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UNPAIRED SPINS IN MOLECULAR PHYSICS AND CHEMISTRY

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Résumé. - L'interprétation des grandeurs physiques liées au spin dans le cadre d'une théorie qui fait intervenir le concept de densité de spin requiert des précautions : 1) On ne peut pas toujours calculer les densités de spin ni en discuter les valeurs en partant d'un modèle à particules indépendantes ordinaire (comme la théorie de Hartree-Fock avec contrainte de spin) ou de modèles améliorés du même genre sans contrainte de spin. Les premiers, négligeant les effets de polarisation de spin, sont incapables de reproduire d'éventuelles densités de spin négatives, tandis que le second présente de sérieux inconvénients en raison de la levée des contraintes à caractère self-consistant exprimées par le théorème de Delbrück-Ripka. 2) On ne doit pas confondre les densités de spin avec ce qu'on entend par populations de spin car ces dernières proviennent d'un partage entre atomes de la densité de spin totale, lequel met en jeu la notion presque insaisissable de l'atome "in situ".

Abstract. - The analysis of physical properties connected to the electron spin in terms of spin densities requires some caution : i) Spin densities cannot be always calculated or discussed in the frame of standard independent-particle model (as the restricted Hartree-Fock theory), neither in the frame of amended spin-unrestricted independent - particle models. The former, neglecting spin-polarization effects, are unable to reproduce possible negative spin densities, where as the latter have serious theoretical drawbacks, due to the relaxation of the self-consistent constraints expressed by the Delbrück-Ripka theorem. ii) Spin densities should not be confused with the so-called spin populations, because the latter are based on an atomic partitioning of the total spin density involving a rather elusive definition of atoms "in situ".

1. UNPAIRED ELECTRONS IN STRUCTURAL CHEMISTRY

Although spin was really included in the description of electron only from 1925 owing to requirements of Atomic Spectroscopy, the concept of unpaired electrons - or, more exactly, that of atoms with non - satisfied valencies in compounds like free radicals, biradicals, etc... goes back much earlier in Chemistry (see, e.g., [1]). The existence of chemically unlinked radicals, affirmed by Frankland and strongly denied by chemists as Gerhardt, Kekulé, Ostwald and many others during the last century, was revived by Gomberg at the outset of the 20th century in his studies on hexaarylethanes : he proved that an equilibrium may take place between some hexaaryl

dimers R-C-C-R and their monomeric moieties R-C with a carbon C retaining one of his valencies free. In spite of lengthy debates about the meaning of chemical formulas where an atom does not exhaust all his capabilities of building, not only the "trivalent" carbon of aryl radicals, but also other types of radical centers were finally accepted. For instance, a "divalent" nitrogen was recongnized in hydrazyl radicals as DPPH, $(C_6H_5)_2N-N-C_6H_5(NO_2)_3$, and a "monovalent" oxygen in nitric oxides, as the Frémy salt $(KSO_3)_2NO$ and the other nitroxides. In fact, the most representative stable radicals were known fifty years ago, and even more.

Between 1920 and 1940, the application of the Lewis electron-pair theory to molecules containing an odd number of electrons and the determination of their paramagnetic susceptibilities (see, e.g., [2]) conferred the status of unpaired electron spins to the unshared atomic valencies of radicals. As a general rule the experimental results can be analyzed in terms of paramagnetic susceptibilities by a spin-only formula :

$$\chi_{para} = (N \beta^2 / 3 k T) \times 4 S(S+1)$$

(β : Bohr magneton, N and k : Avogadro number and Boltzmann constant, T : absolute temperature) ; in other words, a molecular state of multiplicity $2S + 1$ has an effective magnetic moment

$$\mu_{eff} = 2\sqrt{S(S+1)} \beta$$

which can be reexpressed in the form

$$\mu_{eff} = \sqrt{n(n+2)} \beta$$

if we consider the highest spin component for a system of n unpaired electrons.

Classical magnetochemical measurements, by Kuhn, Müller and coworkers, and modern ESR experiments (see [3], [4], [5]) given many examples of compounds verifying this law.

In addition to organic free radicals with $n = 1$, it has been possible to prepare chemically related compounds containing an even number of electrons, but exhibiting a similar paramagnetism with $n = 2$, i.e., biradicals. Some magnetochemists distinguish between true biradicals and biradicaloids, the former being molecules in triplet ground states and the latter diamagnetic singlet ground states with thermally accessible triplets (see [6]). Generally, organic biradicals have their two paramagnetic centers located in distinct parts of the molecule, so that the electron exchange between the two moieties, as given by recent ESR studies, depend on structure peculiarities. In a just published monography, the hyperfine parameters of about 250 stable biradicals are listed [7]: as insulating factors between the unpaired electrons, we can mention the distance of their atomic centers, the steric arrangement of the two parts of the molecule and, sometimes, the lack of classical chemical formula. The three possibilities, indeed, are realized in pure hydrocarbon series [6] and in nitroxides series [4].

Most interesting from the theoretical viewpoint are those pairs of corresponding biradicals and biradicaloids, as the Schlenk hydrocarbon, bis-(1,3 phenylene diphenylmethyl) to which no Kékulé formula corresponds and the Chichibabin hydrocar-

bon, bis - (1,4 phenylenediphenylmethyl), which has a classical quinonoid structure.

After many years of controversy, ESR hyperfine studies have proved that, in accordance with the predictions of the resonance theory, Schlenk's hydrocarbon is a paramagnetic triplet ground state and Chichibabin's hydrocarbon a diamagnetic singlet, ESR signals in the fluid solution of the latter being produced by another paramagnetic species [8], [9].

In the last decades, polyradicals with more than two radical centers have been prepared (see [3]), in particular aryl, verdazyl and nitroxide triradicals. For instance, the hyperfine structure of the ESR spectra suggests that 1,3,5 - tris (di-p-biphenylmethyl) benzene has the form of a quartet ground state with $n = 3$ [10], whereas 1,3,5 - tris - (1,5 diphenylverdazyl - 3 yl) benzene is a mixture of the doublet and quartet states formed from almost degenerate configurations with three unpaired electrons [11].

A rather different case of magnetism, formerly known by the name of "magneto-photochromism" [2] happens when a diamagnetic molecule is optically excited in some states. However, the identification of the resulting paramagnetic species was delayed till the assignment, by Lewis and Kasha in 1945, of the metastable state in the Jablonski diagram [12] to the first excited triplet [13]. Before, spectroscopy has not contributed very much to our understanding of unpaired-electron systems, in spite of the use of colorimetric methods in free - radical chemistry. Probably, this is due to the fact that the study of relationships between colour and constitution was still largely based on classical considerations (see [14]). Let us mention that, if we try to assign the first excited doublets observed in the near U.V. and visible regions for an aromatic radical, for instance benzyl $C_6H_5CH_2$ [15] [16], we have to begin with all the configurations built from a basic three-electron system (Fig.1). The intricate sequence of the corresponding energy levels [17] [18] could be hardly discussed in a semi-classical approach, even without significant correlation effects.

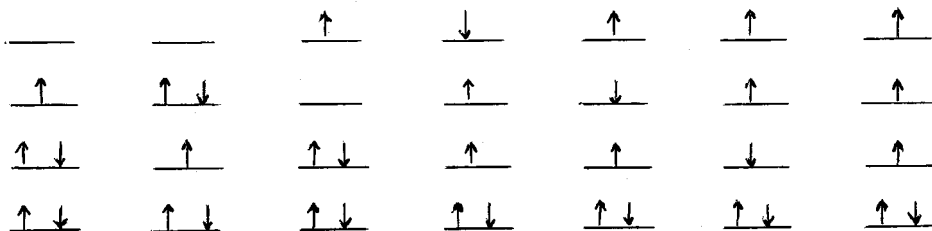


Fig. 1 - Lower-energy configurations of the three-electron systems ($M_S = 1/2, 3/2$)

2. SPINS IN QUANTUM CHEMISTRY

Even if it is perfectly true that all the properties of an electron system governed by a non-relativistic spin-free Hamiltonian could be described in the frame of theories involving no spin function at all (using permutational symmetry instead [19]), the concept of spinorbitals is still the most popular way of constructing and computing electronic wave functions for atoms, molecules and solids. In Quantum Chemistry, we normally begin with a set of one - electron functions including spin that are products of space and spin functions, i.e., with spinorbitals $\psi(\vec{r}, \sigma)$ obtained by multiplying orbitals $\varphi(\vec{r})$ by fixed spin functions $\theta(\sigma)$, where \vec{r} denotes the vector position of the electron in question and σ a two-valued discrete variable describing its spin in the standard Pauli theory. Next, we can solve the spin problem of the system by constructing either determinantal wave functions Φ of definite values for the total spin operations S_z and S^2 of the N electrons as a whole, or more limited building - blocks Ω where the electrons are gradually paired. The first approach is that of the molecular orbital method, the second that of the valence - bond method and various electron-pair theories (see [20]). The resulting many-electron functions form a convenient set of zeroth-order functions if we have to study special spin properties, as the ones which are not described by a spin - free Hamiltonian, for instance the spin - orbit and spin - spin interactions, or others which are not correctly taken into account in the first steps of the theory, for instance the so - called "spin polarization effects" not included in a single Slater determinant (see below).

Starting with the previous general framework we are accustomed to introduce more and more drastic assumptions on the spinorbitals $\psi = \varphi\theta$, with the object of having trial wave functions more or less closely related to our intuitive picture of the matter at the atomic or molecular level. There are :

- i) Spin functions $\theta(\sigma)$ written $\alpha(\pm 1/2) = 1$ or 0 and $\beta(\pm 1/2) = 0$ or 1 , instead of the more general form $c_\alpha \alpha(\sigma) + c_\beta \beta(\sigma)$, in order to have integers or half-integers for the average values (in \hbar units) of the total S_z operator.
- ii) Same space functions $\varphi(\vec{r})$ for both sets of α -spinorbitals and β -spinorbitals, in conformity with Aufbau principles based on the double-occupancy concept of orbitals.
- iii) Space functions $\varphi(\vec{r})$ transforming as basis vectors of irreducible representations for atomic or molecular systems belonging to some symmetry groups, which enables us to expand the total wave function in terms of many-electron functions with well-defined symmetry properties.

From assumptions i) and ii), we can immediately build trial wave functions that are, in addition, eigenfunctions of the S_z and S^2 operators of the electron system. Assumption iii) in configurational approaches ensures that the final wave function is also an eigenfunction of the operators describing the space symmetries

of the nuclear skeleton. Taking advantage of the spin and symmetry equivalences of the orbitals forming incomplete electron shells [21], we can easily fulfil the requirements of the Wigner theorem concerning the total wave function. This recipe, mentioned by Brillouin as far back as 1933 [22], is the basis of the usual electronic picture of atoms and the conventional starting point of the S C F and C I theories for molecules.

Here, we must add that there is no reason why the properties expected from a total wave function should be reflected by its building-blocks: Transferring the spin and space symmetries of, e.g., a configurational function to its orbital components is not a necessity, but only a matter of convenience for the calculations. Although such an approach would have no consequence if the expansion basis set was complete, the spin and symmetry equivalence conditions should be really considered as restrictions on the form of the orbitals; and this may have an effect on the final results in truncated theories, such as the S C F calculations where the wave function is reduced to one Slater determinant or, in the case of open-shell systems, a fixed combination of equivalent determinants. This point has been often overlooked in the S C F theory, owing to a too large interpretation of the symmetry properties of the Fock operator. A theorem put forward by Delbrück in 1930 for closed-shell atoms [23] and generalized to molecules by Roothaan in 1951 [24] states that the eigenfunctions of the one-electron Hamiltonian of the S C F method can be written in the form of symmetry-adapted orbitals, to be occupied by two paired electrons at most. As pointed out by Ripka in 1967 for nuclear structure calculations [25], this result expresses nothing but the self-consistency properties of the iterative calculation itself. If from the beginning we take doubly and singly occupied orbitals of symmetry-adapted form with respect to some group G leaving the effective Hamiltonian invariant, we recover corresponding "restricted" solutions at the end of the S C F iterative process. The Delbrück-Ripka theorem, however, does not preclude that "unrestricted" solutions may exist if one or several equivalence conditions imposed on the spinorbitals are relaxed. This usually happens in the case of Hartree-Fock instability, that is to say when a variational calculation with constraints does not yield the expected energy minimum, but another type of extremum [26].

An exact appraisal of the consequences of spin and symmetry equivalence conditions enables us to realize the limitations of the restricted S C F treatments as concerns the spin-density problems in systems with unpaired electrons and to understand the origin of the so-called unrestricted methods. Using the normalized one-electron operator

$$O_{spin}(\nu) = (1/M_s) S_z \delta(\vec{r}_p - \vec{r}_\nu)$$

where M_s is the average value of the total S_z spin [27], the spin density at each point P

$$\rho_{spin}(\vec{r}_p) = \langle \Phi | \sum_{\nu} O(\nu) | \Phi \rangle$$

reduces, in the restricted S C F picture, to the contributions coming from the singly

occupied orbitals $\varphi_{n+1} \dots \varphi_{n+p}$:

$$\rho_{\text{spin}}^{\text{RHF}}(\vec{r}_p) = (1/M_s) \times (1/2) \sum_{i=n+1}^p \varphi_i^*(\vec{r}_p) \varphi_i(\vec{r}_p)$$

Assuming an excess of α -spins ($M_s > 0$), we see that it is impossible to obtain negative spin densities anywhere; and so we should go beyond the S C F monoconfiguration treatment in order to have, in addition, β -spin pilings due to spin polarization effects in some particular points. In a C I expansion, spin polarization is described by the mixing of the S C F ground-state wave function with unpaired electrons ${}^{2S+1}\Phi_0$ with the monoexcited ones ${}^{2S+1}\Phi_{i \rightarrow k}$ involving an electron jump from a doubly occupied orbital φ_i to a virtual orbital φ_k , for which no Brillouin theorem can be laid down [28]:

$$\langle \Phi_0 | \mathcal{H} | \Phi_{i \rightarrow k} \rangle \neq 0$$

In the case of doublet states for instance (radicals), such a circumstance occurs with one of the two familiar functions with three unpaired electrons:

$$|\varphi_i \varphi_i \bar{\varphi}_n| \rightarrow (1/\sqrt{6}) \{ 2 |\varphi_i \varphi_k \bar{\varphi}_n| - |\varphi_i \bar{\varphi}_k \varphi_n| - |\bar{\varphi}_i \varphi_k \varphi_n| \}$$

The result is interpreted in terms of spin polarization because a mixing between Φ_0 and $\Phi_{i \rightarrow k}$ yields a first-order change in the spin density, the value of which can be derived from a function of the form:

$$\Phi_0 + \lambda \Phi_{i \rightarrow k} \simeq |(\varphi_i + \frac{\lambda}{\sqrt{6}} \varphi_k)(\bar{\varphi}_i - \frac{\lambda}{\sqrt{6}} \bar{\varphi}_k) \varphi_n| + \frac{2\lambda}{\sqrt{6}} |\varphi_i \varphi_k \bar{\varphi}_n| + \dots$$

where only the first term involving a splitting of the doubly occupied orbital in a non-zero spin system, contributes to $\rho_{\text{spin}}(\vec{r}_p)$ [29], [30]. As a matter of fact, a double perturbation limited to the first-order can be used with some success in spin-density calculations for radicals, giving [31]:

$$\rho_{\text{spin}}^{\text{CI}}(\vec{r}_p) = \rho_{\text{spin}}^{\text{RHF}} + 2 \frac{\sum \langle \Phi_0 | \mathcal{H} | \Phi_{i \rightarrow k} \rangle \langle \Phi_{i \rightarrow k} | \sum \mathcal{O}(\psi) | \Phi_0 \rangle}{\langle \Phi_0 | \mathcal{H} | \Phi_0 \rangle - \langle \Phi_{i \rightarrow k} | \mathcal{H} | \Phi_{i \rightarrow k} \rangle} + \dots$$

but precise numerical values requires a second-order perturbation treatment using the $\Phi_{i \rightarrow k}$ functions [32].

We can trace back the interpretation of the principle of double occupancy of the one-electron functions of atomic and molecular orbital theories in terms of spin constraints to the early days of Quantum Chemistry. The alternative concept of "different orbitals for different spins" was put forward by Löwdin in 1953, in order to go beyond the independent-particle model by simply relaxing the α and β spin equivalence [33]. In the frame of the S C F theory, the possibility of renouncing the double-occupancy hypothesis was recognized for a long time, for instance by Slater, Gombás and others..., but explicit introduction of this idea in the L C A O - M O method is to be found in two papers independently published in January [34] and March 1954 [35]. More exactly, an S C F - M O calculation method using different space functions for the two families of α and β spin orbitals of systems containing a subshell of unpaired electrons with parallel spins -i.e., doublet radicals, triplet states etc...- was suggested instead of a normal open-shell treatment, thought to be too difficult. It is based on the fact that the effective Hamiltonians acting on the

α and β spinorbitals contain different exchange parts K_α and K_β ; consequently, we can write two almost-independent Hartree-Fock equations for the space components

$$\begin{aligned} \varphi_i^\alpha \text{ and } \varphi_i^\beta \text{ of the spinorbitals:} \\ [H^{\text{core}} + \sum_{\text{occ}} (J_j^\alpha + J_j^\beta - K_j^\alpha)] \varphi^\alpha = e^\alpha \varphi^\alpha \\ [H^{\text{core}} + \sum_{\text{occ}} (J_j^\alpha + J_j^\beta - K_j^\beta)] \varphi^\beta = e^\beta \varphi^\beta \end{aligned}$$

where the sum of the K_j^α is not equal to the sum of the K_j^β , as in standard closed-shell systems, since the number of α and β spins are different ($M_S \neq 0$).

The same form of unrestricted method was called "spin-polarized Hartree-Fock theory" by the Slater group in connection with calculations of electronic structure for atoms and crystals [36], [37], [38], because it yields a spin density of the form:

$$\rho_{\text{spin}}^{\text{UHF}}(\vec{r}_P) = (1/M_S) \left[\frac{1}{2} \sum_{\text{occ}} \varphi_i^{\alpha*}(\vec{r}_P) \varphi_i^\alpha(\vec{r}_P) - \frac{1}{2} \sum_{\text{occ}} \varphi_i^{\beta*}(\vec{r}_P) \varphi_i^\beta(\vec{r}_P) \right]$$

where a negative sign somewhere is interpreted in terms of spin-polarization effects. Although the numerical concordance of the UHF spin density $\rho_{\text{spin}}^{\text{UHF}}$ with the above-defined quantity $\rho_{\text{spin}}^{\text{CI}}$ is by no means guaranteed, an UHF approach preserving the simplicity of the independent-particle model has many advantages from computational and descriptive purposes. As noticed by Mc Connell for E.S.R. coupling constants of organic free radicals [39] and by Watson and Freeman for crystalline form factors of iron-series ions [29], the UHF Hartree-Fock theory is particularly well suited to the study of magnetic properties of atoms, molecules and solids, hence a huge number of calculations of this type performed in connection with experimental data coming from E.S.R. studies of radicals (see [40]) or conductivity studies of solids [38].

Relaxing the spin constraint connected to the double-occupancy principle has a major drawback as regards the treatment of unpaired electron systems by the unrestricted SCF method in its simplest form, namely that the resulting total wave function is not an eigenfunction of the S^2 spin operator. Given a determinantal function without spin and symmetry equivalence conditions, it is always possible to select the component of right spin or space properties by projecting it onto the appropriate subspace. Unfortunately, this procedure destroys the simplicity of the independent-particle model if it is performed before the variational calculation or the variational character of the results if it is performed after. The second recipe, however is commonly adopted in E.S.R. calculations, using projected spin densities or, more simply spin densities obtained after purifying the doublet state from its contamination by the next quadruplet component [41], [42]. This expedient may improve the agreement between theory and experiment in some cases, but we must admit that we are computing observables with something else than the primitive SCF wave function, especially if the value found for of the S^2 operator deviates from $S(S+1)$ too strongly. To the S^2 problem, we can add a second drawback recently discovered in unrestricted SCF calculations at large interatomic distances [43]: except in very

simple centrosymmetry systems, it is not possible to remove the double-occupancy spin constraints without affecting the space constraints connected with the different asymptotic behavior of the R H F and U H F functions. Consequently, the interpretation of the U H F results in terms of spin polarization effects only is not valid for all distances.

3. SPECTROSCOPIC AND CRYSTALLOGRAPHIC APPLICATIONS

Experimentally, we have access to spin densities through two different techniques, the electron magnetic resonance which gives local values $\rho(\vec{r}_P)$ of the spin density for points P where nuclear spins N are located, and the polarized neutron scattering which yields spin density maps $\rho(\vec{r})$ on convenient projection planes. The first method involves an analysis of the hyperfine structure of E S R spectra in terms of electron nucleus coupling constants a_N resulting, in isotropic conditions, from a contact (or Fermi) term of the form :

where \vec{I}_N and $\vec{S} = \sum_V \vec{S}(V)$ are the non-zero interacting spins of some nucleus N and an atomic or molecular system with unpaired electrons. The second method describes the observed diffraction pattern at each Bragg reflection (hkl) by the superposition of a known nuclear structure factor F_N and a magnetic structure factor F_M extracted from the experimental data ; the latter are the Fourier transforms of the unknown spin density through the scattering vector K for the (hkl) reflection :

$$F_M = \int_V \rho_{spin}(r) e^{2\pi i K \vec{r}} dV$$

(V unit cell volume).

From a quantum-mechanical point of view, electron spin resonance and polarized neutron scattering give us molecular observables which can be considered as being derived, as regards their electronic part, from the spin density operator $\hat{\rho}$. A theoretical determination of the corresponding average value ρ_{spin} includes one-electron integrals between occupied or virtual molecular orbitals φ_i and φ_j , to be calculated from their expansion in terms of atomic basis orbitals χ_p and χ_q :

$$\langle \varphi_i | \hat{\rho} | \varphi_j \rangle = (1 M_S)(\pm 1/2) \sum_P \sum_Q c_{pi}^* c_{qj} \chi_p(\vec{r}) \chi_q(\vec{r}) \equiv \rho_{ij}$$

(\vec{r} : vector locating the point where the spin density is computed, i.e., a nucleus N for electron magnetic resonance, an arbitrary point P for polarized neutron scattering. The spin density expressions ρ_{spin}^{RHF} and ρ_{spin}^{UHF} given by restricted and unrestricted S C F calculations include no off-diagonal elements $\langle \varphi_i | \hat{\rho} | \varphi_j \rangle$, but only diagonal elements $\langle \varphi_i | \hat{\rho} | \varphi_i \rangle$ corresponding to occupied molecular orbitals. Cross-terms multiplied by C I interaction integrals involving virtual orbitals φ arise in more complete treatments.

In addition to many semi-empirical studies successful ab-initio calculation of hyperfine coupling constants starting with spin-restricted wave functions have been carried out for simple hydrocarbon and nitroxide radicals [31], [44], [45].

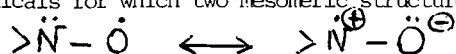
The spin densities computed in these (S C F + C I) approaches contain a first, purely S C F, contribution usually called the "direct interaction term" in the E S R terminology, because the value $\rho_{spin}^{RHf}(\vec{r}_N)$ coincides with the probability of finding, in frame of the singly-occupied molecular orbital picture, an unpaired electron at nucleus N. The final spin density ρ_{spin}^{CI} collects spin polarization and, ideally, correlation effects, which can be considered in the same context as due to some "indirect" interactions. For the former, chemists often speak of "through-space mechanism" in structural analyses of hyperfine coupling constants, whereas they connect the latter, in some cases, to "through-bond" mechanisms (see [46]). Unrestricted S C F calculations carried out at the ab-initio level by the molecular orbital method for simple radical systems including nitroxides [47], [48], and by the X_α method for transition-metal radicals [49] do not lend themselves to such a dichotomy between S C F direct and spin-polarization indirect interactions.

By definition, all the atomic basis orbitals χ forming the L C A O - expansion of each molecular orbital ψ_i contained in $\rho_{spin}^{RHf}(\vec{r}_P)$ or $\rho_{spin}^{UHf}(\vec{r}_P)$ contribute to the value of the S C F spin density at an arbitrary point P, except those which have just a node on P. Similar considerations hold for the pair of orbitals ψ_i and ψ_j in the indirect interaction term in the spin-restricted approach. If the electron system has a radical center with a nuclear spin N at point $\vec{r}_P \equiv \vec{r}_N$ the value taken by the contributions of the molecular orbital ψ_i to the spin density at nucleus N :

$$\rho_{ii}(\vec{r}_N) \propto \sum_{p,q} c_{pc}^* c_{qc} \chi_p(\vec{r}_N) \chi_q(\vec{r}_N)$$

gives a theoretical basis to the distinction between σ and π free radicals [50]. The rather large hyperfine coupling constants a_N found in the former can be directly connected, in the R H F picture of an unpaired electron occupying the orbital ψ_i , with the magnitude of the non-zero density $\rho_{ii}(\vec{r}_N)$ due to the nodeless atomic orbitals of the radical center (e.g., s orbitals of nucleus N). On the other hand, the smaller couplings a_N observed in the latter, where $\rho_{ii}(\vec{r}_N)$ is practically zero because all the atomic components of ψ_i located at the radical centers are orbitals having nodes with respect to the some symmetry plane, will be interpreted by an indirect spin-polarisation mechanism (e.g., the coupling constants a_H of hydrogens attached to carbons with $2p\pi$ orbitals in aryl radicals).

We can try to go a little farther by means of an appropriate partitioning of the molecular spin density in atomic contributions, with the hope of finding a relationship between experimental data and chemical formulas. For instance, in the case of the nitroxide radicals for which two mesomeric structures can be written :



the hyperfine splittings due to the nitrogen and oxygen nuclei in the E S R spectra and the corresponding coupling constants obtained by semi-empirical evaluations [51] and ab-initio calculations [45], [48] can be rationalized by assuming a predominance

of the first formula, while the polarized-neutron experiments indicate an equal sharing of the unpaired electron between nitrogen and oxygen [52].

To cope with the difficulties of specifying the notion of atoms in molecules theoretically, it is customary to introduce the so-called "atomic spin populations" in imitation of the Coulson charges and bond orders or the Mulliken population analysis. The partial atomic population of an atom A in a molecular orbital ψ_i is defined as follows :

$$n_i^A = \sum_{p \in A} (c_{pi}^2 + \sum_{q \neq p} c_{pi} c_{qi} S_{pq})$$

where S_{pq} is the overlap integral between an orbital χ_p belonging to A and any other orbital χ_q centered on A or not). Now, if we assume that the matrix elements of a delta operator with respect to the basis atomic functions can be approximated by a Mulliken formula, that is to say :

$$\chi_p^*(\vec{r}) \chi_q(\vec{r}) = S_{pq} [\chi_p^*(\vec{r}) \chi_p(\vec{r}) + \chi_q^*(\vec{r}) \chi_q(\vec{r})] / 2$$

the molecular matrix element e_{ii} becomes :

$$e_{ii}(\vec{r}) \propto \sum_{p \in A} (c_{pi}^2 + \sum_{q \neq p} c_{pi}^* c_{qi} S_{pq}) \chi_p^*(\vec{r}) \chi_p(\vec{r})$$

so that the partial population n_{pi}^A of the atomic orbital χ_p centered on atom A can be considered as the spin population of χ_p in the singly occupied molecular orbital ψ_i of the RHF picture. In the more sophisticated UHF model, the atomic spin population will be defined as a difference between the sum of the populations coming from the α and β spinorbitals. The concept of spin populations is all right in semi-empirical evaluations not only for studying direct interactions due to non-zero spin densities, but also indirect interactions roughly proportional to π atomic densities [53] ; but it has to be avoided in non-empirical computations, because it is based on a Ruedenberg expansion of the χ orbitals limited to the first-order terms

$$\chi_q(\vec{r}) = \sum_{p \in A} S_{qp} \chi_p(\vec{r}) \quad (q \in B \neq A)$$

an approximation questionable for a delta operator in an ab-initio basis set, and non-valid for an orbital χ_q centered on the same atom as χ_p . Consequently, the experimental ESR splittings are compared - after, possibly, vibrational corrections [54] - to RHF, RHF + CI or UHF hyperfine coupling constants exactly computed from the standard expression of the spin coupling operator. The same procedure could be applied to the structure factors coming from polarized-neutron experiments, using the Fourier transform of the theoretical spin density, in conformity with the quantum-mechanical definition of an observable ; and then, best form factors for atoms "in situ" could be extracted from a spherical least-square fitting [55] ...

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