are attached to the same donor unit and their corresponding orbital sets are formally nondisjoint, upon one-electron

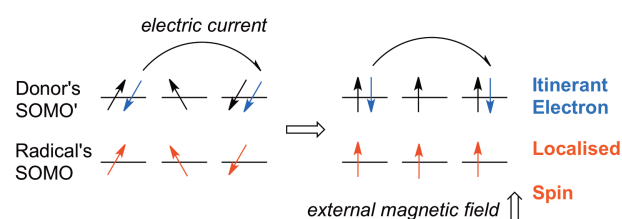
oxidation the newly formed spin on the donor affords strong ferromagnetic coupling of the dynamic molecular high-spin system (Figure 14).^{97,98}

The resulting high-spin molecules have at least two nondegenerate singly occupied MOs. The higher energy one, localized on the donor unit, is therefore capable to accept an itinerant electron, i.e., to conduct electric current (Scheme 4). The second SOMO,

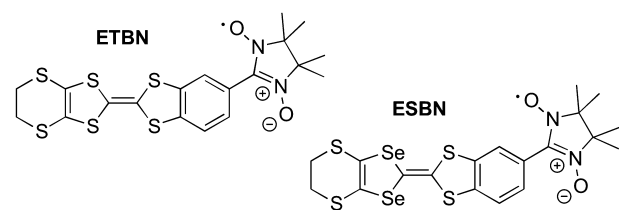
localized on the radical unit, is characterized by large on-site Coulomb repulsion toward the entering conducting electron and thus will not contribute to conductivity; instead, its spin is responsive toward an external magnetic field. Given the strong ferromagnetic coupling of such units, the system overall is expected to display significant magnetoresistance. Such systems therefore offer unique, dual *conductivity and magnetism* properties to the field of molecular electronics.^{99–101}

In practical terms, the conductivity will be achieved in the crystal of a radical coupled to the spin-polarized donor through the stacked donor units. At the same time, the radical unit needs to be stabilized by bulky substituents in order to maintain kinetic stability, which complicates the stacking. This obstacle has been overcome in ion-radical perchlorate salts of ETBN and ESNB with extended donor units (Scheme 5). The corresponding crystals represent first genuine paramagnetic conductors, in which the itinerant electron passes through the donors' stack and at the same time undergoes spin alignment with the radical's localized spin. The theoretically predicted non-aufbau configuration is consistent with the measured magnetic susceptibility and electron transport properties of the crystals, as well the ESR spectra, CVs and DFT calculations on isolated molecules. Neutral crystals of these and similar salts exhibit negative magnetoresistance, as expected, and can function as field-effect transistors.^{102–106}

Oxidation of spin-polarized donors induces magnetization and can be employed to switch



SCHEME 4 | Conductivity and magnetism in non-aufbau high-spin polyradicals.



SCHEME 5 | Systems combining conductivity and magnetism, realized in practice.

between the closed-shell and open-shell states. For example, an NN with a phenol-based spin-polarized donor operates as a pH sensor due to its ability to fluctuate between the triplet and closed-shell singlet states upon (de)protonation (Figure 15(a)).¹⁰⁷ Spin-polarized donors, coupled to verdazyl radical unit, such as anthracene-*p*-phenylene-oxoverdazyl (AnOV), have also been reported to form high-spin oxidation products (Figure 15(b)).^{108,109}

Another broad class of systems with SOMO–HOMO orbital conversion—distonic radical anions—has been reported very recently (Figure 16).^{110,111} A combination of a resonance stabilized radical, such as diallyl or nitroxide, and virtually any anionic group, non- π -conjugated to stabilizing molecular fragments, yields species, in which anion's HOMO(s) have energy(ies) higher than radical's SOMO. Moreover, the two moieties mutually stabilize each other, leading to higher radical stability and enhanced acidity of the conjugate acid. Importantly, if the anion is protonated, the aufbau orbital occupation is restored—thus, for the first time it is possible to switch between aufbau and non-aufbau configurations by association with H^+ (and hence *via* changing pH) or other cations. This stabilizing effect has been confirmed experimentally, while

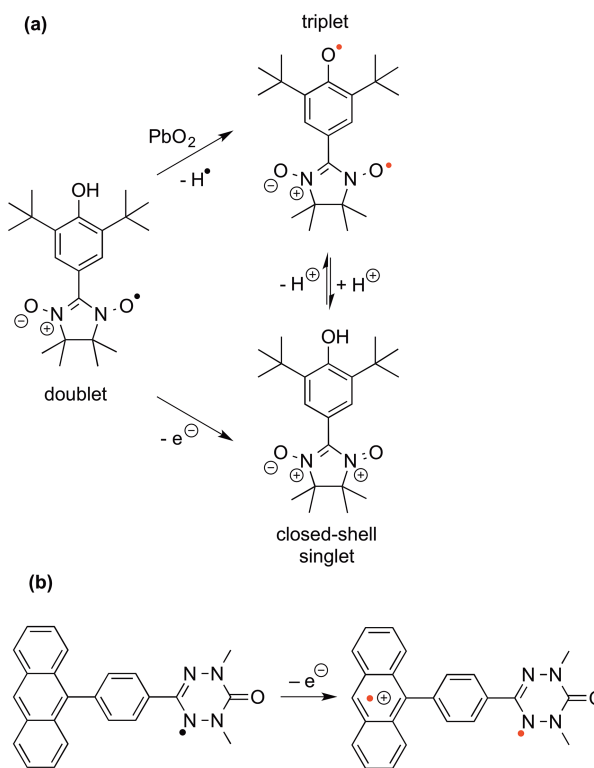


FIGURE 15 | Spin-polarized donors with radicals other than NN. Red dots denote spin-up (α) electrons.

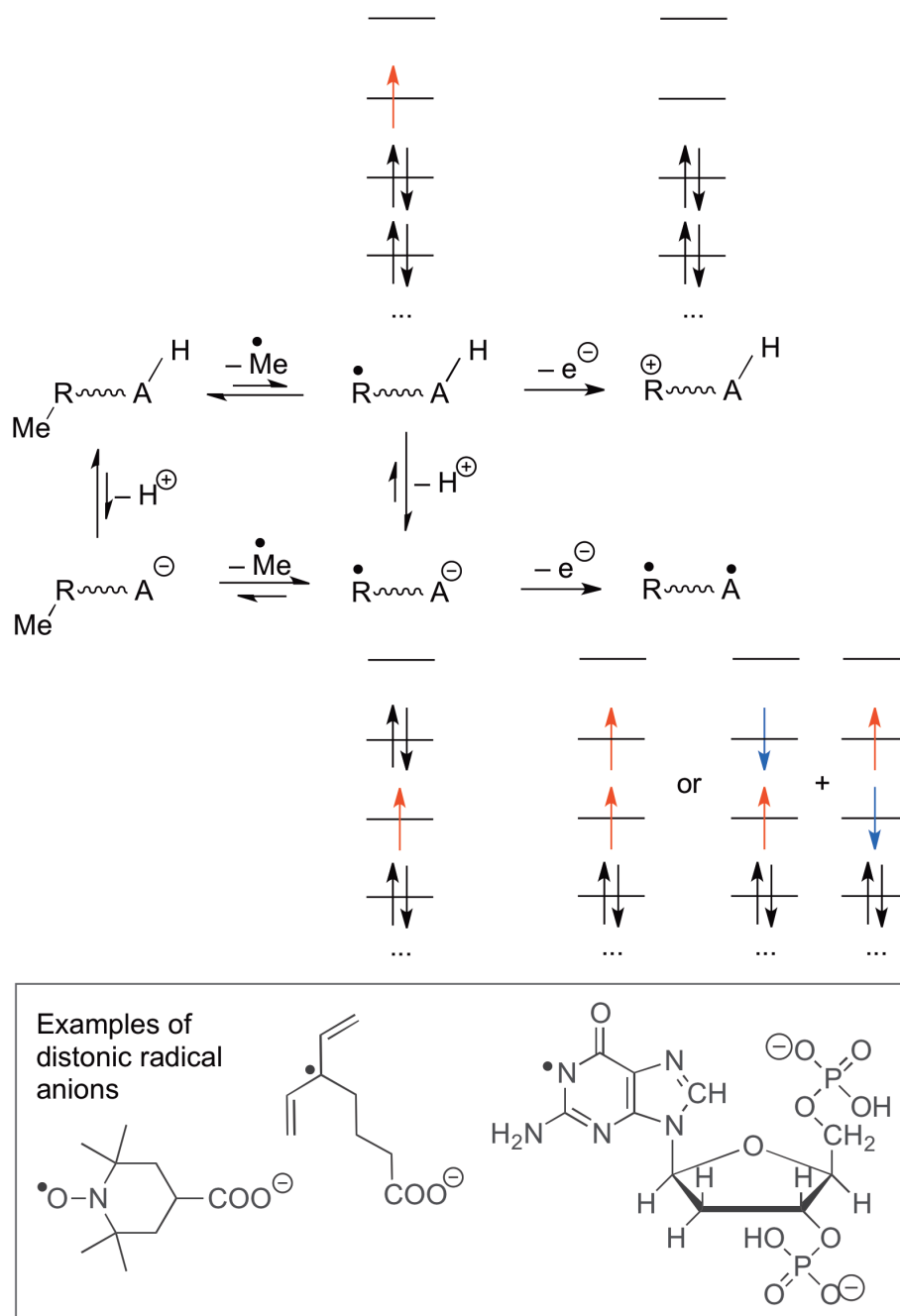


FIGURE 16 | Non-aufbau distonic radical anions.

the associated non-aufbau orbital configuration has been shown computationally to yield diradical species preferentially over the closed-shell zwitterion upon one-electron oxidation. Given the abundance of distonic radical anions in nature and practice, the scope of the discovered effect ranges from biomolecules, such as nucleobase pairs,¹¹² to potential molecular electronics applications.

While the examples above involved mostly the oxidation as both the diagnostic of a non-aufbau configuration and a practical tool of achieving the high-spin states, several studies report formation of non-aufbau polyradicals with nondegenerate SOMOs upon *electron addition*. For example, spiro-biphenalenyl radical VI is reduced to an open-shell singlet state (Figure 17(a)). It crystallizes without

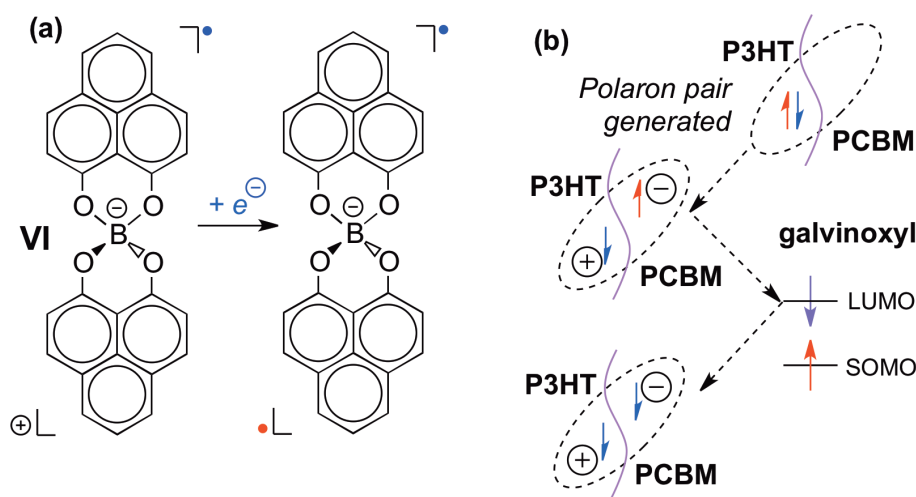


FIGURE 17 | Non-aufbau occupations formed by electron addition. Red dots denote spin-up (α) electrons and blue dots represent spin-down (β) electrons.

undergoing dimerization and functions as an intrinsic molecular metal.¹¹³ Doping the active layer of P3HT/PCBM with galvinoxyl radical massively improves its photovoltaic efficiency, because galvinoxyl allows its LUMO to transmit an intersystem crossing of a polaron pair from the singlet to the triplet *via* exchange interactions with its unpaired electron, preventing the undesired polaron recombination (Figure 17(b)).¹¹⁴

Finally, orbital energy level conversion has been observed in radicals, formed by *self-doping*. Specifically, radical autogeneration in TTF *via* protonation-assisted disproportionation is well established; in crystals of ammonium tetrathiafulvalene-2-carboxylate, TTF⁺•COO⁻NH₄⁺, intermolecular hydrogen bonding promotes similar self-doping, establishing a new type of carrier generation mechanism in organic semiconductors. Importantly, the SOMO of the TTF⁺•COO⁻NH₄⁺ unit is not the highest occupied orbital, according to the single- and multireference calculations on the model tetramer.^{115–118}

Clearly, molecules with quasi closed-shell configuration are not only unusual, but also extremely attractive as components of molecular electronic devices and various switches. Moreover, they elegantly illustrate how a purely theoretical concept—an orbital approximation—provides solid ground for their unexpected yet experimentally detected behavior. While to date only two major classes and very few isolated organic molecules have been reported to possess an orbital converted configuration, more and more systems are likely to be discovered and designed once the reasons causing their nontypical electronic structure are better understood. The

limited explanations, given in the literature, are based on qualitative rules of thumb, and a rigorous theoretical analysis of such molecules with the inclusion of multiple configurations, is in demand. Nonetheless, it is evident that the quasi close-shell configuration is achieved by combination of spatially separated stable radical center and molecular fragment serving as a source of high-energy doubly occupied orbitals, possessing sufficiently dissimilar reactivities (e.g., ionization potentials).

CONCLUSION

In the present review, we have discussed how various unconventional electronic configurations can be rationalized and realized in organic molecules for smart materials and molecular electronic applications. In diradicals, the multiplicity of the ground state and its separation from the next low-lying state are dependent upon static correlation in the multireference open-shell singlet wavefunction, as well as the dynamic correlation effect in both the singlet and triplet states. Various simple rules of thumb have been proposed and employed to explain the electronic structure of diradicals, yet their validity is limited by their intrinsic assumptions. Using rigorous state-of-the-art computational methods and various experimental techniques, diverse organic diradicals have been shown to possess a fluctuating spin state and thus be capable of transitioning between the triplet and open-shell, or between open- and closed-shell singlet configurations, in response to external stimuli, e.g., pH, radiation and temperature.

While MO theory struggles to model multireference systems accurately, it provides intuitive explanations for the fascinating chemistry of the so-called quasi closed-shell systems. These are the molecules in which a singly occupied MO is energetically lower than one or more doubly occupied MOs. As a result, they form polyradicals upon removal or attachment of electron(s), while keeping the initial unpaired spin intact. Such orbital configurations are in formal violation of an aufbau principle, however the latter is in fact in contradiction with the modern quantum chemistry. In this work, we have

highlighted several examples of such species being characterized experimentally and computationally, and outlined their peculiar chemical properties and practical applications as conducting magnets and pH switches.

These examples illustrate the obsolescence of qualitative rules, such as aufbau principle and Hund's multiplicity rule, given the contemporary understanding of the complex electronic configurations. These artifact textbook dogmas, therefore, should not remain a hindrance to future discoveries of molecules with unusual spin states and properties.

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