PROTON SPLITTINGS IN ELECTRON SPIN RESONANCE SPECTROSCOPY

W. J. VAN DER HART

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Aan de nagedachtenis van
mijn Moeder
aan mijn Vader
aan Jopie en Hugo

CONTENTS

CHAPTER I

INTRODUCTION

Electron spin resonance (e.s.r.) has become an important tool in the study of paramagnetic molecules and ions [1,2]. Besides the purely chemical applications such as the detection and identification of free radicals occurring in chemical reactions, it offers a possibility to investigate the electron distribution in paramagnetic molecules in a rather direct way. Especially the hyperfine structure of e.s.r. spectra is a valuable addition to data obtained e.g. from absorption spectroscopy in the ultraviolet and visible region.
In this thesis we shall give a critical survey and an extension of the theory of proton splittings in the e.s.r. spectra of organic radicals in solution. This will be followed by a discussion of the e.s.r. spectra of triphenylmethyl and related compounds.

When a system containing an unpaired electron spin is placed in a magnetic field $\vec{H}$, the spin momentum will be quantized parallel or anti-parallel with respect to the direction of the magnetic field. The energy difference between these two states is

$$\Delta E = g \beta H$$

where g is the spectroscopic splitting factor and β is the Bohr magneton. Transitions between the two states can be induced by irradiation when the radiation frequency ν satisfies the condition

$$h \nu = \Delta E = g \beta H$$

Instead of one single line, e.s.r. measurements usually give a number of lines because of the additional dipole-dipole interaction between the magnetic moments of the electron and nuclear spins. The corresponding term in the Hamiltonian can be written

$$H_{op} = (\vec{\mu}_e \cdot \vec{\nabla}_e)(\vec{\mu}_N \cdot \vec{\nabla}_N)(\frac{1}{r}) - \frac{8\pi}{3}\,\delta(\vec{r}_e - \vec{r}_N)\,\vec{\mu}_e \cdot \vec{\mu}_N \qquad 1.1$$

where $\vec{\mu}_e$ and $\vec{\mu}_N$ are the operators for the magnetic moments of electron and nucleus respectively, r is the distance between electron and nucleus and $\delta(\vec{r}_e - \vec{r}_N)$ is the Dirac delta function. The first term can only be used outside a small sphere surrounding the nucleus which can be taken infinitely small after the integrations in the calculation of matrix elements have been carried out.

The last term in 1.1, which is called the Fermi contact interaction, is isotropic. The first term is the anisotropic dipole-dipole interaction. For e.s.r. measurements in solution, where the orientation of the molecules changes rapidly, the first term averages out although it may influence the line widths in the e.s.r. spectrum (see e.g. reference 3 for a review of line width effects). Then the hyperfine structure depends on the second term only.

Because of the weakness of the hyperfine interaction, it will not have any significant influence on the orbital motion of the electrons. Therefore it is allowed to average the Hamiltonian over the orbital part of the wave function whereby a spin-Hamiltonian remains containing spin-dependent operators only. For measurements on solutions in strong magnetic fields 1.1 can be written

$$H^S_{op} = a^N S^z I^z_N \qquad 1.2$$

where S^z and I^z_N are the electron and nuclear spin angular momentum operators in the direction of the magnetic field and a^N is the splitting constant of nucleus N. Because of the Dirac delta function in 1.1, a^N is proportional to the electron spin density $\rho(\vec{r}_N)$ at the position of the nucleus where $\rho(\vec{r}_N)$ is defined as the probability of finding and electron with α-spin at $\vec{r}_N$ minus the probability of finding an electron with β-spin at $\vec{r}_N$. When more than one nuclei are present, equation 1.2 must be summed over all nuclei.

In most of the radicals studied in organic chemistry the unpaired spin is part of the π-electron system. The wave function for the ground state is therefore antisymmetric with respect to a reflection in the nodal plane of the π-electron system and consequently the spin density in the nodal plane is zero. At first sight one should expect that the splitting constants of nuclei in this nodal plane vanish. This is not in agreement with the experiments, however. The reason why this is so, is now well understood although there still remain difficulties in the actual calculation of splitting constants (see chapter IV).

Besides the hyperfine structure due to nuclei in the nodal plane of the π-electron system, further splittings can be observed caused by substituent groups. This offers a possibility to study the interaction between a π-electron system and a substituent in a direct way. Usually substituent effects are studied by an investigation of the influence of a substituent on the properties of the π-electron system (or of the whole molecule). In e.s.r. measurements, however, the splitting constants of the nuclei of substituents give a direct information about the transmission of a property of the π-electron system (the unpaired spin) into the substituent. This is especially important because it might give an answer to the much discussed question of the significance of hyperconjugation [4,5,6].

Hyperconjugation, which can be defined as the influence of the mixing of the usual wave function for the ground state with wave functions in which an electron is transferred between a π-electron system and an alkyl substituent, is one of the possible explanations of the electron-donating character of a methyl substituent. The electron-donating character will be more effective in positive ions than in negative ions so, if hyperconjugation is the mechanism which causes the spin density in the methyl group, we should expect that methyl proton splittings are relatively larger in positive ions than in negative ions. From the observed large differences between positive and negative ions Bolton, Carrington and McLachlan [7] and Colpa and de Boer [8] concluded that the hyperfine splitting due to methyl protons must be ascribed to hyperconjugation. These authors calculated the splitting constants according to a molecular orbital approximation for the complete system including π-electrons and electrons of the methyl group. This type of approximation differs essentially from the usual theory of the splitting constants of protons directly bonded to the unsaturated system where the wave functions for the separated π- and σ-electron systems are assumed to be calculated in the best possible way before the systems are coupled together. From the comparison with the latter theory it will be clear that the molecular orbital calculation of methyl proton splitting constants has several disadvantages:

1. It is often assumed that a valence bond approximation yields a better wave function for a σ-bond than a molecular orbital calculation. This can not be taken into account in a molecular orbital calculation for the complete system.

2. Since the π-electron system and the methyl group are from the beginning considered as one system, the calculation does not yield a simple relation between the spin density in the methyl group and the spin density distribution in the π-electron system. This applies especially for substituents bonded to atoms for which the π-electron spin density is negative, e.g. the meta carbon atoms in triphenylmethyl.

We have tried to evaluate a more general model in which the wave functions for the π- and σ-systems are assumed to be calculated in the best possible way before coupling effects due to the influence of charge transfer and mixing with triplet states of the σ-bonds are taken into account. The derivation of formulas for the spin density in several types of σ-bonds in organic radicals will be discussed in chapter II. Because the derivation is rather lengthy and intricate, we shall discuss a simple system in the introduction of chapter II.

Both the general formulas and the best possible wave functions for the separated systems are too complicated for practical calculations. Therefore approximations must be introduced. The approximations used in the calculations for the π-electron system are discussed in chapter III.

In chapter IV we shall discuss the application of the formulas in the calculation of the splitting constants of protons directly bonded to the unsaturated system and of the α- and β-protons of alkyl substituents. In the literature a large number of papers on proton splittings have been published but in many of these papers the theoretical foundation is rather questionable. Therefore the discussion in chapter IV is combined with a critical survey of the existing literature.

In chapter V we shall discuss the e.s.r. spectra of a number of substituted triphenylmethyl radicals and corresponding 'biradicals'. This part of our investigations is an extension of Lupinski's study of triphenylmethyl radicals [9]. The improvement of e.s.r. spectrometers since the time of Lupinski's measurements enabled us to obtain much more accurate conclusions from the observed spectra.

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CHAPTER II

THEORY OF THE SPIN DENSITY IN THE σ-BONDS OF A π-ELECTRON RADICAL

A. INTRODUCTION

For many organic radicals the wave function for the ground state is antisymmetric with respect to reflection in the plane of the molecule. These radicals are usually described as consisting of a π-electron system having an odd number of electrons and of a number of σ-bonds each containing two electrons with opposite spin. In this description the spin density on nuclei in the nodal plane of the π-electron system vanishes because the π-electron density is zero whereas in the σ-bonds the probability of finding an electron with α-spin is equal to the probability of finding an electron with β-spin. As has been remarked in chapter I, the hyperfine structure of e.s.r. spectra in solution depends on the spin density on the nuclei so for radicals such as the naphtalene anion, where all nuclei are in the nodal plane, we should expect one single line without hyperfine structure. Experimentally, however, a complex hyperfine structure is observed which must be attributed to the hydrogen nuclei of the naphtalene anion [1].

In order to explain this splitting several mechanisms might be proposed:

1. A non-zero spin density on the nuclei due to the out-of-plane vibrations.
2. Spin-orbit coupling effects.
3. A change of the spin density distribution in the σ-bonds due to the presence of an unpaired spin in the π-electron system (spin polarization).

These possibilities will be discussed in some more detail:

1. The amplitude of the out-of-plane vibrations depends on the mass of the nuclei so from this explanation of the hyperfine structure we should expect that deuterium splittings are relatively smaller than hydrogen splittings. Experimentally, however, it appears that the ratio of corresponding hydrogen and deuterium splittings is nearly equal to the ratio of the gyromagnetic factors of these nuclei [2]. Therefore it is generally assumed that the influence of the out-of-plane vibrations is of minor importance. In recent publications it has been shown that this effect is not entirely negligible because it might explain the slightly anomalous ratio of hydrogen and deuterium splittings and the temperature dependence of the hyperfine structure which is observed e.g. in the methyl radical (see references 3 and 4 and references cited therein).

2. McConnell and Chesnut [5] have discussed the possible influence of pseudo-hyperfine interactions, i.e. cross terms obtained from the coupling between the electron orbital momentum and the electron spin and nuclear spin. For radicals containing only light nuclei this term is negligible but in other cases it may be of some importance [6].
Besides, one might wonder whether the electron-spin electron-orbit coupling could mix the wave function for the ground state with wave functions in which the number of σ-electrons is odd. This mixing yields in second order a spin density in the σ-bond. With a crude estimate it can easily be shown, however, that the calculated splitting is much smaller than the observed one.

3. Spin polarization is generally accepted to be the correct explanation. In the theoretical treatment of this effect the wave function for the ground state is mixed with wave functions in which the σ-part is a triplet function [5, 7]. In these theories the zeroth order wave functions are written as products of the wave functions for the separated π- and σ-electron systems which are assumed to be calculated in the best possible way. The mixing of these wave functions is obtained by introduction of the π-σ exchange interaction.

Besides splittings due to nuclei within the nodal plane, splittings are observed caused by other nuclei such as the protons of a methyl substituent. In this case the value of the π-electron wave functions at the position of the nuclei does not vanish but a simple calculation shows that this explanation of the observed splitting constants is wholly unsatisfactory. Bolton, Carrington and McLachlan [8] and Colpa and de Boer [9] have shown that the sign and the magnitude of methyl proton splittings provide strong evidence for the importance of hyperconjugation. It is noteworthy that a calculation according to the hyperconjugation model differs essentially from the calculation of the splitting constants of nuclei within the nodal plane mentioned above. In the latter case the wave functions for the π- and σ-electron systems are calculated in the best possible way before the systems are coupled together. In the hyperconjugation method, however, the interaction within the π- and σ-systems and the interaction between the two systems are introduced simultaneously. In view of the smallness of the interaction between a π-electron system and a methyl substituent we should expect that a more realistic model is obtained when the calculation of splitting constants of methyl protons is also performed by calculating the wave functions for the π- and σ-systems in the best possible way before the interaction between the separated systems is introduced. The theoretical evaluation of this model is presented in this chapter.

In order to illustrate the essential points in the rather lengthy discussion, we first consider a simple system consisting of a carbon $2p_z$-orbital and a CH-bond which will be described with the bonding and antibonding molecular orbitals σ and σ*. The wave function for the ground state is

$$\psi_0 = \mathscr{A}\,p(1)\sigma(2)\sigma(3)\,\frac{\alpha(1)\{\alpha(2)\beta(3) - \beta(2)\alpha(3)\}}{\sqrt{2}}$$

where $\mathscr{A}$ is the antisymmetrization operator and α and β are the spin functions for one electron.

As has been remarked above, the spin density in a σ-bond in the nodal plane is obtained from the mixing of ψ_0 with a doublet wave function in which the σ-part is a triplet function:

$$\psi_T = \mathscr{A}\,\frac{p(1)\{\sigma(2)\sigma^*(3) - \sigma^*(2)\sigma(3)\}}{\sqrt{2}}\;\frac{\{2\beta(1)\alpha(2)\alpha(3) - \alpha(1)\alpha(2)\beta(3) - \alpha(1)\beta(2)\alpha(3)\}}{\sqrt{6}}$$

For σ-bonds which are not located within the nodal plane ψ_0 can also mix with wave functions in which an electron is transferred from the σ-bond to the $2p_z$-orbital or vice versa:

$$\psi_{\sigma p} = \mathscr{A}\,p(1)p(2)\sigma(3)\,\frac{\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}\,\alpha(3)}{\sqrt{2}}$$

$$\psi_{p\sigma} = \mathscr{A}\,\sigma^*(1)\sigma(2)\sigma(3)\,\frac{\alpha(1)\{\alpha(2)\beta(3) - \beta(2)\alpha(3)\}}{\sqrt{2}}$$

The final wave function

$$\psi = \frac{1}{\sqrt{N}} \{ \psi_0 + \lambda\psi_T + \mu\psi_{\sigma p} + \nu\psi_{p\sigma} \}$$

where N is the normalization constant, is easily calculated with second order perturbation theory. The spin density becomes

$$\rho = \langle \psi | \rho_{op} | \psi \rangle$$

where ρ_{op}, the spin density operator, is defined by

$$\rho_{op}(\vec{r}_x) = \sum_i \delta(\vec{r}_i - \vec{r}_x) 2S_i^z$$

in which the Dirac delta function $\delta(\vec{r}_i - \vec{r}_x)$ yields the probability of finding electron i at $\vec{r}_x$ whereas the operator $2S_i^z$ multiplies this probability by +1 when electron i has α-spin and by -1 when electron i has β-spin.

The spin density contribution due to the mixing of ψ_T depends on the matrix element

$$\langle \psi_0 | \rho_{op} | \psi_T \rangle$$

and is therefore proportional to λ. The spin density matrix elements of $\psi_{\sigma p}$ and $\psi_{p\sigma}$ with other wave functions are negligibly small for the protons of a methyl substituent so, in this case, contributions are obtained from

$$\langle \psi_{\sigma p} | \rho_{op} | \psi_{\sigma p} \rangle \quad \text{and} \quad \langle \psi_{p\sigma} | \rho_{op} | \psi_{p\sigma} \rangle$$

only. These contributions are proportional to μ^2 and ν^2 respectively. Besides, the introduction of $\psi_{\sigma p}$ and $\psi_{p\sigma}$ causes a change in the coefficient λ of ψ_T because of the mixing of ψ_T via the interaction with $\psi_{\sigma p}$ and $\psi_{p\sigma}$. The corresponding term in the spin density has a magnitude comparable to the magnitude of the terms proportional to μ^2 and ν^2.

For a real radical with a larger number (N, say) of π-electrons and a more complicated wave function for the σ-bond the calculation becomes more difficult. The main reason for this is the fact that wave functions for a system having more than two electrons can not be written as a simple product of space and spin functions.

Consider e.g. the interaction between ψ_0 and $\psi_{\sigma p}$. Apart from the differences in the spin functions, these wave functions differ by a replacement of $\sigma(2)$ in ψ_0 by p(2) in $\psi_{\sigma p}$ so the interaction depends on the resonance integral $\beta_{p\sigma}$. A simple calculation of the necessary overlap integrals of spin functions shows that in fact

$$\langle \psi_0 | H_{op} | \psi_{\sigma p} \rangle = - \langle p | H_{op} | \sigma \rangle = - \beta_{p\sigma}$$

In a general case the product $p(1)\alpha(1)$ in ψ_0 is replaced by the wave function for the ground state of the π-electron system

$$\pi_0(1..N) = \sum_{\mu} \pi_{0,\mu}(1..N)\, \chi_{\mu}(1..N)$$

where $\chi_{\mu}(1..N)$ is one of the possible spin functions for N electrons.
In the same way, the product

$$p(1)p(2)\, \frac{\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}}{\sqrt{2}}$$

in $\psi_{\sigma p}$ is replaced by a function

$$\pi_j(1..N+1) = \sum_{\nu} \pi_{j\nu}(1..N+1)\, \chi_{\nu}(1..N+1)$$

which is the wave function for one of the possible (ground and excited) states of the system of (N+1) electrons.
In the calculation of the matrix element

$$\langle \psi_0 | H_{op} | \psi_{\sigma p} \rangle$$

the overlap integrals of the spin functions were easily calculated. In the general case this is not possible without a further specification of the spin functions $\chi_{\mu}(1..N)$ and $\chi_{\nu}(1..N+1)$. This problem can be solved by choosing the $\chi_{\nu}(1..N+1)$ to be built up from the spin functions $\chi_{\mu}(1..N)$ by a combination with the spin functions for one electron (section B.1). In this way a relation between spin functions for different numbers of electrons is obtained which enables a straightforward calculation of the overlap integrals.
In the further evaluation of the matrix elements we obtain instead of $\beta_{p\sigma}$ an

interaction between functions of the type

$$\underline{P}_j^-(N+1) = \int \pi_{0,\mu}(1..N)\pi_{j\mu}(1..N+1)d\tau_1..d\tau_N$$

and corresponding functions for the σ-systems. The exact form of the functions $\underline{P}_j^-$ is given in section B. 2 where they are written $\underline{\varphi}_j^-$. In the same way the matrix elements between ψ_0 and $\psi_{p\sigma}$ can be reduced to an interaction between functions $\underline{\varphi}_j^+$ and corresponding functions for the σ-systems.

In section C it will be shown that the derivation of formulas for the spin density in the σ-bond can now be performed in the same way as for the simple system discussed above. First the choice of the zeroth order wave functions will be considered (C. 1). In section C. 2 the formula for σ-bonds within the nodal plane of the π-electron system is derived. Our result is practically identical with the formula given by McLachlan, Dearman and Lefebvre [7] but their derivation differs from ours in so far as their wave functions are not eigenfunctions of the total S^2-operator.

The formula for an arbitrary σ-bond is derived in section C. 3.

A simple formula for the spin density distribution in the π-electron system in terms of the functions $\underline{\varphi}_j^+$ and $\underline{\varphi}_j^-$ is derived in section B. 3. A comparison of this formula with the formula for the spin density in an arbitrary σ-bond shows that a clear relation exists between the spin density in the σ-bond and the spin density distribution in the π-electron system.

In several cases splittings have been observed due to protons for which the direct interaction with the π-electron system is very small e. g. the protons of tert. butyl substituents. A formula for the spin density on these protons, in which both the direct interaction with the π-electron system and the interaction via other σ-bonds is included, has been derived by a straightforward but lengthy calculation. This is discussed in section D.

B. WAVE FUNCTIONS FOR N-ELECTRON SYSTEMS

1. The spin functions

We consider a system of N electrons for which the wave functions are eigenfunctions of the S^2 and S^z operators (in the matrix elements of these operators the factors $h/2\pi$ will always be omitted). For each value of $m = \langle S^z \rangle$

the number of linearly independent spin functions ${}^{S}\chi_{\mu}^{m}$ is [10]

$$n(S,N) = \frac{(2S+1)N!}{(\frac{N}{2}-S)!\ (\frac{N}{2}+S+1)!} \qquad 2.1$$

These spin functions will be constructed from orthogonal spin functions for systems consisting of a smaller number of electrons according to the theory of angular momentum [11]. In this theory it is shown that, when two systems of K and L electrons with spin quantum numbers S_1 and S_2 are coupled together, the spin functions for the total system can be written

$$ {}^{S}\chi_{\mu}^{m}(1..K+L) = \sum_{m_1}\sum_{m_2} C(S_1,S_2,S;m_1,m_2,m)\ {}^{S_1}\chi_{\lambda}^{m_1}(1..K)\ {}^{S_2}\chi_{\nu}^{m_2}(K+1,...K+L) \qquad 2.2$$

in which the coefficients $C(S_1,S_2,S;m_1,m_2,m)$, which are called Clebsch-Gordan coefficients, are zero unless S takes one of the values $|S_1-S_2|, ...(S_1+S_2)$ and $m = m_1+m_2$. The values for $S_2 = 1/2$ and for $S_2 = 1$ are given in tables 2.1 and 2.2.

	$m_2 = 1/2$	$m_2 = -1/2$
$S = S_1+1/2$	$\sqrt{\frac{S_1+m+1/2}{2S_1+1}}$	$\sqrt{\frac{S_1-m+1/2}{2S_1+1}}$
$S = S_1-1/2$	$-\sqrt{\frac{S_1-m+1/2}{2S_1+1}}$	$\sqrt{\frac{S_1+m+1/2}{2S_1+1}}$

Table 2.1. Clebsch-Gordan coefficients for $S_2 = 1/2$.

	$m_2 = 1$	$m_2 = 0$	$m_2 = -1$
$S = S_1+1$	$\sqrt{\frac{(S_1+m)(S_1+m+1)}{2(2S_1+1)(S_1+1)}}$	$\sqrt{\frac{(S_1-m+1)(S_1+m+1)}{(2S_1+1)(S_1+1)}}$	$\sqrt{\frac{(S_1-m)(S_1-m+1)}{2(2S_1+1)(S_1+1)}}$
$S = S_1$	$-\sqrt{\frac{(S_1+m)(S_1-m+1)}{2S_1(S_1+1)}}$	$m\sqrt{\frac{1}{S_1(S_1+1)}}$	$\sqrt{\frac{(S_1-m)(S_1+m+1)}{2S_1(S_1+1)}}$
$S = S_1-1$	$\sqrt{\frac{(S_1-m)(S_1-m+1)}{2S_1(S_1+1)}}$	$-\sqrt{\frac{(S_1-m)(S_1+m)}{S_1(2S_1+1)}}$	$\sqrt{\frac{(S_1+m)(S_1+m+1)}{2S_1(2S_1+1)}}$

Table 2.2. Clebsch-Gordan coefficients for $S_2 = 1$.

For a system which can be described as consisting of two or more sub-systems, e.g. the π- and σ-systems of an aromatic radical, the total spin functions are calculated from the spin functions for the sub-systems according to equation 2.2. The spin functions for the sub-systems are obtained from the spin functions α and β for one electron by successively adding one electron, each time calculating the new spin function with the coefficients given in table 2.1.

2. The total wave function

Since the total wave function is an eigenfunction of S^2 and S^z we may write it as a linear combination of the n(S, N) possible spin functions [10]. The space dependent part of the wave function is then given by the coefficients of the spin functions.

$$\psi(1..N) = \frac{1}{\sqrt{n}} \sum_{\mu=1}^{n} \varphi_\mu(1..N)\chi_\mu(1..N) \qquad 2.3$$

We shall introduce as a rule that the spin functions ${}^{S}\chi_\mu(1..N)$ in this expansion are obtained from the p spin functions ${}^{S-1/2}\chi_\mu(1..N-1)$ for $\mu = 1..p$ and from the q spin functions ${}^{S+1/2}\chi_{\mu-p}(1..N-1)$ for $\mu = p+1,..p+q$, where $p+q = n$.

From the Pauli principle

$$\psi(1..N) = \delta_P P\psi(1..N)$$

in which P is a permutation operator

$\delta_P = +1$ for even permutations

$\delta_P = -1$ for odd permutations

we obtain by multiplying by χ_ν and integrating

$$\varphi_\nu = \delta_P \sum_{\alpha=1}^{n} \langle P\chi_\alpha|\chi_\nu\rangle P\varphi_\alpha \qquad 2.4$$

which yields

$$\langle\varphi_\nu|\varphi_\mu\rangle = \sum_{\alpha=1}^{n}\sum_{\beta=1}^{n} \langle P\chi_\alpha|\chi_\nu\rangle\langle\chi_\mu|P\chi_\beta\rangle\langle\varphi_\alpha|\varphi_\beta\rangle \qquad 2.5$$

On summing over all permutations the left-hand side is multiplied by N!. The right-hand side can be simplified with the orthogonality relations from group theory [10, 12].

$$\sum_{P=1}^{N!} \langle P\chi_{\alpha} | \chi_{\nu} \rangle \langle \chi_{\mu} | P\chi_{\beta} \rangle = \frac{N!}{n} \delta_{\alpha\beta} \delta_{\mu\nu}$$

in which $\delta_{\alpha\beta} = 0$ if $\alpha \neq \beta$

$= 1$ if $\alpha = \beta$

Equation 2.5 then becomes

$$\langle \varphi_{\nu} | \varphi_{\mu} \rangle = \delta_{\mu\nu} \sum_{\alpha=1}^{n} \frac{\langle \varphi_{\alpha} | \varphi_{\alpha} \rangle}{n}$$

which states that the φ_{μ} are orthogonal and $\langle \varphi_{\mu} | \varphi_{\mu} \rangle$ is independent of μ. This result can of course also be obtained from a direct application of group theory to the φ_{μ}. The φ_{μ} constitute an irreducible set of eigenfunctions of the spinless Hamiltonian which must be combined with an irreducible set of spin functions having the same dimension to obtain the completely antisymmetric total wave function. When we take

$$\langle \varphi_{\nu} | \varphi_{\mu} \rangle = \delta_{\mu\nu} \qquad 2.6$$

then $\psi(1..N)$ will be normalized.

On a permutation of the electron numbers 1..N the $\varphi_{\mu}(1..N)$ are transformed into each other according to 2.4. When the $\varphi_{\mu}(1..N)$ are divided in groups dependent on the multiplicity of the spin functions $\chi_{\nu}(1..N\text{-}1)$ from which $\chi_{\mu}(1..N)$ is built up, then a permutation of the electron numbers 1..N-1 will cause a similar transformation within these groups. For functions $\varphi_{\mu}(1..N)$ belonging to the same group we then obtain besides 2.6

$\int \varphi_{\mu}(1..N)\varphi_{\nu}(1..N)d\tau_1 \ldots d\tau_{N-1}$ vanishes if $\mu \neq \nu$ whereas the integral is independent of μ if $\mu = \nu$ 2.7

whereas for integrals over products of N- and (N-1)-electron functions

$\int \varphi_{\mu}(1..N)\varphi_{\nu}(1..N\text{-}1)d\tau_1 \ldots d\tau_{N-1}$ vanishes if $\chi_{\mu}(1..N)$ is not built up from $\chi_{\nu}(1..N\text{-}1)$ whereas the integral is independent of μ if $\chi_{\mu}(1..N)$ is built up from $\chi_{\nu}(1..N\text{-}1)$ 2.8

The integrals in 2.8 are very important in calculations with charge-transfer wave functions. Therefore we introduce a short-hand notation for these integrals. In our calculations on π-electron radicals we shall use for integrals over π-electron functions

$$\underline{\varphi}_j^{+}(N) = \sqrt{\frac{N+3}{4}} \int {}^{0}\varphi_{j,1}(1..N-1)\, {}^{1/2}\varphi_1(1..N)\, d\tau_1 \ldots d\tau_{N-1} \quad \text{for singlet } j$$

$$2.9$$

$$\text{or} \quad \underline{\varphi}_j^{+}(N) = \sqrt{\frac{N-1}{4}} \int {}^{1}\varphi_{j,1}(1..N-1)\, {}^{1/2}\varphi_{p+1}(1..N)\, d\tau_1 \ldots d\tau_{N-1} \quad \text{for triplet } j$$

$$\underline{\varphi}_j^{-}(N+1) = \sqrt{\frac{N+1}{2}} \int {}^{1/2}\varphi_1(1..N)\, {}^{0}\varphi_{j,1}(1..N+1)\, d\tau_1 \ldots d\tau_N \quad \text{for singlet } j$$

$$2.10$$

$$\text{or} \quad \underline{\varphi}_j^{-}(N+1) = \sqrt{\frac{N+5}{6}} \int {}^{1/2}\varphi_1(1..N)\, {}^{1}\varphi_{j,1}(1..N+1)\, d\tau_1 \ldots d\tau_N \quad \text{for triplet } j$$

in which j enumerates the possible singlet and triplet states of the (N-1)- and (N+1)-electron system.

The coefficients in 2.9 and 2.10 are chosen in such a way that simple formulas will be obtained for the spin density distribution.

For integrals over the σ-bonds the indices are altered somewhat:

$$\underline{\sigma}_{jS}^{+}(2) = \int {}^{0}\sigma(1,2)\, {}^{1/2}\sigma_j(1)\, d\tau_1$$

$$2.11$$

$$\underline{\sigma}_{jT}^{+}(2) = \int {}^{1}\sigma(1,2)\, {}^{1/2}\sigma_j(1)\, d\tau_1$$

$$\underline{\sigma}_{jS}^{-}(3) = \sqrt{\frac{3}{2}} \int {}^{0}\sigma(1,2)\, {}^{1/2}\sigma_{j,1}(1,2,3)\, d\tau_1 d\tau_2$$

$$2.12$$

$$\underline{\sigma}_{jT}^{-}(3) = \sqrt{\frac{1}{2}} \int {}^{1}\sigma(1,2)\, {}^{1/2}\sigma_{j,2}(1,2,3)\, d\tau_1 d\tau_2$$

3. The charge and spin density

The charge density $Q(\vec{r}_x)$ is defined as the probability of finding an electron at $\vec{r}_x$. The spin density $\rho(\vec{r}_x)$ is the difference between the probability of finding an electron with α-spin and the probability of finding an electron with β-spin. The corresponding operators for a system of N electrons are

$$Q_{op}(\vec{r}_x) = \sum_{j=1}^{N} \delta(\vec{r}_j - \vec{r}_x)$$

$$\rho_{op}(\vec{r}_x) = \sum_{j=1}^{N} \delta(\vec{r}_j - \vec{r}_x) 2S_j^z$$

in which $\delta(\vec{r}_j - \vec{r}_x)$ is the Dirac delta function.

Because all electrons are equivalent, the matrix elements can be written

$$Q_{ij}(\vec{r}_x) = N \langle \psi_i(1..N) | \delta(\vec{r}_N - \vec{r}_x) | \psi_j(1..N) \rangle$$

$$\rho_{ij}(\vec{r}_x) = 2N \langle \psi_i(1..N) | \delta(\vec{r}_N - \vec{r}_x) S_N^z | \psi_j(1..N) \rangle$$

The charge and spin densities in a particular state are given by the corresponding diagonal matrix elements. The non-diagonal matrix elements are usually called transition charge densities and transition spin densities. Because Q_{op} is independent of spin, transition charge densities can only be obtained between states having the same multiplicity. Transition spin densities may exist between states of different multiplicity when the spin functions are partly built up from the same spin functions $\chi_\mu(1..N-1)$ as is the case e.g. for singlets and triplets.

On substitution of the wave function 2. 3 and application of 2. 7 we obtain for the (transition) charge densities

$$Q_{ij}(\vec{r}_x) = \frac{N}{p+q} \{ p \langle \varphi_{i,1}(1..N) | \delta(\vec{r}_N - \vec{r}_x) | \varphi_{j,1}(1..N) \rangle + q \langle \varphi_{i,p+1}(1..N) | \delta(\vec{r}_N - \vec{r}_x) | \varphi_{j,p+1}(1..N) \rangle \} \tag{2.13}$$

whereas (transition) spin densities between states of the same multiplicity are given by

$$\rho_{ij}(\vec{r}_x) = \frac{2N}{p+q} \{ p \langle \varphi_{i,1}(1..N) | \delta(\vec{r}_N - \vec{r}_x) | \varphi_{j,1}(1..N) \rangle \langle \chi_1(1..N) | S_N^z | \chi_1(1..N) \rangle + q \langle \varphi_{i,p+1}(1..N) | \delta(\vec{r}_N - \vec{r}_x) | \varphi_{j,p+1}(1..N) \rangle \langle \chi_{p+1}(1..N) | S_N^z | \chi_{p+1}(1..N) \rangle \} \tag{2.14a}$$

and transition spin densities between states of different multiplicity by

$$\rho_{ij}(\vec{r}_x) = \frac{2N}{\sqrt{(p_i+q_i)(p_j+q_j)}} \{ p_i \langle \varphi_{i,1}(1..N) | \delta(\vec{r}_N - \vec{r}_x) | \varphi_{j,p_j+1}(1..N) \rangle \tag{2.14b}$$

$$\times \langle \chi_{i,1}(1..N) | S_N^z | \chi_{j,p_j+1}(1..N) \rangle + q_i \langle \varphi_{i,p_i+1}(1..N) | \delta(\vec{r}_N - \vec{r}_x) | \varphi_{j,1}(1..N) \rangle$$

$$\times \langle \chi_{i,p_i+1}(1..N) | S_N^z | \chi_{j,1}(1..N) \rangle \}$$

The values of p and q can be substituted from 2.1 when the multiplicity of the wave functions is known.

Instead of 2.13 and 2.14 it is more practical to use density matrices [13]. The (transition) charge density matrix (or spinless one-particle density matrix) is defined by

$$Q_{ij}(N,M) = \frac{N}{p+q} [p \int \frac{1}{2} \{ \varphi_{i,1}(1..N-1,N) \varphi_{j,1}(1..N-1,M)$$

$$+ \varphi_{j,1}(1..N-1,N) \varphi_{i,1}(1..N-1,M) \} d\tau_1 \dots d\tau_{N-1} \tag{2.15}$$

$$+ q \int \frac{1}{2} \{ \varphi_{i,p+1}(1..N-1,N) \varphi_{j,p+1}(1..N-1,M)$$

$$+ \varphi_{j,p+1}(1..N-1,N) \varphi_{i,p+1}(1..N-1,M) \} d\tau_1 \dots d\tau_{N-1}]$$

The (transition) spin density matrix is defined in an analogous way. Instead of the general formula we shall give the formulas for some special cases. These are obtained from 2.14 by substitution of spin functions $\chi_\mu(1..N)$ which are calculated from spin functions $\chi_\mu(1..N-1)$ according to 2.2. The values for p and q were calculated from 2.1.

The (transition) spin density matrix for doublets i and j becomes

$$\rho_{ij}(N,M) = \frac{(N+3)}{4} \int \frac{1}{2} \{ \varphi_{i,1}(1..N-1,N) \varphi_{j,1}(1..N-1,M)$$

$$+ \varphi_{j,1}(1..N-1,N) \varphi_{i,1}(1..N-1,M) \} d\tau_1 \dots d\tau_{N-1} \tag{2.16}$$

$$- \frac{(N-1)}{4} \int \frac{1}{2} \{ \varphi_{i,p+1}(1..N-1,N) \varphi_{j,p+1}(1..N-1,M)$$

$$+ \varphi_{j,p+1}(1..N-1,N) \varphi_{i,p+1}(1..N-1,M) \} d\tau_1 \dots d\tau_{N-1}$$

For i and j triplet states with m = +1 we obtain

$$\begin{aligned}\rho_{ij}(N,M) = {} & \frac{(N+4)}{3}\int \frac{1}{2}\,\{\varphi_{i,1}(1..N-1,N)\varphi_{j,1}(1..N-1,M) \\ & \qquad + \varphi_{j,1}(1..N-1,N)\varphi_{i,1}(1..N-1,M)\}\,d\tau_1\ldots d\tau_{N-1} \\ & - \frac{(N-2)}{3}\int \frac{1}{2}\,\{\varphi_{i,p+1}(1..N-1,N)\varphi_{j,p+1}(1..N-1,M) \\ & \qquad + \varphi_{j,p+1}(1..N-1,N)\varphi_{i,p+1}(1..N-1,M)\}\,d\tau_1\ldots d\tau_{N-1}\end{aligned} \qquad 2.17$$

The transition spin density matrix between a singlet and a triplet with m = 0 becomes

$$\begin{aligned}\rho_{ij}(N,M) = {} & -\sqrt{\frac{N(N+4)}{3}}\int \frac{1}{2}\,\{{}^{0}\varphi_{i,1}(1..N-1,N)\,{}^{1}\varphi_{j,1}(1..N-1,M) \\ & \qquad + {}^{1}\varphi_{j,1}(1..N-1,N)\,{}^{0}\varphi_{i,1}(1..N-1,M)\}\,d\tau_1\ldots d\tau_{N-1}\end{aligned} \qquad 2.18$$

In the following we shall prove that for a doublet state $\rho\,(N,M)$ can also be written

$$\rho(N,M) = \sum_j \delta_j \underline{\varphi}_j^{+}(N)\, \underline{\varphi}_j^{+}(M) \qquad 2.19$$

$$\rho(N,M) = \sum_j \delta_j \underline{\varphi}_j^{-}(N)\, \underline{\varphi}_j^{-}(M) \qquad 2.20$$

in which $\delta_j = +1$ for singlet j
$ = -1$ for triplet j

2.19 can easily be proved by expanding the functions $\varphi_\mu(1..N-1,N)$ in a complete set of functions $\varphi_{r\mu}(1..N-1)\varphi_s(N)$. The proof of 2.20, however, is more difficult. First $\rho(N,M)$ is expressed in terms of a complete set of one-electron functions φ_r.

$$\rho\,(N,M) = \sum_r \sum_s \rho_{rs}\varphi_r(N)\varphi_s(M)$$

$$\begin{aligned}\rho_{rs} &= \int \rho(N,M)\varphi_r(N)\varphi_s(M)d\tau_N d\tau_M \\ &= \frac{(N+3)}{4}\langle \varphi_1(1..N-1,M)\varphi_r(N)|\varphi_1(1..N-1,N)\varphi_s(M)\rangle \\ &\qquad - \frac{(N-1)}{4}\langle \varphi_{p+1}(1..N-1,M)\varphi_r(N)|\varphi_{p+1}(1..N-1,N)\varphi_s(M)\rangle\end{aligned}$$

Next the functions $\varphi(1..N-1,M)\varphi_r(N)$ and $\varphi(1..N-1,N)\varphi_s(M)$ are expanded in a complete set of (N+1)-electron singlet and triplet functions. In general this is not possible because these functions are not wave functions so the Pauli principle does not hold. When $\varphi_\mu(1..N-1,M)$ is written in terms of products of one-electron functions, then terms will occur in $\varphi_\mu(1..N-1,M)\varphi_r(N)$ in which φ_r contains three electrons. From the orthogonality of φ_r and φ_s it follows that these terms can only give contributions for $r = s$. From a calculation for $N = 3$ it appears that the contributions from the two terms cancel out. The expansion in terms of (N+1)-electron functions is therefore permitted.

$$\begin{aligned}\rho_{rs} = \frac{(N+3)}{4}\sum_j\sum_k &\langle \varphi_1(1..N-1,M)\varphi_r(N)|\varphi_{j,1}(1..N-1,M,N)\rangle \\ \times &\langle \varphi_{j,1}(1..N-1,M,N)|\varphi_{k,1}(1..N-1,N,M)\rangle\langle \varphi_{k,1}(1..N-1,N,M)|\varphi_1(1..N-1,N)\varphi_s(M)\rangle \\ - \frac{(N-1)}{4}\sum_j\sum_k &\langle \varphi_{p+1}(1..N-1,M)\varphi_r(N)|\varphi_{j,p+1}(1..N-1,M,N)\rangle \\ \times &\langle \varphi_{j,p+1}(1..N-1,M,N)|\varphi_{k,p+1}(1..N-1,N,M)\rangle \\ &\qquad \times \langle \varphi_{k,p+1}(1..N-1,N,M)|\varphi_{p+1}(1..N-1,N)\varphi_s(M)\rangle\end{aligned}$$

The second integral in both terms vanishes for $j \neq k$. From 2.8 we then obtain

$$\begin{aligned}\rho_{rs} = \sum_j &\langle \varphi_1(1..N-1,M)\varphi_r(N)|\varphi_{j,1}(1..N-1,M,N)\rangle\langle \varphi_{j,1}(1..N-1,N,M)|\varphi_1(1..N-1,N)\varphi_s(M)\rangle \\ &\times\left\{\frac{(N+3)}{4}\langle \varphi_{j,1}(1..N-1,M,N)|\varphi_{j,1}(1..N-1,N,M)\rangle\right. \\ &\qquad \left. - \frac{(N-1)}{4}\langle \varphi_{j,p+1}(1..N-1,M,N)|\varphi_{j,p+1}(1..N-1,N,M)\rangle\right\}\end{aligned} \tag{2.21}$$

The overlap terms between brackets are calculated from the overlap of the corresponding spin functions. The two functions in the integrals differ by an odd number of permutations so, according to 2.4 and 2.6, the overlap is opposite to the overlap of the spin functions. After construction of the spin functions according to 2.2 we obtain

for singlet j $\quad \langle \varphi_{j,1}(1..N\text{-}1,M,N)|\varphi_{j,1}(1..N\text{-}1,N,M)\rangle = +1$

$\langle \varphi_{j,p+1}(1..N\text{-}1,M,N)|\varphi_{j,p+1}(1..N\text{-}1,N,M)\rangle = -1$

for triplet j $\quad \langle \varphi_{j,1}(1..N\text{-}1,M,N)|\varphi_{j,1}(1..N\text{-}1,N,M)\rangle = -1$

$\langle \varphi_{j,p+1}(1..N\text{-}1,M,N)|\varphi_{j,p+1}(1..N\text{-}1,N,M)\rangle = -1/3$

After substitution 2.21 can be written

$$\rho_{rs} = \sum_j \delta_j \langle \varphi_r(N)|\underline{\varphi}_j^-(N)\rangle \langle \underline{\varphi}_j^-(M)|\varphi_s(M)\rangle$$

Because ρ_{rs} is the representation of ρ in the complete set φ_r, φ_s it follows immediately that 2.20 holds.

It can easily be shown that analogous to 2.19 the charge density matrix for a doublet state can be written

$$Q(N,M) = \sum_j \epsilon_j \underline{\varphi}_j^+(N)\underline{\varphi}_j^+(M) \qquad 2.22$$

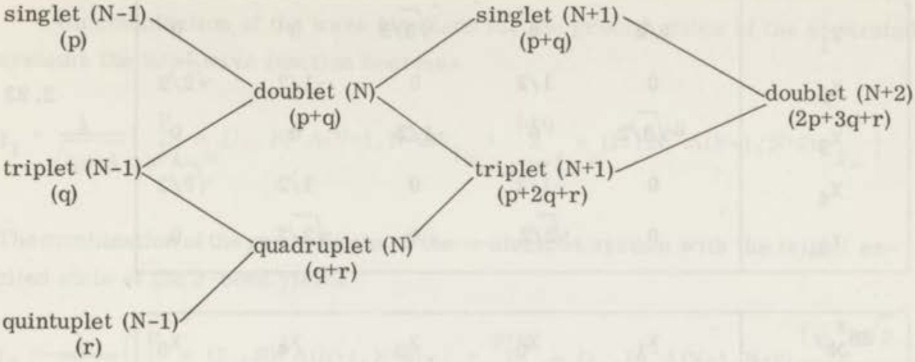
in which $\epsilon_j = +1$ for singlet j
$= +3$ for triplet j

An equation analogous to 2.20 could not be obtained because in this case the expansion in a complete set of (N+1)-electron functions is not possible.

C. σ-BONDS DIRECTLY COUPLED TO THE π-ELECTRON SYSTEM

1. The zeroth order wave functions

We consider a doublet π-electron system of N electrons and a σ-bond A which will be regarded as a two-electron system.
According to the branching diagram [10]



we obtain from the p singlet and q triplet functions for (N-1) electrons (2p+3q) doublet spin functions for the (N+2)-electron system. The total wave functions will be written in terms of the following expressions for these spin functions.

$$\chi_{1\mu} = {}^{0}\chi_{\mu}(1..N-1)\alpha(N)\,{}^{0}\chi(N+1,N+2)$$

$$\chi_{2\mu} = 1/\sqrt{6}\{2\,{}^{1}\chi^{+1}_{\mu-p}(1..N-1)\beta(N) - \sqrt{2}\,{}^{1}\chi^{0}_{\mu-p}(1..N-1)\alpha(N)\}\;{}^{0}\chi(N+1,N+2)$$

$$\chi_{3\mu} = {}^{0}\chi_{\mu}(1..N-1)\;1/\sqrt{6}\{-2\beta(N)\,{}^{1}\chi^{+1}(N+1,N+2) + \sqrt{2}\,\alpha(N)\,{}^{1}\chi^{0}(N+1,N+2)\}$$

$$\chi_{4\mu} = 1/\sqrt{3}\{-\,{}^{1}\chi^{0}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{0}(N+1,N+2) + {}^{1}\chi^{-1}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{+1}(N+1,N+2)$$
$$+\,{}^{1}\chi^{+1}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{-1}(N+1,N+2)\}$$

$$\chi_{5\mu} = 1/\sqrt{6}\{-\sqrt{2}\,{}^{1}\chi^{0}_{\mu-p}(1..N-1)\beta(N)\,{}^{1}\chi^{+1}(N+1,N+2) + \sqrt{2}\,{}^{1}\chi^{+1}_{\mu-p}(1..N-1)\beta(N)\,{}^{1}\chi^{0}(N+1,N+2)$$
$$-\,{}^{1}\chi^{+1}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{-1}(N+1,N+2) + {}^{1}\chi^{-1}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{+1}(N+1,N+2)\}$$

in which $\mu = 1\ldots p$ for $\chi_{1\mu}$ and $\chi_{3\mu}$
$= p+1,\ldots p+q$ for $\chi_{2\mu}$, $\chi_{4\mu}$ and $\chi_{5\mu}$

The functions $\chi_{1\mu}$, $\chi_{2\mu}$, $\chi_{3\mu}$ and $1/\sqrt{3}\{\chi_{4\mu}+\sqrt{2}\,\chi_{5\mu}\}$ may be regarded as being built up from doublet spin functions for N electrons whereas $1/\sqrt{3}\{\sqrt{2}\,\chi_{4\mu}-\chi_{5\mu}\}$ can be obtained from the quadruplet functions for N electrons which are built up from the triplet functions for N-1 electrons.

In our calculations use will be made of the transformation matrix for a transposition of electrons N and N+2 and of the matrix elements of the operators $2S^{z}_{N}$, $2S^{z}_{N+1}$ and $2S^{z}_{N+2}$. These are given in 2.23 and 2.24a, b and c.

$T_{N,N+2}$	χ_1	χ_2	χ_3	χ_4	χ_5
χ_1	$1/2$	0	$-\sqrt{3}/2$	0	0
χ_2	0	$1/2$	0	$-1/2$	$\sqrt{2}/2$
χ_3	$-\sqrt{3}/2$	0	$-1/2$	0	0
χ_4	0	$-1/2$	0	$1/2$	$\sqrt{2}/2$
χ_5	0	$\sqrt{2}/2$	0	$\sqrt{2}/2$	0

2.23

$2S^z_N$	χ_1	χ_2	χ_3	χ_4	χ_5
χ_1	1	0	0	0	0
χ_2	0	$-1/3$	0	0	0
χ_3	0	0	$-1/3$	0	0
χ_4	0	0	0	1	0
χ_5	0	0	0	0	$-1/3$

2.24a

$2S^z_{N+1}$	χ_1	χ_2	χ_3	χ_4	χ_5
χ_1	0	0	$\sqrt{3}/3$	0	0
χ_2	0	0	0	$1/3$	$\sqrt{2}/3$
χ_3	$\sqrt{3}/3$	0	$2/3$	0	0
χ_4	0	$1/3$	0	0	$\sqrt{2}/3$
χ_5	0	$\sqrt{2}/3$	0	$\sqrt{2}/3$	$1/3$

2.24b

$2S^z_{N+2}$	χ_1	χ_2	χ_3	χ_4	χ_5
χ_1	0	0	$-\sqrt{3}/3$	0	0
χ_2	0	0	0	$-1/3$	$-\sqrt{2}/3$
χ_3	$-\sqrt{3}/3$	0	$2/3$	0	0
χ_4	0	$-1/3$	0	0	$\sqrt{2}/3$
χ_5	0	$-\sqrt{2}/3$	0	$\sqrt{2}/3$	$1/3$

2.24c

On combination of the wave functions for the ground states of the separated systems the total wave function becomes

$$\psi_1 = \frac{1}{\sqrt{(p+q)}}\{ \sum_{\mu=1}^{p} \pi_{\mu}(1..N)^0 A(N+1,N+2)\chi_{1\mu} + \sum_{\mu=p+1}^{p+q} \pi_{\mu}(1..N)^0 A(N+1,N+2)\chi_{2\mu} \}$$

The combination of the ground state of the π-electron system with the triplet excited state of the σ-bond yields

$$\psi_2 = \frac{1}{\sqrt{(p+q)}}\left\{ \sum_{\mu=1}^{p} \pi_{\mu}(1..N)^1 A(N+1,N+2)\chi_{3\mu} + \sum_{\mu=p+1}^{p+q} \pi_{\mu}(1..N)^1 A(N+1,N+2)\frac{\{\chi_{4\mu}+\sqrt{2}\,\chi_{5\mu}\}}{\sqrt{3}}\right\}$$

On transfer of one electron from the π-electron system to the σ-bond a doublet function for the total system can be obtained in four different ways:

1. π(1..N-1) singlet and A(N+1, N+2, N) doublet
2. π(1..N-1) triplet and A(N+1, N+2, N) doublet
3. π(1..N-1) triplet and A(N+1, N+2, N) quadruplet
4. π(1..N-1) quintuplet and A(N+1, N+2, N) quadruplet

From 2.8 it is obvious that

$$\int {}^0A(1,2)\ {}^{3/2}A(1,2,3)d\tau_1 d\tau_2 = 0$$

From the further calculations it may be inferred that in consequence of this result the wave functions corresponding to 3. and 4. do not mix with ψ_1 and can be neglected. The wave functions corresponding to 1. and 2. are

$$\psi_{3j} = \frac{1}{\sqrt{2p}} \sum_{\mu=1}^{p} {}^0\pi_{j\mu}(1..N-1)\ \{A_1(N+1,N+2,N)\chi_{1\mu} - A_2(N+1,N+2,N)\chi_{3\mu}\}$$

$$\psi_{4j} = \frac{1}{\sqrt{2q}} \sum_{\mu=p+1}^{p+q} {}^1\pi_{j,\mu-p}(1..N-1)\left\{A_1(N+1,N+2,N)\chi_{2\mu} - A_2(N+1,N+2,N)\ \frac{\{\chi_{4\mu}-\sqrt{2}\,\chi_{5\mu}\}}{\sqrt{3}}\right.$$

On transfer of one electron from the σ-bond to the π-electron system a doublet function for the total system is obtained from the combination of the A(N+1) doublet functions with the π(1..N, N+2) singlet and triplet functions. The corresponding wave functions are

$$\psi_{5j} = \frac{1}{\sqrt{p+q}} \left\{ \sum_{\mu=1}^{p} {}^{0}\pi_{j\mu}(1..N, N+2)A(N+1) \frac{\{\chi_{1\mu} + \sqrt{3}\,\chi_{3\mu}\}}{2} + \sum_{\mu=p+1}^{p+q} {}^{0}\pi_{j\mu}(1..N, N+2)A(N+1) \times \frac{\{\chi_{2\mu} + \chi_{4\mu} + \sqrt{2}\,\chi_{5\mu}\}}{2} \right\}$$

$$\psi_{6j} = \frac{1}{\sqrt{p+2q+r}} \left\{ \sum_{\mu=1}^{p} {}^{1}\pi_{j\mu}(1..N, N+2)A(N+1) \frac{\{-\sqrt{3}\,\chi_{1\mu} + \chi_{3\mu}\}}{2} + \sum_{\mu=p+1}^{p+q} {}^{1}\pi_{j\mu}(1..N, N+2) \times A(N+1) \frac{\{-3\chi_{2\mu} + \chi_{4\mu} + \sqrt{2}\,\chi_{5\mu}\}}{2\sqrt{3}} + \sum_{\mu=p+q+1}^{p+2q+r} \{\text{quadruplet (N) terms}\} \right\}$$

The wave functions $\psi_1 \ldots \psi_{6j}$ are not antisymmetrized with respect to the permutation of σ and π electrons. The antisymmetrized wave functions shall be written $\mathscr{A}\psi_1 \ldots \mathscr{A}\psi_{6j}$. In this antisymmetrization and in all further calculations the overlap integrals between σ- and π-functions will be neglected. A further approximation is the neglect of all wave functions in which the σ-system is excited (except the lowest triplet state in ψ_2) and of all wave functions in which two electrons are transferred.

In the usual theories for the spin density in σ-bonds within the nodal plane the zeroth order wave functions are assumed to be calculated with neglect of all σ-π exchange integrals. In our method this is not necessary.
We consider two systems with wave functions

$$\sum_{\mu=1}^{r} \frac{1}{\sqrt{r}} \Phi_{1\mu}(1..N)\chi_{\mu}(1..N)$$

$$\sum_{\nu=1}^{s} \frac{1}{\sqrt{s}} \psi_{1\nu}(N+1, .. N+M)\chi_{\nu}(N+1, .. N+M)$$

which are coupled together. The wave function for the total system becomes

$$\Theta_1(1..N+M) = \sum_{\mu=1}^{r} \sum_{\nu=1}^{s} \frac{1}{\sqrt{rs}} \Phi_{1\mu}(1..N)\,\psi_{1\nu}(N+1, .. N+M)\,\chi_{\mu\nu}(1..N+M)$$

in which $\chi_{\mu\nu}$ is the spin function obtained from χ_μ and χ_ν by application of 2.2. The wave function for the Φ-system will now be calculated in such a way that a wave function

$$\Theta_j(1..N{+}M) = \sum_{\mu=1}^{r} \sum_{\nu=1}^{s} \frac{1}{\sqrt{rs}}\, \Phi_{j\mu}(1..N)\, \psi_{1\nu}(N{+}1,..N{+}M)\, \chi_{\mu\nu}(1..N{+}M)$$

in which the Φ-system is excited without a change of the spin function, does not mix in first order with Θ_1 which means

$$\langle \mathscr{A}\Theta_1 |H| \mathscr{A}\Theta_j \rangle = 0$$

Because in Θ_j all electrons within the Φ- and ψ-system are equivalent we may write this

$$\langle \Theta_1 |H| \Theta_j \rangle - NM\langle \Theta_1 | HT_{N,N+M} | \Theta_j \rangle = 0$$

in which $T_{N,N+M}$ is the operator for a transposition of electrons N and N+M. Higher order permutations do not contribute because the two systems are supposed to be orthogonal.

On substitution of the Hamiltonian

$$H(1..N{+}M) = H_\Phi(1..N) + H_\psi(N{+}1,..N{+}M) + \sum_{i=1}^{N} \sum_{j=N+1}^{N+M} \frac{1}{r_{ij}}$$

we obtain as condition for the calculation of Φ_1:

$$\langle \Phi_{11} |H| \Phi_{j1} \rangle + \sum_{\mu=1}^{r} \sum_{\nu=1}^{s} \frac{NM}{rs} \langle \Phi_{1\mu}\psi_{1\nu} \left| \frac{1}{r_{N,N+M}} \right| \Phi_{j\mu}\psi_{1\nu} \rangle \qquad 2.25$$

$$- \frac{NM}{rs} \sum_{\mu=1}^{r} \sum_{\nu=1}^{s} \langle \Phi_{1\mu}\psi_{1\nu} \left| \frac{1}{r_{N,N+M}} T_{N,N+M} \right| \Phi_{j\mu}\psi_{1\nu} \rangle \langle \chi_{\mu\nu} | T_{N,N+M} | \chi_{\mu\nu} \rangle = 0$$

In terms of charge density matrices the second term becomes

$$\int Q^{\Phi}_{1j}(1,1) \frac{1}{r_{12}} Q^{\psi}_{11}(2,2)\, d\tau_1 d\tau_2$$

The evaluation of the third term depends on the multiplicity of Φ, ψ and Θ. As an example we shall discuss the calculation of the zeroth order wave functions

ψ_1 and ψ_2.

For singlet-singlet, doublet-singlet and singlet-doublet combinations 2.25 becomes after substitution of the spin functions calculated from 2.2

$$\langle \Phi_{11}|H|\Phi_{j1}\rangle + \int Q_{1j}^{\Phi}(1,1)\frac{1}{r_{12}}Q_{11}^{\psi}(2,2)d\tau_1 d\tau_2 - \frac{1}{2}\int Q_{1j}^{\Phi}(1,2)\frac{1}{r_{12}}Q_{11}^{\psi}(1,2)d\tau_1 d\tau_2 = 0 \tag{2.26}$$

This formula, which is the formula used in the theory of separated electron pairs [14] and in McWeeny's group function method [13], is assumed to be used in an iterative process for the calculation of the ground state of the π- and σ-systems.

For a triplet-doublet combination, for which the total wave function is a doublet function, the condition for the calculation of the triplet state becomes

$$\langle {}^1\Phi_{11}|H|{}^1\Phi_{j1}\rangle + \int Q_{1j}^{\Phi}(1,1)\frac{1}{r_{12}}Q_{11}^{\psi}(2,2)d\tau_1 d\tau_2 - \frac{1}{2}\int Q_{1j}^{\Phi}(1,2)\frac{1}{r_{12}}Q_{11}^{\psi}(1,2)d\tau_1 d\tau_2$$

$$+ \int \rho_{1j}^{\Phi}(1,2)\frac{1}{r_{12}}\rho_{11}^{\psi}(1,2)d\tau_1 d\tau_2 = 0 \tag{2.27}$$

The triplet excited state of the σ-bond is assumed to be calculated from 2.27. In this calculation the wave function for the π-system is taken to be the one obtained from 2.26.

The charge transfer wave functions can be calculated in a similar way.

2. σ-bonds in the nodal plane

For σ-bonds in the nodal plane the interaction between ψ_1 and $\psi_{3j} \cdots \psi_{6j}$ vanishes for symmetry reasons. The spin density is therefore determined solely by ψ_1 and ψ_2 and becomes in first order

$$\rho^A(\vec{r}_x) = -2\,\frac{\langle \mathscr{A}\psi_1|H|\mathscr{A}\psi_2\rangle\langle \mathscr{A}\psi_2|\rho|\mathscr{A}\psi_1\rangle}{(E_2-E_1)}$$

in which $E_1 = \langle \mathscr{A}\psi_1|H|\mathscr{A}\psi_1\rangle$

$E_2 = \langle \mathscr{A}\psi_2|H|\mathscr{A}\psi_2\rangle$

The Hamiltonian matrix element in the numerator

$$\langle \mathscr{A}\psi_1 | H | \mathscr{A}\psi_2 \rangle = \langle \psi_1 | H | \psi_2 \rangle - 2N \langle \psi_1 | H\, T_{N,N+2} | \psi_2 \rangle$$

becomes on substitution of the wave functions, evaluation of the integrals over the spin functions with the values given in 2.23 and application of 2.7

$$= \frac{Np\sqrt{3}}{(p+q)} \langle \pi_1(1..N-1,N)\, {}^0A(N+1,N+2) \left| \frac{1}{r_{N,N+2}} \right| \pi_1(1..N-1,N+2)\, {}^0A(N+1,N) \rangle$$

$$- \frac{Nq\sqrt{3}}{3(p+q)} \langle \pi_{p+1}(1..N-1,N)\, {}^0A(N+1,N+2) \left| \frac{1}{r_{N,N+2}} \right| \pi_{p+1}(1..N-1,N+2)\, {}^1A(N+1,N) \rangle \qquad 2.28$$

According to 2.16 and 2.18 this is identical to

$$\langle \mathscr{A}\psi_1 | H | \mathscr{A}\psi_2 \rangle = -\frac{1}{2}\sqrt{3} \int \rho^{\pi}(1,2) \frac{1}{r_{12}} \rho^{A}_{ST}(1,2)\, d\tau_1 d\tau_2$$

in which ρ^{A}_{ST} is the transition spin density matrix between the singlet and triplet state of the σ-bond.

In the calculation of the matrix element of the spin density operator the permutations between π- and σ-electrons can be omitted because ρ_{op} is a sum of one-electron terms. From the integral values given in 2.24c we obtain

$$\langle \mathscr{A}\psi_1 | \rho | \mathscr{A}\psi_2 \rangle = -\frac{2}{3}\sqrt{3} \langle {}^0A(N+1,N+2) | \delta(\vec{r}_{N+2} - \vec{r}_x) | {}^1A(N+1,N+2) \rangle$$

Substitution of the matrix elements yields for the spin density

$$\rho(\vec{r}_x) = -2 \frac{\int \rho^{\pi}(1,2) \frac{1}{r_{12}} \rho^{A}_{ST}(1,2)\, d\tau_1 d\tau_2}{\Delta E^{T}_{A}} \langle {}^0A(N+1,N+2) | \delta(\vec{r}_{N+2} - \vec{r}_x) | {}^1A(N+1,N+2) \rangle$$

in which $\Delta E^{T}_{A} = E_2 - E_1$, the triplet excitation energy of the σ-bond

In terms of spin density matrices this becomes

$$\rho^{A}(1,2) = \frac{\int \rho^{\pi}(1,2)\,\frac{1}{r_{12}}\,\rho^{A}_{ST}(1,2)\,d\tau_1 d\tau_2}{\Delta E^{T}_{A}}\,\rho^{A}_{ST}(1,2) \qquad 2.29$$

This formula can be generalized by a summation of the right-hand side over all possible triplet states of bond A.

3. σ-bonds not located in the nodal plane

For σ-bonds which are not located in the nodal plane the π- and σ-functions are no longer orthogonal. The first order term 2. 29 must therefore be used in a more general form in which the $1/r_{12}$ operator is replaced by the complete Hamiltonian. This is especially important in valence bond calculations.

$$\Delta_{T}\rho^{A}(1,2) = \frac{\int \rho^{\pi}(1,2)\,H\,\rho^{A}_{ST}(1,2)\,d\tau_1 d\tau_2}{\Delta E^{T}_{A}}\,\rho^{A}_{ST}(1,2) \qquad 2.30$$

It must be noted that for an exact calculation the integral in the numerator must be regarded as a short-hand notation of the complete term which is obtained from 2. 28 by replacing $1/r_{N,\,N+2}$ by the complete Hamiltonian and multiplying by $-2\sqrt{3}/3$. In the usual valence bond approximation, however, 2. 30 may be regarded as the correct expression.

Besides 2. 30, contributions will be obtained from the charge-transfer wave functions $\psi_{3j}\cdots\psi_{6j}$. In a first order approximation matrix elements of the spin density operator between σ- and π-functions occur. In calculations of the spin density on methyl protons these terms are usually neglected but it is by no means sure that this is correct for all types of σ-bonds. Therefore, this term will also be considered. Second order terms are obtained from the diagonal matrix elements of the spin density for $\psi_{3j}\cdots\psi_{6j}$ and from the mixing of ψ_2 via $\psi_{3j}\cdots\psi_{6j}$ with ψ_1. Second order terms from the mixing of $\psi_{3j}\cdots\psi_{6j}$ via ψ_2 and from the direct mixing of ψ_2 with ψ_1 are neglected with respect to the first order term 2. 30.

On neglect of the overlap integrals of σ- and π-functions the contribution from the charge-transfer wave functions is then given by

$$\Delta_{CT}\rho^{A} = -2 \sum_{i=3}^{6} \sum_{j} \frac{\langle \mathscr{A}\psi_1 |H| \mathscr{A}\psi_{ij}\rangle \langle \mathscr{A}\psi_{ij} |\rho| \mathscr{A}\psi_1\rangle}{(E_{ij}-E_1)} + \sum_{i=3}^{6} \sum_{j} \left\{ \frac{\langle \mathscr{A}\psi_1 |H| \mathscr{A}\psi_{ij}\rangle}{(E_{ij}-E_1)} \right\}^2 \qquad 2.31$$

$$\times \langle \mathscr{A}\psi_{ij} |\rho| \mathscr{A}\psi_{ij}\rangle + 2 \sum_{i=3}^{6} \sum_{j} \frac{\langle \mathscr{A}\psi_1 |H| \mathscr{A}\psi_{ij}\rangle \langle \mathscr{A}\psi_{ij} |H| \mathscr{A}\psi_2\rangle \langle \mathscr{A}\psi_2 |\rho| \mathscr{A}\psi_1\rangle}{(E_{ij}-E_1)(E_2-E_1)}$$

In the calculation of the matrix elements between ψ_1, ψ_2 and $\psi_{3j} \cdots \psi_{6j}$ it is important to note that the number of permutations with respect to which the wave functions are already antisymmetrized is not the same for all wave functions. These numbers are for

$$\begin{array}{llcl} \psi_{cov} & = \psi_1, \psi_2 & : & N!\ 2! \\ \psi_{\pi\sigma} & = \psi_{3j}, \psi_{4j} & : & (N-1)!\ 3! \\ \psi_{\sigma\pi} & = \psi_{5j}, \psi_{6j} & : & (N+1)! \end{array}$$

The energy matrix elements are obtained as follows

$$\langle \mathscr{A}\psi_{cov} |H| \mathscr{A}\psi_{\pi\sigma}\rangle = \sqrt{\frac{(N-1)!\ 3!}{N!\ 2!}} \langle \psi_{cov} \left| H(1-\sum_{j=1}^{N-1} T_{jN}) \right| \psi_{\pi\sigma}\rangle$$

From $T_{jN}\psi_{cov} = -\psi_{cov}$ we obtain

$$\langle \mathscr{A}\psi_{cov} |H| \mathscr{A}\psi_{\pi\sigma}\rangle = \sqrt{3N} \langle \psi_{cov} |H| \psi_{\pi\sigma}\rangle$$

whereas

$$\langle \mathscr{A}\psi_{cov} |H| \mathscr{A}\psi_{\sigma\pi}\rangle = \sqrt{\frac{(N+1)!}{N!\ 2!}} \langle \psi_{cov} \left| H(1-T_{N+1,N+2}) \right| \psi_{\sigma\pi}\rangle$$

$$= \sqrt{2(N+1)} \langle \psi_{cov} |H| \psi_{\sigma\pi}\rangle$$

Now we assume that in the evaluation of these matrix elements the Hamiltonian operator may be approximated by an effective one-electron operator (this is identical with neglect of differential overlap). In this way we obtain on substitution of 2.9, 2.10, 2.11 and 2.12

$$\begin{aligned}
\langle \mathscr{A}\psi_1|H|\mathscr{A}\psi_{3j}\rangle &= \langle \underline{\pi}_j^+|H|\underline{A}_S^-\rangle & \langle \mathscr{A}\psi_1|H|\mathscr{A}\psi_{5j}\rangle &= \langle \underline{\pi}_j^-|H|\underline{A}_S^+\rangle \\
\langle \mathscr{A}\psi_1|H|\mathscr{A}\psi_{4j}\rangle &= \sqrt{3}\,\langle \underline{\pi}_j^+|H|\underline{A}_S^-\rangle & \langle \mathscr{A}\psi_1|H|\mathscr{A}\psi_{6j}\rangle &= -\sqrt{3}\,\langle \underline{\pi}_j^-|H|\underline{A}_S^+\rangle \\
\langle \mathscr{A}\psi_2|H|\mathscr{A}\psi_{3j}\rangle &= -\sqrt{3}\,\langle \underline{\pi}_j^+|H|\underline{A}_T^-\rangle & \langle \mathscr{A}\psi_2|H|\mathscr{A}\psi_{5j}\rangle &= \sqrt{3}\,\langle \underline{\pi}_j^-|H|\underline{A}_T^+\rangle \\
\langle \mathscr{A}\psi_2|H|\mathscr{A}\psi_{4j}\rangle &= \langle \underline{\pi}_j^+|H|\underline{A}_T^-\rangle & \langle \mathscr{A}\psi_2|H|\mathscr{A}\psi_{6j}\rangle &= \langle \underline{\pi}_j^-|H|\underline{A}_T^+\rangle
\end{aligned}$$

The spin density matrix elements between ψ_1 and $\psi_{3j} \cdots \psi_{6j}$ are obtained in the same way:

$$\begin{aligned}
\langle \mathscr{A}\psi_{cov}|\rho|\mathscr{A}\psi_{\pi\sigma}\rangle &= \sqrt{3N}\,\langle \psi_{cov}|\rho|\psi_{\pi\sigma}\rangle \\
\langle \mathscr{A}\psi_{cov}|\rho|\mathscr{A}\psi_{\sigma\pi}\rangle &= \sqrt{2(N+1)}\,\langle \psi_{cov}|\rho|\psi_{\sigma\pi}\rangle
\end{aligned}$$

which yields

$$\begin{aligned}
\langle \mathscr{A}\psi_1|\rho|\mathscr{A}\psi_{3j}\rangle &= \langle \underline{\pi}_j^+(1)|\delta(\vec{r}_1-\vec{r}_x)|\underline{A}_S^-(1)\rangle \\
\langle \mathscr{A}\psi_1|\rho|\mathscr{A}\psi_{4j}\rangle &= -1/\sqrt{3}\,\langle \underline{\pi}_j^+(1)|\delta(\vec{r}_1-\vec{r}_x)|\underline{A}_S^-(1)\rangle \\
\langle \mathscr{A}\psi_1|\rho|\mathscr{A}\psi_{5j}\rangle &= -\,\langle \underline{\pi}_j^-(1)|\delta(\vec{r}_1-\vec{r}_x)|\underline{A}_S^+(1)\rangle \\
\langle \mathscr{A}\psi_1|\rho|\mathscr{A}\psi_{6j}\rangle &= -1/\sqrt{3}\,\langle \underline{\pi}_j^-(1)|\delta(\vec{r}_1-\vec{r}_x)|\underline{A}_S^+(1)\rangle
\end{aligned}$$

In the diagonal matrix elements of the spin density operator for $\psi_{3j} \cdots \psi_{6j}$ only the contributions in the σ-bond are of importance. In terms of spin density matrices these are

$$\begin{aligned}
\langle \mathscr{A}\psi_{3j}|\rho|\mathscr{A}\psi_{3j}\rangle &: \quad \rho_3^A(1,2) \\
\langle \mathscr{A}\psi_{4j}|\rho|\mathscr{A}\psi_{4j}\rangle &: \quad -1/3\ \rho_3^A(1,2) \\
\langle \mathscr{A}\psi_{5j}|\rho|\mathscr{A}\psi_{5j}\rangle &: \quad \rho_1^A(1,2) \\
\langle \mathscr{A}\psi_{6j}|\rho|\mathscr{A}\psi_{6j}\rangle &: \quad -1/3\ \rho_1^A(1,2)
\end{aligned}$$

in which ρ_1 and ρ_3 are the spin density matrices according to 2.16 for N=1 and N=3 respectively.

The excitation energies of the charge-transfer states are approximated for

$$\begin{aligned}
&\psi_{3j}, \psi_{4j} \quad \text{as} \quad I_\pi - E_A + \Delta E_j^+ + C_{jA} \\
&\psi_{5j}, \psi_{6j} \quad \text{as} \quad I_A - E_\pi + \Delta E_j^- + C_{Aj}
\end{aligned}$$

in which

I_π, I_A	the ionization energies of the π and A system
E_π, E_A	the electron affinities of the π and A system
$\Delta E_j^+, \Delta E_j^-$	the excitation energies of the π-electron system after charge transfer
C_{jA}, C_{Aj}	correction terms for the difference in Coulomb energy before and after charge transfer

On substitution in 2.31 and combination with 2.30 the spin density in the σ-bonds becomes in terms of spin density matrices:

$$\begin{aligned}
\rho^A(1,2) = &- 2 \sum_j \delta_j \frac{\langle \underline{\pi}_j^+ |H| \underline{A}_S^- \rangle \frac{1}{2} \{ \underline{\pi}_j^+(1) \underline{A}_S^-(2) + \underline{A}_S^-(1) \underline{\pi}_j^+(2) \}}{(I_\pi - E_A + \Delta E_j^+ + C_{jA})} \\
&+ 2 \sum_j \delta_j \frac{\langle \underline{\pi}_j^- |H| \underline{A}_S^+ \rangle \frac{1}{2} \{ \underline{\pi}_j^-(1) \underline{A}_S^+(2) + \underline{A}_S^+(1) \underline{\pi}_j^-(2) \}}{(I_A - E_\pi + \Delta E_j^- + C_{Aj})} + \sum_j \delta_j \frac{\langle \underline{\pi}_j^+ |H| \underline{A}_S^- \rangle^2}{(I_\pi - E_A + \Delta E_j^+ + C_{jA})^2} \rho_3^A(1,2) \\
&+ \sum_j \delta_j \frac{\langle \underline{\pi}_j^- |H| \underline{A}_S^+ \rangle^2}{(I_A - E_\pi + \Delta E_j^- + C_{Aj})^2} \rho_1^A(1,2) + 2 \Big\{ - \sum_j \delta_j \frac{\langle \underline{\pi}_j^+ |H| \underline{A}_S^- \rangle \langle \underline{A}_T^- |H| \underline{\pi}_j^+ \rangle}{(I_\pi - E_A + \Delta E_j^+ + C_{jA}) \Delta E_A^T} \qquad 2.32 \\
&+ \sum_j \delta_j \frac{\langle \underline{\pi}_j^- |H| \underline{A}_S^+ \rangle \langle \underline{A}_T^+ |H| \underline{\pi}_j^- \rangle}{(I_A - E_\pi + \Delta E_j^- + C_{Aj}) \Delta E_A^T} + \frac{1}{2} \frac{\int \rho^\pi(1,2)\, H\, \rho_{ST}^A(1,2)\, d\tau_1 d\tau_2}{\Delta E_A^T} \Big\} \rho_{ST}^A(1,2)
\end{aligned}$$

The application of this formula to actual problems and the relation to more usual methods such as hyperconjugation will be discussed in chapter IV.

D. σ-BONDS COUPLED VIA ANOTHER σ-BOND

We consider a system consisting of N π-electrons, 2 σ-electrons in bond A and 2 σ-electrons in bond B. The π-B interaction is assumed to be much smaller than the π-A interaction. Consequently the spin density in B is calculated by first taking into account the π-A interaction and then coupling B to the π-A system.

1. The zeroth order wave functions

In the calculation of the spin density in B the following wave functions will be considered:

$\psi_1 \cdots \psi_6$	:	the wave functions given in section C multiplied by the singlet ground state wave function of B
$\psi_7 \cdots \psi_{12}$	:	wave functions obtained from $\psi_1 \cdots \psi_6$ by excitation of B to the lowest triplet state
ψ_{13}, ψ_{14}	:	$\pi \rightarrow$ B charge-transfer wave functions
ψ_{15}, ψ_{16}	:	B $\rightarrow \pi$ charge-transfer wave functions
ψ_{17}, ψ_{18}	:	A $\rightarrow$ B charge-transfer wave functions
ψ_{19}, ψ_{20}	:	B $\rightarrow$ A charge-transfer wave functions

In $\psi_{13} \cdots \psi_{16}$ the σ-bond A is in its singlet ground state; in $\psi_{17} \cdots \psi_{20}$ the π-electron system is in its ground state. ψ_{17} and ψ_{19} will be chosen in such a way that the π-A system is in a singlet state whereas in ψ_{18} and ψ_{20} it is in a triplet state. From the ground state of the π-A system, which is calculated from $\psi_1 \cdots \psi_6$ as in section C, wave functions can be obtained by transfer of one electron in which A contains zero or four electrons and wave functions in which the π-system contains (N-2) or (N+2) electrons. These are neglected.

From the p singlet and q triplet spin functions for (N-1) electrons (5p+9q) doublet spin functions for (N+4) electrons can be built up. These are given in table 2.3. The total wave functions expressed in terms of these spin functions are given in table 2.4.

Table 2.3. Spin functions for (N+4) electrons built up from singlet and triplet spin functions for (N-1) electrons

$$\chi_{1\mu} = {}^0\chi_{\mu}(1..N-1)\alpha(N)\,{}^0\chi(N+1,N+2)\,{}^0\chi(N+3,N+4)$$

$$\chi_{2\mu} = 1/\sqrt{6}\{2\,{}^1\chi^{+}_{\mu-p}(1..N-1)\beta(N) - \sqrt{2}\,{}^1\chi^{0}_{\mu-p}(1..N-1)\alpha(N)\}\,{}^0\chi(N+1,N+2)\,{}^0\chi(N+3,N+4)$$

$$\chi_{3\mu} = {}^0\chi_{\mu}(1..N-1)\,1/\sqrt{6}\{-2\beta(N)\,{}^1\chi^{+}(N+1,N+2) + \sqrt{2}\,\alpha(N)\,{}^1\chi^{0}(N+1,N+2)\}\,{}^0\chi(N+3,N+4)$$

$$\chi_{4\mu} = 1/\sqrt{3}\{-{}^1\chi^{0}_{\mu-p}(1..N-1)\,{}^1\chi^{0}(N+1,N+2) + {}^1\chi^{-}_{\mu-p}(1..N-1)\,{}^1\chi^{+}(N+1,N+2)$$

$$+\,{}^1\chi^{+}_{\mu-p}(1..N-1)\,{}^1\chi^{-}(N+1,N+2)\}\alpha(N)\,{}^0\chi(N+3,N+4)$$

$$\chi_{5_\mu} = 1/\sqrt{6}\{-\sqrt{2}\,{}^{1}\chi^{0}_{\mu-p}(1..N-1)\beta(N)\,{}^{1}\chi^{+}(N+1,N+2)+\sqrt{2}\,{}^{1}\chi^{+}_{\mu-p}(1..N-1)\beta(N)\,{}^{1}\chi^{0}(N+1,N+2)$$

$$-{}^{1}\chi^{+}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{-}(N+1,N+2)+{}^{1}\chi^{-}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{+}(N+1,N+2)\}\,{}^{0}\chi(N+3,N+4)$$

$$\chi_{6_\mu} = {}^{0}\chi_{\mu}(1..N-1)\,{}^{0}\chi(N+1,N+2)\ 1/\sqrt{6}\{-2\beta(N)\,{}^{1}\chi^{+}(N+3,N+4)+\sqrt{2}\alpha(N)\,{}^{1}\chi^{0}(N+3,N+4)\}$$

$$\chi_{7_\mu} = \alpha(N)\,{}^{0}\chi(N+1,N+2)\ 1/\sqrt{3}\{-{}^{1}\chi^{0}_{\mu-p}(1..N-1)\,{}^{1}\chi^{0}(N+3,N+4)+{}^{1}\chi^{-}_{\mu-p}(1..N-1)\,{}^{1}\chi^{+}(N+3,N+4)$$

$$+{}^{1}\chi^{+}_{\mu-p}(1..N-1)\,{}^{1}\chi^{-}(N+3,N+4)\}$$

$$\chi_{8_\mu} = {}^{0}\chi(N+1,N+2)\ 1/\sqrt{6}\{-\sqrt{2}\,{}^{1}\chi^{0}_{\mu-p}(1..N-1)\beta(N)\,{}^{1}\chi^{+}(N+3,N+4)+\sqrt{2}\,{}^{1}\chi^{+}_{\mu-p}(1..N-1)\beta(N)$$

$$\times\,{}^{1}\chi^{0}(N+3,N+4)-{}^{1}\chi^{+}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{-}(N+3,N+4)+{}^{1}\chi^{-}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{+}(N+3,N+4)\}$$

$$\chi_{9_\mu} = {}^{0}\chi_{\mu}(1..N-1)\alpha(N)\ 1/\sqrt{3}\{-{}^{1}\chi^{0}(N+1,N+2)\,{}^{1}\chi^{0}(N+3,N+4)+{}^{1}\chi^{-}(N+1,N+2)\,{}^{1}\chi^{+}(N+3,N+4)$$

$$+{}^{1}\chi^{+}(N+1,N+2)\,{}^{1}\chi^{-}(N+3,N+4)\}$$

$$\chi_{10_\mu} = {}^{0}\chi_{\mu}(1..N-1)\ 1/\sqrt{6}\{-\sqrt{2}\,\beta(N)\,{}^{1}\chi^{0}(N+1,N+2)\,{}^{1}\chi^{+}(N+3,N+4)+\sqrt{2}\,\beta(N)\,{}^{1}\chi^{+}(N+1,N+2)$$

$$\times\,{}^{1}\chi^{0}(N+3,N+4)-\alpha(N)\,{}^{1}\chi^{+}(N+1,N+2)\,{}^{1}\chi^{-}(N+3,N+4)+\alpha(N)\,{}^{1}\chi^{-}(N+1,N+2)\,{}^{1}\chi^{+}(N+3,N+4)\}$$

$$\chi_{11_\mu} = 1/\sqrt{18}\{2\,{}^{1}\chi^{0}_{\mu-p}(1..N-1)\beta(N)\,{}^{1}\chi^{0}(N+1,N+2)\,{}^{1}\chi^{+}(N+3,N+4)-\sqrt{2}\,{}^{1}\chi^{0}_{\mu-p}(1..N-1)\alpha(N)$$

$$\times\,{}^{1}\chi^{0}(N+1,N+2)\,{}^{1}\chi^{0}(N+3,N+4)-2\,{}^{1}\chi^{-}_{\mu-p}(1..N-1)\beta(N)\,{}^{1}\chi^{+}(N+1,N+2)\,{}^{1}\chi^{+}(N+3,N+4)$$

$$+\sqrt{2}\,{}^{1}\chi^{-}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{+}(N+1,N+2)\,{}^{1}\chi^{0}(N+3,N+4)-2\,{}^{1}\chi^{+}_{\mu-p}(1..N-1)\beta(N)\,{}^{1}\chi^{-}(N+1,N+2)$$

$$\times\,{}^{1}\chi^{+}(N+3,N+4)+\sqrt{2}\,{}^{1}\chi^{+}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{-}(N+1,N+2)\,{}^{1}\chi^{0}(N+3,N+4)\}$$

$$\chi_{12_\mu} = 1/6[-2\{-\sqrt{2}\,{}^{1}\chi^{0}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{-}(N+1,N+2)+\sqrt{2}\,{}^{1}\chi^{-}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{0}(N+1,N+2)$$

$$-{}^{1}\chi^{-}_{\mu-p}(1..N-1)\beta(N)\,{}^{1}\chi^{+}(N+1,N+2)+{}^{1}\chi^{+}_{\mu-p}(1..N-1)\beta(N)\,{}^{1}\chi^{-}(N+1,N+2)\}\,{}^{1}\chi^{+}(N+3,N+4)$$

$$+\sqrt{2}\{-\sqrt{2}\,{}^{1}\chi^{0}_{\mu-p}(1..N-1)\beta(N)\,{}^{1}\chi^{+}(N+1,N+2)+\sqrt{2}\,{}^{1}\chi^{+}_{\mu-p}(1..N-1)\beta(N)\,{}^{1}\chi^{0}(N+1,N+2)$$

$$-{}^{1}\chi^{+}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{-}(N+1,N+2)+{}^{1}\chi^{-}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{+}(N+1,N+2)\}\,{}^{1}\chi^{0}(N+3,N+4)]$$

$$
\begin{aligned}
\chi_{13_\mu} = 1/6\{ & -\sqrt{2}\,{}^{1}\chi^{+}_{\mu-p}(1..N-1)\beta(N)\,{}^{1}\chi^{0}(N+1,N+2)\,{}^{1}\chi^{0}(N+3,N+4)+\sqrt{2}\,{}^{1}\chi^{0}_{\mu-p}(1..N-1)\beta(N) \\
& \times{}^{1}\chi^{+}(N+1,N+2)\,{}^{1}\chi^{0}(N+3,N+4)+\sqrt{2}\,{}^{1}\chi^{+}_{\mu-p}(1..N-1)\beta(N)\,{}^{1}\chi^{-}(N+1,N+2)\,{}^{1}\chi^{+}(N+3,N+4) \\
& -\sqrt{2}\,{}^{1}\chi^{-}_{\mu-p}(1..N-1)\beta(N)\,{}^{1}\chi^{+}(N+1,N+2)\,{}^{1}\chi^{+}(N+3,N+4)+3\,{}^{1}\chi^{+}_{\mu-p}(1..N-1)\alpha(N) \\
& \times{}^{1}\chi^{0}(N+1,N+2)\,{}^{1}\chi^{-}(N+3,N+4)-3\,{}^{1}\chi^{0}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{+}(N+1,N+2)\,{}^{1}\chi^{-}(N+3,N+4) \\
& +{}^{1}\chi^{0}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{-}(N+1,N+2)\,{}^{1}\chi^{+}(N+3,N+4)-{}^{1}\chi^{-}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{0}(N+1,N+2) \\
& \times{}^{1}\chi^{+}(N+3,N+4)-2\,{}^{1}\chi^{+}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{-}(N+1,N+2)\,{}^{1}\chi^{0}(N+3,N+4) \\
& +2\,{}^{1}\chi^{-}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{+}(N+1,N+2)\,{}^{1}\chi^{0}(N+3,N+4)\}
\end{aligned}
$$

$$
\begin{aligned}
\chi_{14_\mu} = 1/6\sqrt{5}\{ & \sqrt{2}\,{}^{1}\chi^{+}_{\mu-p}(1..N-1)\beta(N)\,{}^{1}\chi^{-}(N+1,N+2)\,{}^{1}\chi^{+}(N+3,N+4)+\sqrt{2}\,{}^{1}\chi^{-}_{\mu-p}(1..N-1)\beta(N) \\
& \times{}^{1}\chi^{+}(N+1,N+2)\,{}^{1}\chi^{+}(N+3,N+4)+2\sqrt{2}\,{}^{1}\chi^{0}_{\mu-p}(1..N-1)\beta(N)\,{}^{1}\chi^{0}(N+1,N+2)\,{}^{1}\chi^{+}(N+3,N+4) \\
& -3\sqrt{2}\,{}^{1}\chi^{+}_{\mu-p}(1..N-1)\beta(N)\,{}^{1}\chi^{0}(N+1,N+2)\,{}^{1}\chi^{0}(N+3,N+4)-3\sqrt{2}\,{}^{1}\chi^{0}_{\mu-p}(1..N-1)\beta(N) \\
& \times{}^{1}\chi^{+}(N+1,N+2)\,{}^{1}\chi^{0}(N+3,N+4)+6\sqrt{2}\,{}^{1}\chi^{+}_{\mu-p}(1..N-1)\beta(N)\,{}^{1}\chi^{+}(N+1,N+2)\,{}^{1}\chi^{-}(N+3,N+4) \\
& -3\,{}^{1}\chi^{0}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{-}(N+1,N+2)\,{}^{1}\chi^{+}(N+3,N+4)-3\,{}^{1}\chi^{-}_{\mu-p}(1..N-1)\alpha(N) \\
& \times{}^{1}\chi^{0}(N+1,N+2)\,{}^{1}\chi^{+}(N+3,N+4)+2\,{}^{1}\chi^{+}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{-}(N+1,N+2)\,{}^{1}\chi^{0}(N+3,N+4) \\
& +2\,{}^{1}\chi^{-}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{+}(N+1,N+2)\,{}^{1}\chi^{0}(N+3,N+4)+4\,{}^{1}\chi^{0}_{\mu-p}(1..N-1)\alpha(N) \\
& \times{}^{1}\chi^{0}(N+1,N+2)\,{}^{1}\chi^{0}(N+3,N+4)-3\,{}^{1}\chi^{+}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{0}(N+1,N+2)\,{}^{1}\chi^{-}(N+3,N+4) \\
& -3\,{}^{1}\chi^{0}_{\mu-p}(1..N-1)\alpha(N)\,{}^{1}\chi^{+}(N+1,N+2)\,{}^{1}\chi^{-}(N+3,N+4)\}
\end{aligned}
$$

Table 2.4. Wave functions used in the calculation of the spin density in B.

$$
\psi_1 = \frac{1}{\sqrt{p+q}}\{\sum_{\mu=1}^{p}\pi_\mu(1..N)\chi_{1_\mu}+\sum_{\mu=p+1}^{p+q}\pi_\mu(1..N)\chi_{2_\mu}\}\,{}^{0}A(N+1,N+2)\,{}^{0}B(N+3,N+4)
$$

$$
\psi_2 = \frac{1}{\sqrt{p+q}}\left[\sum_{\mu=1}^{p}\pi_\mu(1..N)\chi_{3_\mu}+\sum_{\mu=p+1}^{p+q}\pi_\mu(1..N)\frac{\{\chi_{4_\mu}+\sqrt{2}\,\chi_{5_\mu}\}}{\sqrt{3}}\right]{}^{1}A(N+1,N+2)\,{}^{0}B(N+3,N+4)
$$

$$\psi_{3j} = \frac{1}{\sqrt{2p}} \sum_{\mu=1}^{p} {}^{0}\pi_{j\mu}(1..N-1)\{A_1(N+1,N+2,N)\chi_{1\mu} - A_2(N+1,N+2,N)\chi_{3\mu}\}\,{}^{0}B(N+3,N+4)$$

$$\psi_{4j} = \frac{1}{\sqrt{2q}} \sum_{\mu=p+1}^{p+q} {}^{1}\pi_{j,\mu-p}(1..N-1)\left[A_1(N+1,N+2,N)\chi_{2\mu} - A_2(N+1,N+2,N)\,\frac{\{\chi_{4\mu} - \sqrt{2}\,\chi_{5\mu}\}}{\sqrt{3}}\right]$$

$$\times\, {}^{0}B(N+3, N+4)$$

$$\psi_{5j} = \frac{1}{\sqrt{p+q}}\left[\sum_{\mu=1}^{p} {}^{0}\pi_{j\mu}(1..N,N+2)\,\frac{\{\chi_{1\mu} + \sqrt{3}\,\chi_{3\mu}\}}{2} + \sum_{\mu=p+1}^{p+q} {}^{0}\pi_{j\mu}(1..N,N+2)\right.$$

$$\left.\times\,\frac{\{\chi_{2\mu} + \chi_{4\mu} + \sqrt{2}\,\chi_{5\mu}\}}{2}\right] A(N+1)\,{}^{0}B(N+3,N+4)$$

$$\psi_{6j} = \frac{1}{\sqrt{p+2q+r}}\left[\sum_{\mu=1}^{p} {}^{1}\pi_{j\mu}(1..N,N+2)\,\frac{\{-\sqrt{3}\,\chi_{1\mu} + \chi_{3\mu}\}}{2} + \sum_{\mu=p+1}^{p+q} {}^{1}\pi_{j\mu}(1..N,N+2)\right.$$

$$\left.\times\,\frac{\{-3\chi_{2\mu} + \chi_{4\mu} + \sqrt{2}\,\chi_{5\mu}\}}{2\sqrt{3}} + \sum_{\mu=p+q+1}^{p+2q+r} \{\text{quadruplet}(N)\ \text{terms}\}\right] A(N+1)\,{}^{0}B(N+3,N+4)$$

$$\psi_{7} = \frac{1}{\sqrt{p+q}}\left[\sum_{\mu=1}^{p} \pi_{\mu}(1..N)\chi_{6\mu} + \sum_{\mu=p+1}^{p+q} \pi_{\mu}(1..N)\,\frac{\{\chi_{7\mu} + \sqrt{2}\,\chi_{8\mu}\}}{\sqrt{3}}\right] {}^{0}A(N+1,N+2)\,{}^{1}B(N+3,N+4)$$

$$\psi_{8} = \frac{1}{\sqrt{p+q}}\left[\sum_{\mu=1}^{p} \pi_{\mu}(1..N)\,\frac{\{-\chi_{9\mu} - \sqrt{2}\,\chi_{10\mu}\}}{\sqrt{3}} + \sum_{\mu=p+1}^{p+q} \pi_{\mu}(1..N)\,\frac{\{\chi_{11\mu} + \sqrt{2}\,\chi_{12\mu}\}}{\sqrt{3}}\right]$$

$$\times\, {}^{1}A(N+1, N+2)\,{}^{1}B(N+3, N+4)$$

$$\psi_{9j} = \frac{1}{\sqrt{2p}} \sum_{\mu=1}^{p} {}^{0}\pi_{j\mu}(1..N-1)\left[A_1(N+1,N+2,N)\chi_{6\mu} + A_2(N+1,N+2,N)\,\frac{\{\chi_{9\mu} + \sqrt{2}\,\chi_{10\mu}\}}{\sqrt{3}}\right]$$

$$\times\, {}^{1}B(N+3, N+4)$$

$$\psi_{10j} = \frac{1}{\sqrt{2q}} \sum_{\mu=p+1}^{p+q} {}^{1}\pi_{j,\mu-p}(1..N-1)\left[A_1(N+1,N+2,N)\,\frac{\{\chi_{7\mu} + \sqrt{2}\,\chi_{8\mu}\}}{\sqrt{3}} - A_2(N+1,N+2,N)\right.$$

$$\left.\times\,\frac{\{\chi_{11\mu} - \sqrt{2}\,\chi_{12\mu}\}}{\sqrt{3}}\right] {}^{1}B(N+3, N+4)$$

$$\psi_{11j} = \frac{1}{\sqrt{p+q}}\left[\sum_{\mu=1}^{p} {}^{0}\pi_{j\mu}(1..N,N+2)\,\frac{\{\chi_{6\mu}-\chi_{9\mu}-\sqrt{2}\,\chi_{10\mu}\}}{2} + \sum_{\mu=p+1}^{p+q} {}^{0}\pi_{j\mu}(1..N,N+2)\right.$$

$$\left.\times\,\frac{\{\chi_{7\mu}+\sqrt{2}\,\chi_{8\mu}+\sqrt{3}\,\chi_{11\mu}+\sqrt{6}\,\chi_{12\mu}\}}{2\sqrt{3}}\right] A(N+1)\,{}^{1}B(N+3,N+4)$$

$$\psi_{12j} = \frac{1}{\sqrt{p+2q+r}}\left[\sum_{\mu=1}^{p} {}^{1}\pi_{j\mu}(1..N,N+2)\,\frac{\{-3\chi_{6\mu}-\chi_{9\mu}-\sqrt{2}\,\chi_{10\mu}\}}{2\sqrt{3}} + \sum_{\mu=p+1}^{p+q} {}^{1}\pi_{j\mu}(1..N,N+2)\right.$$

$$\left.\times\,\frac{\{-\sqrt{3}\,\chi_{7\mu}-\sqrt{6}\,\chi_{8\mu}+\chi_{11\mu}+\sqrt{2}\,\chi_{12\mu}\}}{2\sqrt{3}} + \sum_{\mu=p+q+1}^{p+2q+r}\{\text{quadruplet(N) terms}\}\right]$$

$$\times\,A(N+1)\,{}^{1}B(N+3,\,N+4)$$

$$\psi_{13j} = \frac{1}{\sqrt{2p}}\sum_{\mu=1}^{p} {}^{0}\pi_{j\mu}(1..N-1)\,{}^{0}A(N+1,N+2)\,\{B_1(N+3,N+4,N)\,\chi_{1\mu} - B_2(N+3,N+4,N)\,\chi_{6\mu}\}$$

$$\psi_{14j} = \frac{1}{\sqrt{2q}}\sum_{\mu=p+1}^{p+q} {}^{1}\pi_{j,\,\mu-p}(1..N-1)\,{}^{0}A(N+1,N+2)\left[B_1(N+3,N+4,N)\,\chi_{2\mu} + B_2(N+3,N+4,N)\right.$$

$$\left.\times\,\frac{\{-\chi_{7\mu}+\sqrt{2}\,\chi_{8\mu}\}}{\sqrt{3}}\right]$$

$$\psi_{15j} = \frac{1}{\sqrt{p+q}}\left[\sum_{\mu=1}^{p} {}^{0}\pi_{j\mu}(1..N,N+4)\,\frac{\{\chi_{1\mu}+\sqrt{3}\,\chi_{6\mu}\}}{2} + \sum_{\mu=p+1}^{p+q} {}^{0}\pi_{j\mu}(1..N,N+4)\right.$$

$$\left.\times\,\frac{\{\chi_{2\mu}+\chi_{7\mu}+\sqrt{2}\,\chi_{8\mu}\}}{2}\right] {}^{0}A(N+1,\,N+2)\,B(N+3)$$

$$\psi_{16j} = \frac{1}{\sqrt{p+2q+r}}\left[\sum_{\mu=1}^{p} {}^{1}\pi_{j\mu}(1..N,N+4)\,\frac{\{-\sqrt{3}\,\chi_{1\mu}+\chi_{6\mu}\}}{2} + {}^{1}\pi_{j\mu}(1..N,N+4)\,\frac{\{-3\chi_{2\mu}+\chi_{7\mu}+\sqrt{2}\,\chi_{8\mu}\}}{2\sqrt{3}}\right.$$

$$\left. + \sum_{\mu=p+q+1}^{p+2q+r}\{\text{quadruplet(N) terms}\}\right] {}^{0}A(N+1,\,N+2)\,B(N+3)$$

$$\psi_{17} = \frac{1}{\sqrt{2(p+q)}}\left[\sum_{\mu=1}^{p} \pi_{\mu}(1..N)\,A(N+1)\left\{B_1(N+3,\,N+4,\,N+2)\,\frac{\{-\chi_{1\mu}+\sqrt{3}\,\chi_{3\mu}\}}{2} + B_2(N+3,N+4,N+2)\right.\right.$$

$$\times \frac{\{\chi_{6\mu}+\chi_{9\mu}+\sqrt{2}\,\chi_{10\mu}\}}{2}\Big\} + \sum_{\mu=p+1}^{p+q} \pi_{\mu}(1..N)A(N+1)\Big\{B_1(N+3,N+4,N+2)$$

$$\times \frac{\{-\chi_{2\mu}+\chi_{4\mu}+\sqrt{2}\,\chi_{5\mu}\}}{2} + B_2(N+3,N+4,N+2)\ \frac{\{\chi_{7\mu}+\sqrt{2}\,\chi_{8\mu}-\sqrt{3}\,\chi_{11\mu}-\sqrt{6}\,\chi_{12\mu}\}}{2\sqrt{3}}\Big\}\Big]$$

$$\psi_{18} = \frac{1}{\sqrt{2(p+q)}}\Big[\sum_{\mu=1}^{p} \pi_{\mu}(1..N)A(N+1)\Big\{B_1(N+3,N+4,N+2)\ \frac{\{\sqrt{3}\,\chi_{1\mu}+\chi_{3\mu}\}}{2}+B_2(N+3,N+4,N+2)$$

$$\times \frac{\{\chi_{6\mu}-3\chi_{9\mu}+\sqrt{2}\,\chi_{10\mu}\}}{2\sqrt{3}}\Big\} + \sum_{\mu=p+1}^{p+q} \pi_{\mu}(1..N)A(N+1)\Big\{B_1(N+3,N+4,N+2)$$

$$\times \frac{\{3\chi_{2\mu}+\chi_{4\mu}+\sqrt{2}\,\chi_{5\mu}\}}{2\sqrt{3}} + B_2(N+3,N+4,N+2)\{1/6\,\chi_{7\mu}+\sqrt{2}/6\,\chi_{8\mu}+\sqrt{3}/18\,\chi_{11\mu}$$

$$+\sqrt{6}/18\,\chi_{12\mu}-2\sqrt{3}/9\,\chi_{13\mu}-2\sqrt{15}/9\,\chi_{14\mu}\}\Big\}\Big]$$

$$\psi_{19} = \frac{1}{\sqrt{2(p+q)}}\Big[\sum_{\mu=1}^{p} \pi_{\mu}(1..N)B(N+3)\Big\{A_1(N+1,N+2,N+4)\ \frac{\{\chi_{1\mu}+\sqrt{3}\,\chi_{6\mu}\}}{2}+A_2(N+1,N+2,N+4)$$

$$\times \frac{\{\chi_{3\mu}-\chi_{9\mu}-\sqrt{2}\,\chi_{10\mu}\}}{2}\Big\} + \sum_{\mu=p+1}^{p+q} \pi_{\mu}(1..N)B(N+3)\Big\{A_1(N+1,N+2,N+4)$$

$$\times \frac{\{\chi_{2\mu}+\chi_{7\mu}+\sqrt{2}\,\chi_{8\mu}\}}{2} + A_2(N+1,N+2,N+4)\ \frac{\{\chi_{4\mu}+\sqrt{2}\,\chi_{5\mu}+\sqrt{3}\,\chi_{11\mu}+\sqrt{6}\,\chi_{12\mu}\}}{2\sqrt{3}}\Big\}\Big]$$

$$\psi_{20} = \frac{1}{\sqrt{2(p+q)}}\Big[\sum_{\mu=1}^{p} \pi_{\mu}(1..N)B(N+3)\Big\{A_1(N+1,N+2,N+4)\ \frac{\{-\sqrt{3}\,\chi_{1\mu}+\chi_{6\mu}\}}{2}+A_2(N+1,N+2,N+4)$$

$$\times \frac{\{\chi_{3\mu}+3\chi_{9\mu}-\sqrt{2}\,\chi_{10\mu}\}}{2\sqrt{3}} + \sum_{\mu=p+1}^{p+q} \pi_{\mu}(1..N)B(N+3)\Big\{A_1(N+1,N+2,N+4)$$

$$\times \frac{\{-3\chi_{2\mu}+\chi_{7\mu}+\sqrt{2}\,\chi_{8\mu}\}}{2\sqrt{3}} + A_2(N+1,N+2,N+4)\ \{1/6\,\chi_{4\mu}+\sqrt{2}/6\,\chi_{5\mu}-\sqrt{3}/18\,\chi_{11\mu}$$

$$-\sqrt{6}/18\,\chi_{12\mu}+2\sqrt{3}/9\,\chi_{13\mu}+2\sqrt{15}/9\,\chi_{14\mu}\}\Big\}\Big]$$

2. The matrix elements of the Hamiltonian

In the matrix elements of the Hamiltonian terms arise which are determined by the π-A, π-B and A-B interaction but besides these, terms occur which are dependent on integrals such as $\langle \pi A|H|B\pi\rangle$. In order to simplify the calculations, the latter terms are neglected. In this case the non-diagonal matrix elements between the wave functions $\psi_1 \ldots \psi_{6j}$ are equal to the ones given in section C whereas the matrix elements between the wave functions $\psi_7 \ldots \psi_{12j}$ can be obtained by setting

$$\langle \mathscr{A}\psi_r|H|\mathscr{A}\psi_s\rangle = \langle \mathscr{A}\psi_{r-6}|H|\mathscr{A}\psi_{s-6}\rangle$$

for $r, s = 7 \ldots 12j$

The matrix elements between these two groups of functions are dependent on B-(π-A) exchange integrals. The exact form of these terms is not needed because the spin density in B caused by these matrix elements can be calculated directly from the formulas given in section C. The remaining non-diagonal matrix elements as far as they are used in our calculations are given in table 2. 5. The approximation of the excitation energies introduced in section C will be used for the wave functions $\psi_2 \ldots \psi_{16j}$. For ψ_{17} and ψ_{18} and for ψ_{19} and ψ_{20} this would give equal excitation energies. In the spin density in B, however, terms arise which are dependent on

$$\frac{1}{(E_{17}-E_1)} - \frac{1}{(E_{18}-E_1)} \quad \text{and} \quad \frac{1}{(E_{19}-E_1)} - \frac{1}{(E_{20}-E_1)}$$

respectively. In these terms the differences $(E_{17}-E_{18})$ and $(E_{19}-E_{20})$ must be taken into account. In all other terms we assume

$$E_{17}-E_1 = E_{18}-E_1 = I_A - E_B + C_{AB}$$
$$E_{19}-E_1 = E_{20}-E_1 = I_B - E_A + C_{BA}$$

$E_{17}-E_{18}$ and $E_{19}-E_{20}$ can be calculated in a general way. In the molecular orbital theory the energy difference between corresponding singlet and triplet states depends on the exchange integral between the singly occupied orbitals. In our case a similar relation holds:

Suppose two doublet systems with wave functions R(1..N) and S(N+1,... N+M) are coupled together. Then the total wave function is a singlet $\psi_I(1..N+M)$ or a triplet $\psi_{II}(1..N+M)$

$$\psi_I = \frac{1}{\sqrt{n(R)}} \frac{1}{\sqrt{n(S)}} \sum_{\mu=1}^{n(R)} \sum_{\nu=1}^{n(S)} R_\mu(1..N)S_\nu(N+1,..N+M) \frac{1}{\sqrt{2}} \{\chi_\mu^{+1/2}(1..N)\chi_\nu^{-1/2}(N+1,..N+M)$$

$$- \chi_\mu^{-1/2}(1..N)\chi_\nu^{+1/2}(N+1,..N+M)\}$$

$$\psi_{II} = \frac{1}{\sqrt{n(R)}} \frac{1}{\sqrt{n(S)}} \sum_{\mu=1}^{n(R)} \sum_{\nu=1}^{n(S)} R_\mu(1..N)S_\nu(N+1,..N+M) \frac{1}{\sqrt{2}} \{\chi_\mu^{+1/2}(1..N)\chi_\nu^{-1/2}(N+1,..N+M)$$

$$+ \chi_\mu^{-1/2}(1..N)\chi_\nu^{+1/2}(N+1,..N+M)\}$$

The energy difference becomes

$$E_I - E_{II} = \langle \psi_I | H(1 - \sum_{i=1}^{N} \sum_{j=N+1}^{N+M} T_{ij}) | \psi_I \rangle - \langle \psi_{II} | H(1 - \sum_{i=1}^{N} \sum_{j=N+1}^{N+M} T_{ij}) | \psi_{II} \rangle$$

$$= \frac{2NM}{n(R)\, n(S)} \sum_{\mu=1}^{n(R)} \sum_{\nu=1}^{n(S)} \langle R_\mu(1..N)S_\nu(N+1,..N+M) | HT_{N,N+M} | R_\mu(1..N)S_\nu(N+1,..N+M)\rangle$$

$$\times \langle \chi_\mu(1..N)\chi_\nu(N+1,..N+M) | T_{N,N+M} | \chi_\mu(1..N)\chi_\nu(N+1,..N+M)\rangle$$

From the calculation of the integrals over the spin functions as in previous sections we obtain

$$E_I - E_{II} = 2 \int \rho^R(1,2)\, H\, \rho^S(1,2) d\tau_1 d\tau_2$$

which yields

$$E_{17} - E_{18} = 2 \int \rho^\pi(1,2)\, H\, \rho_1^A(1,2) d\tau_1 d\tau_2$$

$$E_{19} - E_{20} = 2 \int \rho^\pi(1,2)\, H\, \rho_3^A(1,2) d\tau_1 d\tau_2$$

Table 2.5. Non-diagonal matrix elements of the Hamiltonian used in the calculation of the spin density in B

	ψ_{13j}	ψ_{14j}	ψ_{15j}	ψ_{16j}	ψ_{17}	ψ_{18}	ψ_{19}	ψ_{20}
ψ_1	$\langle\pi_j^+\vert H\vert\underline{B}_S^-\rangle$	$\sqrt{3}\langle\pi_j^+\vert H\vert\underline{B}_S^-\rangle$	$\langle\pi_j^-\vert H\vert\underline{B}_S^+\rangle$	$-\sqrt{3}\langle\pi_j^-\vert H\vert\underline{B}_S^+\rangle$	$-1/\sqrt{2}\langle\underline{A}_S^+\vert H\vert\underline{B}_S^-\rangle$	$\sqrt{6}/2\langle\underline{A}_S^+\vert H\vert\underline{B}_S^-\rangle$	$1/\sqrt{2}\langle\underline{A}_S^-\vert H\vert\underline{B}_S^+\rangle$	$-\sqrt{6}/2\langle\underline{A}_S^-\vert H\vert\underline{B}_S^+\rangle$
ψ_2					$\sqrt{6}/2\langle\underline{A}_T^+\vert H\vert\underline{B}_S^-\rangle$	$1/\sqrt{2}\langle\underline{A}_T^+\vert H\vert\underline{B}_S^-\rangle$	$\sqrt{6}/2\langle\underline{A}_T^-\vert H\vert\underline{B}_S^+\rangle$	$1/\sqrt{2}\langle\underline{A}_T^-\vert H\vert\underline{B}_S^+\rangle$
ψ_{3j}	$\langle\underline{A}_S^-\vert H\vert\underline{B}_S^-\rangle$						$1/\sqrt{2}\langle\pi_j^+\vert H\vert\underline{B}_S^+\rangle$	$\sqrt{6}/2\langle\pi_j^+\vert H\vert\underline{B}_S^+\rangle$
ψ_{4j}		$\langle\underline{A}_S^-\vert H\vert\underline{B}_S^-\rangle$					$-\sqrt{6}/2\langle\pi_j^+\vert H\vert\underline{B}_S^+\rangle$	$1/\sqrt{2}\langle\pi_j^+\vert H\vert\underline{B}_S^+\rangle$
ψ_{5j}			$-\langle\underline{A}_S^+\vert H\vert\underline{B}_S^+\rangle$		$1/\sqrt{2}\langle\pi_j^-\vert H\vert\underline{B}_S^-\rangle$	$\sqrt{6}/2\langle\pi_j^-\vert H\vert\underline{B}_S^-\rangle$		
ψ_{6j}				$-\langle\underline{A}_S^+\vert H\vert\underline{B}_S^+\rangle$	$\sqrt{6}/2\langle\pi_j^-\vert H\vert\underline{B}_S^-\rangle$	$-1/\sqrt{2}\langle\pi_j^-\vert H\vert\underline{B}_S^-\rangle$		
ψ_7	$-\sqrt{3}\langle\pi_j^+\vert H\vert\underline{B}_T^-\rangle$	$\langle\pi_j^+\vert H\vert\underline{B}_T^-\rangle$	$\sqrt{3}\langle\pi_j^-\vert H\vert\underline{B}_T^+\rangle$	$\langle\pi_j^-\vert H\vert\underline{B}_T^+\rangle$	$\sqrt{6}/2\langle\underline{A}_S^+\vert H\vert\underline{B}_T^-\rangle$	$1/\sqrt{2}\langle\underline{A}_S^+\vert H\vert\underline{B}_T^-\rangle$	$\sqrt{6}/2\langle\underline{A}_S^-\vert H\vert\underline{B}_T^+\rangle$	$1/\sqrt{2}\langle\underline{A}_S^-\vert H\vert\underline{B}_T^+\rangle$
ψ_8					$-3/\sqrt{2}\langle\underline{A}_T^+\vert H\vert\underline{B}_T^-\rangle$	$1/\sqrt{6}\langle\underline{A}_T^+\vert H\vert\underline{B}_T^-\rangle$	$3/\sqrt{2}\langle\underline{A}_T^-\vert H\vert\underline{B}_T^+\rangle$	$-1/\sqrt{6}\langle\underline{A}_T^-\vert H\vert\underline{B}_T^+\rangle$
ψ_{9j}	$-\sqrt{3}\langle\underline{A}_S^-\vert H\vert\underline{B}_T^-\rangle$						$\sqrt{6}/2\langle\pi_j^+\vert H\vert\underline{B}_T^+\rangle$	$-1/\sqrt{2}\langle\pi_j^+\vert H\vert\underline{B}_T^+\rangle$
ψ_{10j}		$1/\sqrt{3}\langle\underline{A}_S^-\vert H\vert\underline{B}_T^-\rangle$					$-3/\sqrt{2}\langle\pi_j^+\vert H\vert\underline{B}_T^+\rangle$	$-1/\sqrt{6}\langle\pi_j^+\vert H\vert\underline{B}_T^+\rangle$
ψ_{11j}			$-\sqrt{3}\langle\underline{A}_S^+\vert H\vert\underline{B}_T^+\rangle$		$-\sqrt{6}/2\langle\pi_j^-\vert H\vert\underline{B}_T^-\rangle$	$1/\sqrt{2}\langle\pi_j^-\vert H\vert\underline{B}_T^-\rangle$		
ψ_{12j}				$1/\sqrt{3}\langle\underline{A}_S^+\vert H\vert\underline{B}_T^+\rangle$	$-3/\sqrt{2}\langle\pi_j^-\vert H\vert\underline{B}_T^-\rangle$	$-1/\sqrt{6}\langle\pi_j^-\vert H\vert\underline{B}_T^-\rangle$		
ψ_{13j}					$\sqrt{2}\langle\pi_j^+\vert H\vert\underline{A}_S^+\rangle$			
ψ_{14j}						$-\sqrt{2}\langle\pi_j^+\vert H\vert\underline{A}_S^+\rangle$		
ψ_{15j}							$\sqrt{2}\langle\pi_j^-\vert H\vert\underline{A}_S^-\rangle$	
ψ_{16j}								$\sqrt{2}\langle\pi_j^-\vert H\vert\underline{A}_S^-\rangle$

3. Introduction of the π-A interaction

From the matrix elements given in section D. 2 it may be inferred that on introduction of the π-A interaction the following combinations of wave functions are obtained.

The ground state wave function before the coupling with B is

$$\psi'_1 = \left\{1 - \frac{1}{2}\sum_{i=3}^{6}\sum_{j}\frac{\langle \mathscr{A}\psi_1|H|\mathscr{A}\psi_{ij}\rangle^2}{(E_{ij}-E_1)^2}\right\}\Big[\mathscr{A}\psi_1 - \sum_{i=3}^{6}\sum_{j}\frac{\langle \mathscr{A}\psi_1|H|\mathscr{A}\psi_{ij}\rangle}{(E_{ij}-E_1)}\mathscr{A}\psi_{ij}$$

$$+\left\{\sum_{i=3}^{6}\sum_{j}\frac{\langle \mathscr{A}\psi_1|H|\mathscr{A}\psi_{ij}\rangle\langle \mathscr{A}\psi_{ij}|H|\mathscr{A}\psi_2\rangle}{(E_{ij}-E_1)(E_2-E_1)} - \frac{\langle \mathscr{A}\psi_1|H|\mathscr{A}\psi_2\rangle}{(E_2-E_1)}\right\}\mathscr{A}\psi_2\Big]$$

in which, as in the calculation of the spin density in A, the second order terms obtained from the interaction between ψ_2 and ψ_1 are neglected.

The corresponding wave function in which B is excited to the triplet state becomes

$$\psi'_7 = \left\{1 - \frac{1}{2}\sum_{i=9}^{12}\sum_{j}\frac{\langle \mathscr{A}\psi_7|H|\mathscr{A}\psi_{ij}\rangle^2}{(E_{ij}-E_7)^2}\right\}\Big[\mathscr{A}\psi_7 - \sum_{i=9}^{12}\sum_{j}\frac{\langle \mathscr{A}\psi_7|H|\mathscr{A}\psi_{ij}\rangle}{(E_{ij}-E_7)}\mathscr{A}\psi_{ij}$$

$$+\left\{\sum_{i=9}^{12}\sum_{j}\frac{\langle \mathscr{A}\psi_7|H|\mathscr{A}\psi_{ij}\rangle\langle \mathscr{A}\psi_{ij}|H|\mathscr{A}\psi_8\rangle}{(E_{ij}-E_7)(E_8-E_7)} - \frac{\langle \mathscr{A}\psi_7|H|\mathscr{A}\psi_8\rangle}{(E_8-E_7)}\right\}\mathscr{A}\psi_8\Big]$$

From the charge-transfer wave functions ψ_{13j} and ψ_{17} we obtain

$$\psi'_{13j} = \left\{1 - \frac{1}{2}\frac{\langle \mathscr{A}\psi_{13j}|H|\mathscr{A}\psi_{17}\rangle^2}{(E_{17}-E_{13j})^2}\right\}\left\{\mathscr{A}\psi_{13j} - \frac{\langle \mathscr{A}\psi_{13j}|H|\mathscr{A}\psi_{17}\rangle}{(E_{17}-E_{13j})}\mathscr{A}\psi_{17}\right\}$$

$$\psi'_{17} = \left\{1 - \frac{1}{2}\sum_{j}\frac{\langle \mathscr{A}\psi_{17}|H|\mathscr{A}\psi_{13j}\rangle^2}{(E_{13j}-E_{17})^2}\right\}\left\{\mathscr{A}\psi_{17} - \sum_{j}\frac{\langle \mathscr{A}\psi_{17}|H|\mathscr{A}\psi_{13j}\rangle}{(E_{13j}-E_{17})}\mathscr{A}\psi_{13j}\right\}$$

The pairs of wave functions (ψ_{14j}, ψ_{18}), (ψ_{15j}, ψ_{19}) and (ψ_{16j}, ψ_{20}) combine in a similar way.

4. Matrix elements of the spin density operator

The spin density obtained from the first order mixing of $\psi'_{13j} \cdots \psi'_{20}$ with ψ'_1 depends on matrix elements of the spin density operator between π and B functions and between A and B functions. In the calculation of proton splittings we may neglect the matrix elements between A and B functions but matrix elements between π and B functions can easily be of importance e.g. for the protons of tert. butyl substituents. Then the matrix elements needed in the first order calculation are:

$$\begin{array}{llll}
\langle \mathscr{A}\psi_1 |\rho| \mathscr{A}\psi_{13j}\rangle = & \langle \underline{\pi}_j^+ |\delta| \underline{B}_S^-\rangle & \langle \mathscr{A}\psi_{4j} |\rho| \mathscr{A}\psi_{19}\rangle = & \sqrt{6}/2 \langle \underline{\pi}_j^+ |\delta| \underline{B}_S^+\rangle \\
\langle \mathscr{A}\psi_1 |\rho| \mathscr{A}\psi_{14j}\rangle = & -1/\sqrt{3} \langle \underline{\pi}_j^+ |\delta| \underline{B}_S^-\rangle & \langle \mathscr{A}\psi_{4j} |\rho| \mathscr{A}\psi_{20}\rangle = & \sqrt{2}/6 \langle \underline{\pi}_j^+ |\delta| \underline{B}_S^+\rangle \\
\langle \mathscr{A}\psi_1 |\rho| \mathscr{A}\psi_{15j}\rangle = & -\langle \underline{\pi}_j^- |\delta| \underline{B}_S^+\rangle & \langle \mathscr{A}\psi_{5j} |\rho| \mathscr{A}\psi_{17}\rangle = & 1/\sqrt{2} \langle \underline{\pi}_j^- |\delta| \underline{B}_S^-\rangle \\
\langle \mathscr{A}\psi_1 |\rho| \mathscr{A}\psi_{16j}\rangle = & -1/\sqrt{3} \langle \underline{\pi}_j^- |\delta| \underline{B}_S^+\rangle & \langle \mathscr{A}\psi_{5j} |\rho| \mathscr{A}\psi_{18}\rangle = & -1/\sqrt{6} \langle \underline{\pi}_j^- |\delta| \underline{B}_S^-\rangle \\
\langle \mathscr{A}\psi_{3j} |\rho| \mathscr{A}\psi_{19}\rangle = & -1/\sqrt{2} \langle \underline{\pi}_j^+ |\delta| \underline{B}_S^+\rangle & \langle \mathscr{A}\psi_{6j} |\rho| \mathscr{A}\psi_{17}\rangle = & \sqrt{6}/2 \langle \underline{\pi}_j^- |\delta| \underline{B}_S^-\rangle \\
\langle \mathscr{A}\psi_{3j} |\rho| \mathscr{A}\psi_{20}\rangle = & 1/\sqrt{6} \langle \underline{\pi}_j^+ |\delta| \underline{B}_S^+\rangle & \langle \mathscr{A}\psi_{6j} |\rho| \mathscr{A}\psi_{18}\rangle = & \sqrt{2}/6 \langle \underline{\pi}_j^- |\delta| \underline{B}_S^-\rangle
\end{array}$$

where $\langle \underline{\pi}_j^+ |\delta| \underline{B}_S^-\rangle = \langle \underline{\pi}_j^+(1) | \delta(\vec{r}_1 - \vec{r}_x) | \underline{B}_S^-(1)\rangle$ etc.

The first order mixing of ψ'_7 and the second order mixing of ψ'_7, $\psi'_{13j} \cdots \psi'_{20}$ leads (among others) to terms dependent on matrix elements between B functions. In terms of spin density matrices the contributions in B are

$$\begin{array}{lcr}
\langle \psi'_1 |\rho| \psi'_7\rangle & : & 1/\sqrt{3}\ \rho^B_{ST}(1,2) \\
\langle \psi'_{13j} |\rho| \psi'_{13j}\rangle ,\ \langle \psi'_{17} |\rho| \psi'_{17}\rangle & : & \rho^B_3(1,2) \\
\langle \psi'_{14j} |\rho| \psi'_{14j}\rangle ,\ \langle \psi'_{18} |\rho| \psi'_{18}\rangle & : & -1/3\ \rho^B_3(1,2) \\
\langle \psi'_{15j} |\rho| \psi'_{15j}\rangle ,\ \langle \psi'_{19} |\rho| \psi'_{19}\rangle & : & \rho^B_1(1,2) \\
\langle \psi'_{16j} |\rho| \psi'_{16j}\rangle ,\ \langle \psi'_{20} |\rho| \psi'_{20}\rangle & : & -1/3\ \rho^B_1(1,2)
\end{array}$$

5. The spin density in B

The first order term obtained from the interaction of ψ'_7 with ψ'_1 can be written down immediately from the general formula 2.30

$$\Delta_T \rho^B(1,2) = \frac{\int \{\rho^{\pi}(1,2) + \rho^A(1,2)\} H \rho^B_{ST}(1,2) d\tau_1 d\tau_2}{\Delta E^T_B} \rho^B_{ST}(1,2) \qquad 2.33$$

in which $\rho^A(1,2)$ is the spin density in A according to 2. 32.

In the calculation of the spin density contributions caused by the introduction of the wave functions $\psi'_{13j}, \ldots \psi'_{20}$ terms of different order in the π-A, π-B and A-B interaction are obtained. Of each type of term only the lowest order contribution will be considered, e. g. terms in $\langle \pi |H| B\rangle \langle B|\rho| \pi\rangle \langle \pi |H| A\rangle^2$ are neglected with respect to terms in $\langle \pi|H|B\rangle\langle B|\rho|\pi\rangle$.
In this approximation the normalization constants of $\psi'_{13j}, \ldots \psi'_{16j}$ can be omitted and the excitation energies $(E'_{13j}-E'_1), \ldots (E'_{16j}-E'_1)$ can be set equal to $(E_{13j}-E_1), \ldots (E_{16j}-E_1)$ respectively. For $\psi'_{17}, \ldots \psi'_{20}$ the normalization constants must be taken into account whereas e. g. for ψ'_{17} the energy becomes

$$E'_{17} = E_{17} - \sum_j \frac{\langle \mathscr{A}\psi_{17}|H|\mathscr{A}\psi_{13j}\rangle^2}{(E_{13j}-E_{17})}$$

The spin density obtained from the first order mixing of $\psi'_{13j} \ldots \psi'_{20}$ with ψ'_1 is

$$\Delta^{(1)}_{CT} \rho^B = -2 \sum_{i=13}^{20} \sum_j \frac{\langle \psi'_1|H|\psi'_{ij}\rangle}{(E'_{ij}-E'_1)} \langle \psi'_{ij}|\rho|\psi'_1\rangle$$

Substitution of the Hamiltonian matrix elements given in table 2. 5 and of the spin density matrix elements given in section D. 4 yields

$$\begin{aligned}\Delta^{(1)}_{CT} \rho^B(1,2) = &- \sum_j \frac{\delta_j}{(I_\pi - E_B + \Delta E^+_j + C_{jB})} \Big\{ \langle \underline{\pi}^+_j|H|\underline{B}^-_S\rangle + \frac{\langle \underline{\pi}^+_j|H|\underline{A}^+_S\rangle\langle \underline{A}^+_S|H|\underline{B}^-_S\rangle}{(I_A - E_B + C_{AB})} \\ &- \frac{\langle \underline{\pi}^+_j|H|\underline{A}^-_S\rangle\langle \underline{A}^-_S|H|\underline{B}^-_S\rangle}{(I_\pi - E_A + \Delta E^+_j + C_{jA})}\Big\} \{\underline{\pi}^+_j(1)\underline{B}^-_S(2) + \underline{B}^-_S(1)\underline{\pi}^+_j(2)\} \\ &+ \sum_j \frac{\delta_j}{(I_B - E_\pi + \Delta E^-_j + C_{Bj})} \Big\{ \langle \underline{\pi}^-_j|H|\underline{B}^+_S\rangle - \frac{\langle \underline{\pi}^-_j|H|\underline{A}^-_S\rangle\langle \underline{A}^-_S|H|\underline{B}^+_S\rangle}{(I_B - E_A + C_{BA})} \quad + \end{aligned}$$

2. 34

$$+\left.\frac{\langle \underline{\pi}_j^- |H| \underline{A}_S^+\rangle\langle \underline{A}_S^+ |H| \underline{B}_S^+\rangle}{(I_A-E_\pi+\Delta E_j^-+C_{Aj})}\right\} \{\underline{\pi}_j^-(1)\underline{B}_S^+(2)+\underline{B}_S^+(1)\underline{\pi}_j^-(2)\}$$

$$-\sum_j \delta_j \frac{\langle \underline{\pi}_j^- |H| \underline{A}_S^+\rangle\langle \underline{A}_S^+ |H| \underline{B}_S^-\rangle}{(I_A-E_B+C_{AB})(I_A-E_\pi+\Delta E_j^-+C_{Aj})} \{\underline{\pi}_j^-(1)\underline{B}_S^-(2)+\underline{B}_S^-(1)\underline{\pi}_j^-(2)\}$$

$$-\sum_j \delta_j \frac{\langle \underline{\pi}_j^+ |H| \underline{A}_S^-\rangle\langle \underline{A}_S^- |H| \underline{B}_S^+\rangle}{(I_B-E_A+C_{BA})(I_\pi-E_A+\Delta E_j^++C_{jA})} \{\underline{\pi}_j^+(1)\underline{B}_S^+(2)+\underline{B}_S^+(1)\underline{\pi}_j^+(2)\}$$

In the same way the second order charge-transfer contribution

$$\Delta_{CT}^{(2)}\,\rho^B(1,2)=\sum_{i=13}^{20}\sum_j \frac{\langle \psi_1' |H| \psi_{ij}'\rangle^2}{(E_{ij}'-E_1')^2}\langle \psi_{ij}'|\rho|\psi_{ij}'\rangle$$

$$+2\sum_{i=13}^{20}\sum_j \frac{\langle \psi_1' |H| \psi_{ij}'\rangle\langle \psi_{ij}' |H| \psi_7'\rangle}{(E_{ij}'-E_1')(E_7'-E_1')}\langle \psi_7'|\rho|\psi_1'\rangle$$

becomes on substitution of the matrix elements

$$\Delta_{CT}^{(2)}\,\rho^B(1,2)=4\left\{-\sum_j \delta_j \frac{\langle \underline{\pi}_j^+ |H| \underline{A}_S^-\rangle\,\langle \underline{A}_T^- |H| \underline{\pi}_j^+\rangle}{(I_\pi-E_A+\Delta E_j^++C_{jA})\Delta E_A^T}+\sum_j \delta_j \frac{\langle \underline{\pi}_j^- |H| \underline{A}_S^+\rangle\,\langle \underline{A}_T^+ |H| \underline{\pi}_j^-\rangle}{(I_A-E_\pi+\Delta E_j^-+C_{Aj})\Delta E_A^T}\right.$$

$$+\left.\frac{1}{2}\frac{\int \rho^\pi(1,2)\,H\,\rho_{ST}^A(1,2)d\tau_1 d\tau_2}{\Delta E_A^T}\right\}\left[-\frac{\langle \underline{B}_S^- |H| \underline{A}_T^+\rangle\,\langle \underline{A}_S^+ |H| \underline{B}_S^-\rangle}{(I_A-E_B+C_{AB})^2}\,\rho_3^B(1,2)\right.$$

$$+\frac{\langle \underline{B}_S^+ |H| \underline{A}_T^-\rangle\langle \underline{A}_S^- |H| \underline{B}_S^+\rangle}{(I_B-E_A+C_{BA})^2}\,\rho_1^B(1,2)+\left\{\frac{\langle \underline{B}_S^- |H| \underline{A}_S^+\rangle\langle \underline{A}_T^+ |H| \underline{B}_T^-\rangle+\langle \underline{B}_T^- |H| \underline{A}_S^+\rangle\langle \underline{A}_T^+ |H| \underline{B}_S^-\rangle}{(I_A-E_B+C_{AB})\Delta E_B^T}\right.$$

$$+\left.\left.\frac{\langle \underline{B}_S^+ |H| \underline{A}_S^-\rangle\langle \underline{A}_T^- |H| \underline{B}_T^+\rangle+\langle \underline{B}_T^+ |H| \underline{A}_S^-\rangle\,\langle \underline{A}_T^- |H| \underline{B}_S^+\rangle}{(I_B-E_A+C_{BA})\Delta E_B^T}\right\}\rho_{ST}^B(1,2)\right]$$

$$-2\frac{\int \rho^\pi(1,2)\,H\,\rho_1^A(1,2)d\tau_1 d\tau_2}{(I_A-E_B+C_{AB})}\left\{\frac{\langle \underline{B}_S^- |H| \underline{A}_S^+\rangle^2}{(I_A-E_B+C_{AB})^2}\,\rho_3^B(1,2)\right.$$

$$\left.-\frac{\langle \underline{B}_S^- |H| \underline{A}_S^+\rangle\,\langle \underline{A}_S^+ |H| \underline{B}_T^-\rangle}{(I_A-E_B+C_{AB})\Delta E_B^T}\,\rho_{ST}^B(1,2)\right\}+$$

$$-2\int\frac{\rho^{\pi}(1,2)\;H\;\rho_3^A(1,2)d\tau_1 d\tau_2}{(I_B-E_A+C_{BA})}\Bigg\{\frac{\langle \underline{B}_S^+|H|\underline{A}_S^-\rangle^2}{(I_B-E_A+C_{BA})^2}\,\rho_1^B(1,2)+\frac{\langle\underline{B}_S^+|H|\underline{A}_S^-\rangle\langle\underline{A}_S^-|H|\underline{B}_T^+\rangle}{(I_B-E_A+C_{BA})\Delta E_B^T}\,\rho_{ST}^B(1,2)\Bigg\}$$

$$+\Bigg[\sum_j\delta_j\Bigg\{\frac{\langle\underline{\pi}_j^+|H|\underline{B}_S^-\rangle}{(I_\pi-E_B+\Delta E_j^++C_{jB})}+\frac{\langle\underline{\pi}_j^+|H|\underline{A}_S^+\rangle\langle\underline{A}_S^+|H|\underline{B}_S^-\rangle}{(I_A-E_B+C_{AB})}\Bigg\{\frac{1}{(I_A-E_B+C_{AB})}+\frac{1}{(I_\pi-E_B+\Delta E_j^++C_{jB})}\Bigg\}$$

$$-\frac{\langle\underline{\pi}_j^+|H|\underline{A}_S^-\rangle\langle\underline{A}_S^-|H|\underline{B}_S^-\rangle}{(I_\pi-E_B+\Delta E_j^++C_{jB})(I_\pi-E_A+\Delta E_j^++C_{jA})}\Bigg\}^2-\sum_j\delta_j\frac{\langle\underline{\pi}_j^+|H|\underline{A}_S^+\rangle^2\langle\underline{A}_S^+|H|\underline{B}_S^-\rangle^2}{(I_A-E_B+C_{AB})^4}$$

$$+2\sum_j\delta_j\frac{\langle\underline{\pi}_j^-|H|\underline{A}_S^+\rangle\langle\underline{A}_S^+|H|\underline{B}_S^-\rangle\langle\underline{B}_S^-|H|\underline{\pi}_j^-\rangle}{(I_A-E_\pi+\Delta E_j^-+C_{Aj})(I_A-E_B+C_{AB})^2}\Bigg]\rho_3^B(1,2) \tag{2.35}$$

$$+\Bigg[\sum_j\delta_j\Bigg\{\frac{\langle\underline{\pi}_j^-|H|\underline{B}_S^+\rangle}{(I_B-E_\pi+\Delta E_j^-+C_{Aj})}-\frac{\langle\underline{\pi}_j^-|H|\underline{A}_S^-\rangle\langle\underline{A}_S^-|H|\underline{B}_S^+\rangle}{(I_B-E_A+C_{BA})}\Bigg\{\frac{1}{(I_B-E_A+C_{BA})}+\frac{1}{(I_B-E_\pi+\Delta E_j^-+C_{Bj})}\Bigg\}$$

$$+\frac{\langle\underline{\pi}_j^-|H|\underline{A}_S^+\rangle\langle\underline{A}_S^+|H|\underline{B}_S^+\rangle}{(I_B-E_\pi+\Delta E_j^-+C_{Bj})(I_A-E_\pi+\Delta E_j^-+C_{Aj})}\Bigg\}^2-\sum_j\delta_j\frac{\langle\underline{\pi}_j^-|H|\underline{A}_S^-\rangle^2\langle\underline{A}_S^-|H|\underline{B}_S^+\rangle^2}{(I_B-E_A+C_{BA})^4}$$

$$-2\sum_j\delta_j\frac{\langle\underline{\pi}_j^+|H|\underline{A}_S^-\rangle\langle\underline{A}_S^-|H|\underline{B}_S^+\rangle\langle\underline{B}_S^+|H|\underline{\pi}_j^+\rangle}{(I_\pi-E_A+\Delta E_j^++C_{jA})(I_B-E_A+C_{BA})^2}\Bigg]\rho_1^B(1,2)$$

$$+\Bigg[-2\sum_j\delta_j\frac{1}{(I_\pi-E_B+\Delta E_j^++C_{jA})\Delta E_B^T}\Bigg\{\langle\underline{\pi}_j^+|H|\underline{B}_S^-\rangle+\frac{\langle\underline{\pi}_j^+|H|\underline{A}_S^+\rangle\langle\underline{A}_S^+|H|\underline{B}_S^-\rangle}{(I_A-E_B+C_{AB})}$$

$$-\frac{\langle\underline{\pi}_j^+|H|\underline{A}_S^-\rangle\langle\underline{A}_S^-|H|\underline{B}_S^-\rangle}{(I_\pi-E_A+\Delta E_j^++C_{jA})}\Bigg\}\Bigg\{\langle\underline{\pi}_j^+|H|\underline{B}_T^-\rangle+\frac{\langle\underline{\pi}_j^+|H|\underline{A}_S^+\rangle\langle\underline{A}_S^+|H|\underline{B}_T^-\rangle}{(I_A-E_B+C_{AB})}-\frac{\langle\underline{\pi}_j^+|H|\underline{A}_S^-\rangle\langle\underline{A}_S^-|H|\underline{B}_T^-\rangle}{(I_\pi-E_A+\Delta E_j^++C_{jA})}\Bigg\}$$

$$-2\sum_j\delta_j\frac{\langle\underline{\pi}_j^-|H|\underline{A}_S^+\rangle\{\langle\underline{A}_S^+|H|\underline{B}_S^-\rangle\langle\underline{B}_T^-|H|\underline{\pi}_j^-\rangle+\langle\underline{A}_S^+|H|\underline{B}_T^-\rangle\langle\underline{B}_S^-|H|\underline{\pi}_j^-\rangle\}}{(I_A-E_B+C_{AB})(I_A-E_\pi+\Delta E_j^-+C_{Aj})\Delta E_B^T}$$

$$+2\sum_j\delta_j\frac{1}{(I_B-E_\pi+\Delta E_j^-+C_{Bj})\Delta E_B^T}\Bigg\{\langle\underline{\pi}_j^-|H|\underline{B}_S^+\rangle-\frac{\langle\underline{\pi}_j^-|H|\underline{A}_S^-\rangle\langle\underline{A}_S^-|H|\underline{B}_S^+\rangle}{(I_B-E_A+C_{BA})}\quad+$$

$$+ \frac{\langle \underline{\pi}_j^- |H| \underline{A}_S^+\rangle\langle \underline{A}_S^+|H|\underline{B}_S^+\rangle}{(I_A - E_\pi + \Delta E_j^- + C_{Aj})}\Big\} \Big\{ \langle \underline{\pi}_j^-|H|\underline{B}_T^+\rangle - \frac{\langle \underline{\pi}_j^- |H| \underline{A}_S^-\rangle\langle \underline{A}_S^-|H|\underline{B}_T^+\rangle}{(I_B - E_A + C_{BA})} + \frac{\langle \underline{\pi}_j^- |H| \underline{A}_S^+\rangle\langle \underline{A}_S^+|H|\underline{B}_T^+\rangle}{(I_A - E_\pi + \Delta E_j^- + C_{Aj})}\Big\}$$

$$- 2 \sum_j \delta_j \frac{\langle \underline{\pi}_j^+ |H| \underline{A}_S^-\rangle\{\langle \underline{A}_S^-|H|\underline{B}_S^+\rangle\langle \underline{B}_T^+|H|\underline{\pi}_j^+\rangle + \langle \underline{A}_S^-|H|\underline{B}_T^+\rangle\langle \underline{B}_S^+|H|\underline{\pi}_j^+\rangle\}}{(I_B - E_A + C_{BA})(I_\pi - E_A + \Delta E_j^+ + C_{jA})\Delta E_B^T}\Big] \rho_{ST}^B(1,2)$$

On combination of 2.33, 2.34 and 2.35 the total spin density in B can be written

$$\rho^B(1,2) = K(1,2) + L(1,2) + M(1,2) + N(1,2) \qquad 2.36$$

K(1,2) is the spin density obtained from the first order mixing of the B triplet state:

$$K(1,2) = \frac{\int\{\rho^\pi(1,2) + \rho^A(1,2)\}\, H\, \rho_{ST}^B(1,2)d\tau_1 d\tau_2}{\Delta E_B^T}\rho_{ST}^B(1,2)$$

L(1,2) is the charge-transfer contribution in the spin density in B caused by the spin density terms in A which are obtained from the first and second order mixing of the A triplet state:

$$L(1,2) =$$

$$2\Big\{ - \sum_j \delta_j \frac{\langle \underline{\pi}_j^+ |H| \underline{A}_S^-\rangle\langle \underline{A}_T^-|H|\underline{\pi}_j^+\rangle}{(I_\pi - E_A + \Delta E_j^+ + C_{jA})\Delta E_A^T} + \sum_j \delta_j \frac{\langle \underline{\pi}_j^- |H| \underline{A}_S^+\rangle\langle \underline{A}_T^+|H|\underline{\pi}_j^-\rangle}{(I_A - E_\pi + \Delta E_j^- + C_{Aj})\Delta E_A^T}$$

$$+ \frac{1}{2}\frac{\int\rho^\pi(1,2)\, H\, \rho_{ST}^A(1,2)d\tau_1 d\tau_2}{\Delta E_A^T}\Big\}\Big[- 2\frac{\langle \underline{B}_S^- |H| \underline{A}_T^+\rangle\langle \underline{A}_S^+|H|\underline{B}_S^-\rangle}{(I_A - E_B + C_{AB})^2}\rho_3^B(1,2)$$

$$+ 2\frac{\langle \underline{B}_S^+ |H| \underline{A}_T^-\rangle\langle \underline{A}_S^-|H|\underline{B}_S^+\rangle}{(I_B - E_A + C_{BA})^2}\rho_1^B(1,2) + \Big\{2\frac{\langle \underline{B}_S^- |H| \underline{A}_S^+\rangle\langle \underline{A}_T^+|H|\underline{B}_T^-\rangle + \langle \underline{B}_T^- |H| \underline{A}_S^+\rangle\langle \underline{A}_T^+|H|\underline{B}_S^-\rangle}{(I_A - E_B + C_{AB})\Delta E_B^T}$$

$$+ 2\frac{\langle \underline{B}_S^+ |H| \underline{A}_S^-\rangle\langle \underline{A}_T^-|H|\underline{B}_T^+\rangle + \langle \underline{B}_T^+ |H| \underline{A}_S^-\rangle\langle \underline{A}_T^-|H|\underline{B}_S^+\rangle}{(I_B - E_A + C_{BA})\Delta E_B^T}\Big\}\rho_{ST}^B(1,2)\Big]$$

M(1,2) is the spin density in B obtained from the energy differences $(E_{17} - E_{18})$

and $(E_{19}-E_{20})$:

$M(1,2)$ =

$$-\frac{\int \rho^{\pi}(1,2)\,H\,\rho_1^{A}(1,2)d\tau_1 d\tau_2}{(I_A-E_B+C_{AB})}\left\{2\,\frac{\langle \underline{B}_S^-|H|\,\underline{A}_S^+\rangle^2}{(I_A-E_B+C_{AB})^2}\,\rho_3^B(1,2)\right.$$

$$\left.-\,2\,\frac{\langle \underline{B}_S^-|H|\,\underline{A}_S^+\rangle\langle \underline{A}_S^+|H|\,\underline{B}_T^-\rangle}{(I_A-E_B+C_{AB})\Delta E_B^T}\,\rho_{ST}^B(1,2)\right\}$$

$$-\frac{\int \rho^{\pi}(1,2)\,H\,\rho_3^{A}(1,2)d\tau_1 d\tau_2}{(I_B-E_A+C_{BA})}\left\{2\,\frac{\langle \underline{B}_S^+|H|\,\underline{A}_S^-\rangle^2}{(I_B-E_A+C_{BA})^2}\,\rho_1^B(1,2)\right.$$

$$\left.+\,2\,\frac{\langle \underline{B}_S^+|H|\,\underline{A}_S^-\rangle\,\langle \underline{A}_S^-|H|\,\underline{B}_T^+\rangle}{(I_B-E_A+C_{BA})\Delta E_B^T}\,\rho_{ST}^B(1,2)\right\}$$

On inspection of the remaining terms it appears that most of them can be obtained from the charge-transfer terms in the formula for a σ-bond A directly coupled to the π-electron system (2. 32) by replacing A by B and

$$\underline{\pi}_j^+ \quad \text{by} \quad \underline{\pi}_j^+ + \frac{\langle \underline{\pi}_j^+|H|\,\underline{A}_S^+\rangle\,\underline{A}_S^+}{(I_A-E_B+C_{AB})} - \frac{\langle \underline{\pi}_j^+|H|\,\underline{A}_S^-\rangle\,\underline{A}_S^-}{(I_{\pi}-E_A+\Delta E_j^++C_{jA})}$$

$$\underline{\pi}_j^- \quad \text{by} \quad \underline{\pi}_j^- - \frac{\langle \underline{\pi}_j^-|H|\,\underline{A}_S^-\rangle\,\underline{A}_S^-}{(I_B-E_A+C_{BA})} + \frac{\langle \underline{\pi}_j^-|H|\,\underline{A}_S^+\rangle\,\underline{A}_S^+}{(I_A-E_{\pi}+\Delta E_j^-+C_{Aj})}$$

We now assume that this substitution in the formula for one σ-bond is a reasonable approximation of term N. In this way a relatively simple formula is obtained which can easily be generalized for systems having a larger number of σ-bonds. The application of formula 2. 36 in the calculation of β-alkyl proton splittings will be discussed in chapter IV.

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CHAPTER III

THE SPIN DENSITY IN THE π-ELECTRON SYSTEM

In chapter II it has been shown that the functions $\underline{\pi}_j^+$ and $\underline{\pi}_j^-$ and the spin density distribution in the π-electron system $\rho^\pi(1,2)$ play an important role in the calculation of the spin density in the σ-bonds of a π-electron radical. In this chapter we shall discuss how $\underline{\pi}_j^+$, $\underline{\pi}_j^-$ and $\rho^\pi(1,2)$ can be obtained from π-electron wave functions which are written as linear combinations of Slater determinants. This will be applied to wave functions obtained from approximation methods within the molecular orbital theory. The relative validity of these methods will be investigated by calculation of the spin density distribution in naphtalene anion and in benzyl.

A. GENERAL FORMULAS

In calculations on π-electron systems the wave functions are usually written as linear combinations of antisymmetrized products of space and spin functions. In this notation the ground state of the N-electron system and the ground and excited states of the (N-1)- and (N+1)-electron system are

$$^{1/2}\psi_0(1..N) = \sum_s c_s^N \mathscr{A}\pi_s(1..N)\chi_s(1..N)$$

$$^{0,1}\psi_j(1..N-1) = \sum_r c_{jr}^{N-1} \mathscr{A}\pi_r(1..N-1)\chi_r(1..N-1)$$

$$^{0,1}\psi_j(1..N+1) = \sum_t c_{jt}^{N+1} \mathscr{A}\pi_t(1..N+1)\chi_t(1..N+1)$$

We assume that the antisymmetrized products in these wave functions are eigenfunctions of the S^2-operator and that π_s, π_r and π_t are symmetric or antisymmetric with respect to the permutations for which the corresponding spin functions are antisymmetric or symmetric respectively. For all other permutations we assume

$$\langle P\pi | R\pi \rangle = \delta_{PR}$$

Then the functions π_μ introduced in chapter II are

$$^{1/2}\pi_\mu(1..N) = \sqrt{\frac{n(1/2,N)\nu_N}{N!}} \sum_s c_s^N \sum_P^{(N)}{}' \delta_P \, P\pi_s(1..N) \langle P\chi_s(1..N) | \chi_\mu(1..N) \rangle$$

$$^{0,1}\pi_{j\mu}(1..N-1) = \sqrt{\frac{n(S,N-1)\nu_{N-1}}{(N-1)!}} \sum_r c_{jr}^{N-1} \sum_P^{(N-1)}{}' \delta_P \, P\pi_r(1..N-1) \langle P\chi_r(1..N-1) | \chi_\mu(1..N-1) \rangle$$

$$^{0,1}\pi_{j\mu}(1..N+1) = \sqrt{\frac{n(S,N+1)\nu_{N+1}}{(N+1)!}} \sum_t c_{jt}^{N+1} \sum_P^{(N+1)}{}' \delta_P \, P\pi_t(1..N+1) \langle P\chi_t(1..N+1) | \chi_\mu(1..N+1) \rangle$$

where ν_N, ν_{N-1} and ν_{N+1} are the number of permutations for which the spin functions are transformed into itself. The N! permutations for N electrons can be divided in groups of ν_N permutations which give an equal term in $\pi_\mu(1..N)$. In the summation over P we consider only one permutation out of each group. This has been denoted by the prime on the summation symbol.
On substitution in 2.9 we obtain for singlet j

$$\underline{\pi}_j^+(N) = \sqrt{\frac{N+3}{4}} \int \pi_{j,1}(1..N-1)\pi_1(1..N) d\tau_1 \dots d\tau_{N-1}$$

$$= \frac{1}{n(0,N-1)} \sqrt{\frac{N+3}{4}} \sum_{\mu=1}^{n} \int \pi_{j\mu}(1..N-1)\pi_\mu(1..N) d\tau_1 \dots d\tau_{N-1}$$

$$= \sqrt{\frac{(N+3)\, n(1/2,N)\nu_{N-1}\nu_N}{4n(0,N-1)\, N!\, (N-1)!}} \sum_{\mu=1}^{n} \sum_r \sum_s c_s^N c_{jr}^{N-1} \sum_P^{(N-1)}{}' \sum_R^{(N)}{}' \delta_P \delta_R$$

$$\times \langle P\chi_r(1..N-1) | \chi_\mu(1..N-1) \rangle \langle \chi_\mu(1..N) | R\chi_s(1..N) \rangle \int P\pi_r(1..N-1)\, R\pi_s(1..N) d\tau_1 \dots d\tau_{N-1}$$

The summation over μ can be removed by substitution of

$$\langle P\chi_r(1..N-1) | \chi_\mu(1..N-1) \rangle = \langle P\chi_r(1..N) | \chi_\mu(1..N) \rangle$$

where $\chi_r(1..N)$ is the doublet spin function obtained from $\chi_r(1..N-1)$ by combination with the spin function for one electron according to the method described in section B. 1 of chapter II. Then the summation over μ becomes an expansion in a complete set of N-electron spin functions. On removal of this set, substitution of $P^{-1}R = Q$ and application of 2. 1 we obtain

$$\underline{\pi}_j^{+}(N) = \sqrt{\frac{\nu_N}{\nu_{N-1}}} \sum_r \sum_s c_s^{N} c_{jr}^{N-1} \sum_Q^{(N)}{}' \delta_Q \langle \chi_r(1..N) | Q\chi_s(1..N) \rangle$$

$$\times \int \pi_r(1..N-1)\, Q\pi_s(1..N) d\tau_1 \ldots d\tau_{N-1}$$

Because of the fact that the numbers of electron-pairs in $\psi(1..N-1)$ and in $\psi(1..N)$ are equal, the wave functions are in general chosen in such a way that $\nu_N = \nu_{N-1}$, hence for singlet j

$$\underline{\pi}_j^{+}(N) = \sum_r \sum_s c_s^{N} c_{jr}^{N-1} \sum_Q^{(N)}{}' \delta_Q \langle \chi_r(1..N) | Q\chi_s(1..N) \rangle \int \pi_r(1..N-1)\, Q\pi_s(1..N) d\tau_1 \ldots d\tau_{N-1} \qquad 3.1a$$

In the same way it can be shown that for triplet j

$$\underline{\pi}_j^{+}(N) = \frac{1}{\sqrt{3}} \sum_r \sum_s c_s^{N} c_{jr}^{N-1} \sum_Q^{(N)}{}' \delta_Q \langle \chi_r(1..N) | Q\chi_s(1..N) \rangle \int \pi_r(1..N-1)\, Q\pi_s(1..N) d\tau_1 .. d\tau_{N-1} \qquad 3.1b$$

In the calculation of $\underline{\pi}_j^{-}$ it must be noted that we have one more electron-pair in $\psi_j(1..N+1)$ than in $\psi(1..N)$, so $\nu_{N+1} = 2\nu_N$. For both singlet and triplet j we obtain

$$\underline{\pi}_j^{-}(N+1) = \sum_t \sum_s c_{jt}^{N+1} c_s^{N} \sum_Q^{(N+1)}{}' \delta_Q \langle \chi_s(1..N+1) | Q\chi_t(1..N+1) \rangle \int \pi_s(1..N)\, Q\pi_t(1..N+1) d\tau_1 .. d\tau_N \qquad 3.2$$

In many calculations the wave functions are written as linear combinations of antisymmetrized products of one-electron functions Φ_k. From these the functions $\underline{\pi}_j^{+}$ can easily be obtained by adding a 'ghost' orbital Φ_x to the (N-1)-electron system in such a way that the total wave function is a doublet (see section B. 1 of chapter II) and calculation of the overlap of this doublet function with $\psi_0(1..N)$.

When $\psi_0(1..N)$, $\psi_j(1..N-1)$ and $\psi_j(1..N+1)$ are expressed in terms of the same set of one-electron functions, then the overlap has the form

$$S_j = \sum_k a_{jk}^{+} \langle \Phi_k | \Phi_x \rangle$$

Equation 3.1 can now be rewritten as

$$\underline{\pi}_j^+ = \sum_k a_{jk}^+ \Phi_k \qquad \text{for singlet j}$$

$$\underline{\pi}_j^+ = \frac{1}{\sqrt{3}} \sum_k a_{jk}^+ \Phi_k \qquad \text{for triplet j} \qquad 3.3$$

$\underline{\pi}_j^-$ is calculated by adding the 'ghost' orbital to $\psi(1..N)$. For both singlet and triplet j equation 3.2 becomes

$$\underline{\pi}_j^- = \frac{1}{\sqrt{2}} \sum_k a_{jk}^- \Phi_k \qquad 3.4$$

The factor $1/\sqrt{2}$ arises from the fact that $\nu_{N+1} = 2\nu_N$.

The spin density distribution $\rho^{\pi}(1,2)$ is calculated from $\underline{\pi}_j^+$ or $\underline{\pi}_j^-$ by application of 2.19 or 2.20 respectively.

These formulas can be used for wave functions obtained from both molecular orbital and valence bond methods. In the following we shall restrict ourselves to molecular orbital methods.

B. APPLICATION IN THE MOLECULAR ORBITAL THEORY

1. The wave functions

We consider a system of an odd number (N) of π-electrons moving over m atomic orbitals f_μ of $2p_z$-type. From the molecular orbitals

$$\Phi_j = \sum_\mu c_{j\mu} f_\mu$$

which are calculated by a Hückel or self consistent field approximation, the ground state wave function is constructed as an antisymmetrized product function (Slater determinant):

$$\psi_0(1..N) = |\Phi_1 \bar{\Phi}_1 \ldots \bar{\Phi}_{a-1} \Phi_a|$$

in which Φ_1 represents $\Phi_1(j)\alpha(j)$

$\bar{\Phi}_1$ represents $\Phi_1(j)\beta(j)$

Φ_a is the singly occupied orbital

The singly excited states are [1]

$$\psi^{A}_{pa}(1..N) = \left|\Phi_1\bar{\Phi}_1 \cdots \Phi_p\bar{\Phi}_a \cdots \bar{\Phi}_{a-1}\Phi_a\right|$$

$$\psi^{B}_{aq}(1..N) = \left|\Phi_1\bar{\Phi}_1 \cdots \bar{\Phi}_{a-1}\Phi_q\right|$$

$$\psi^{C}_{pq}(1..N) = \frac{1}{\sqrt{2}}\left\{\left|\Phi_1\bar{\Phi}_1 \cdots \Phi_p\bar{\Phi}_q \cdots \bar{\Phi}_{a-1}\Phi_a\right| + \left|\Phi_1\bar{\Phi}_1 \cdots \Phi_q\bar{\Phi}_p \cdots \bar{\Phi}_{a-1}\Phi_a\right|\right\}$$

$$\psi^{D}_{pq}(1..N) = \frac{1}{\sqrt{6}}\left\{2\left|\Phi_1\bar{\Phi}_1 \cdots \Phi_p\bar{\Phi}_a \cdots \bar{\Phi}_{a-1}\Phi_q\right| + \left|\Phi_1\bar{\Phi}_1 \cdots \Phi_p\bar{\Phi}_q \cdots \bar{\Phi}_{a-1}\Phi_a\right| - \left|\Phi_1\bar{\Phi}_1 \cdots \Phi_q\bar{\Phi}_p \cdots \bar{\Phi}_{a-1}\Phi_a\right|\right\}$$

where $1 \leqslant p < a$

$a < q \leqslant m$

After inclusion of configuration interaction with the singly excited states, the wave function for the ground state becomes

$$\Psi_0 = c_0\,\psi_0 + \sum_{p=1}^{a-1} c^{A}_{pa}\,\psi^{A}_{pa} + \sum_{q=a+1}^{m} c^{B}_{aq}\,\psi^{B}_{aq} + \sum_{p=1}^{a-1}\sum_{q=a+1}^{m} c^{C}_{pq}\,\psi^{C}_{pq} + \sum_{p=1}^{a-1}\sum_{q=a+1}^{m} c^{D}_{pq}\,\psi^{D}_{pq}$$

In an exact calculation the wave functions in which two or more electrons are excited must also be considered but in practice this is impossible. For large radicals it is even impossible to calculate the mixing of the singly excited states by a diagonalization of the Hamiltonian matrix. E.g. for the radicals we have studied the number of singly excited states varies from 180 for triphenylmethyl until 684 for tri-p-biphenylylmethyl. These numbers are much too large for practical calculations. Therefore, Ψ_0 is usually calculated by a first order approximation:

$$\Psi_0 = \psi_0 - \sum_j \frac{\langle\psi_0|H|\psi_j\rangle}{(E_j - E_0)}\,\psi_j$$

The matrix elements in this expression are

$$\langle\psi_0|H|\psi^A_{pa}\rangle = h_{pa} + G_{pa} + \langle pa\|aa\rangle$$

$$\langle\psi_0|H|\psi^B_{aq}\rangle = h_{aq} + G_{aq}$$

$$\langle\psi_0|H|\psi^C_{pq}\rangle = \sqrt{2}\{h_{pq} + G_{pq} + \langle pa\|qa\rangle - 1/2\langle pa\|aq\rangle\}$$

$$\langle\psi_0|H|\psi^D_{pq}\rangle = \sqrt{6}/2\,\langle pa\|aq\rangle$$

where h is the operator for the kinetic energy and the interaction with the core (nuclei and σ-electrons),

$$\langle pa\|aq\rangle = \int\Phi_p(1)\Phi_a(2)\,\frac{1}{r_{12}}\,\Phi_a(1)\Phi_q(2)\,d\tau_1 d\tau_2$$

$$G_{pq} = \sum_{j=1}^{a-1}\{2\langle jp\|jq\rangle - \langle jp\|qj\rangle\}$$

On substitution ψ_0 becomes

$$\psi_0 = \psi_0 - \sum_{p=1}^{a-1}\frac{\{h_{pa} + G_{pa} + \langle pa\|aa\rangle\}}{(E^A_{pa} - E_0)}\psi^A_{pa} - \sum_{q=a+1}^{m}\frac{\{h_{aq} + G_{aq}\}}{(E^B_{aq} - E_0)}\psi^B_{aq}$$

$$- \sum_{p=1}^{a-1}\sum_{q=a+1}^{m}\frac{\sqrt{2}\{h_{pq} + G_{pq} + \langle pa\|qa\rangle - 1/2\langle pa\|aq\rangle\}}{(E^C_{pq} - E_0)}\psi^C_{pq} - \sum_{p=1}^{a-1}\sum_{q=a+1}^{m}\frac{\sqrt{6}\langle pa\|aq\rangle}{2(E^D_{pq} - E_0)}\psi^D_{pq} \qquad 3.5$$

The further evaluation of this wave function depends on the method which has been used for the calculation of the molecular orbitals. For radicals different types of self consistent field operators have been proposed in the literature: Molecular orbitals calculated according to Longuet-Higgins and Pople's method [1] satisfy the condition

$$h_{ij} + G_{ij} + \frac{1}{2}\{2\langle ai\|aj\rangle - \langle ai\|ja\rangle\} = 0 \qquad \text{for } i \neq j$$

so, the matrix elements become

$$\langle\psi_0|H|\psi^A_{pa}\rangle = \langle pa\|aa\rangle$$

$$\langle\psi_0|H|\psi^B_{aq}\rangle = -\langle aa\|aq\rangle$$

$$\langle\psi_0|H|\psi^C_{pq}\rangle = 0$$

$$\langle\psi_0|H|\psi^D_{pq}\rangle = \frac{\sqrt{6}}{2}\langle pa\|aq\rangle$$

If Roothaan's method [2] is used, then

$$\langle\psi_0|H|\psi^A_{pa}\rangle = \langle\psi_0|H|\psi^B_{aq}\rangle = \langle\psi_0|H|\psi^C_{pq}\rangle = 0$$

$$\langle\psi_0|H|\psi^D_{pq}\rangle = \frac{\sqrt{6}}{2}\langle pa\|aq\rangle$$

For calculations on positive and negative radical-ions it may be advantageous to use the self consistent field orbitals for the neutral molecule. In this case we have the conditions

$h_{ij} + G_{ij} + 2\langle ia\|ja\rangle - \langle ia\|aj\rangle = 0$ for positive ions

$h_{ij} + G_{ij} = 0$ for negative ions

from which the formulas for the matrix elements are easily obtained.

2. The calculation of the spin density distribution

The functions $\underline{\pi}_j^+$ and $\underline{\pi}_j^-$

The functions $\underline{\pi}_j^+$ and $\underline{\pi}_j^-$ are defined as integrals of products of the exact wave functions for the (N-1)-, N- and (N+1)-electron systems. However, the exact wave functions can not be calculated. When the wave function for the N-electron system is obtained from a Hückel-approximation, then it is reasonable to use the same method in the calculation of the wave functions for the (N-1)- and (N+1)-electron system. In our calculation of the wave function for the N-electron system we use first order configuration interaction. In this case the choice of the wave functions for the (N-1)- and (N+1)-electron system is less obvious. We shall assume that a good approximation of the functions $\underline{\pi}_j^+$ and $\underline{\pi}_j^-$ is obtained when both $\psi_j(1..N-1)$, $\psi_0(1..N)$ and $\psi_j(1..N+1)$ are calculated with first order configuration interaction starting with a common set of molecular orbitals.

In order to illustrate the calculation of $\underline{\pi}_j^+$ and $\underline{\pi}_j^-$ we consider the wave function for the ground state of the (N-1)-electron system before configuration interaction:

$$|\Phi_1\bar{\Phi}_1\ldots\Phi_{a-1}\bar{\Phi}_{a-1}|$$

Combination with a 'ghost' orbital Φ_x according to the method discussed in section A.1 of chapter II yields

$$\left|\Phi_1\bar{\Phi}_1 \cdots \Phi_{a-1}\bar{\Phi}_{a-1}\Phi_x\right|$$

The overlap of this function with $\psi_0(1..N)$ is

$$\langle \Phi_a | \Phi_x \rangle - \sum_{q=a+1}^{m} \frac{\{h_{aq} + G_{aq}\}}{(E^B_{aq} - E_0)} \langle \Phi_q | \Phi_x \rangle$$

so, according to 3.3, $\underline{\pi}_0^+$ becomes on neglect of configuration interaction in the (N-1)-electron system

$$\underline{\pi}_0^+ = \Phi_a - \sum_{q=a+1}^{m} \frac{\{h_{aq} + G_{aq}\}}{(E^B_{aq} - E_0)} \Phi_q \qquad 3.6$$

In the same way we can obtain functions $\underline{\pi}_{pa}^+$ from the $\Phi_p \rightarrow \Phi_a$ singlet and triplet excited states of the (N-1)-electron system. The contribution of other excited states in the spin density appears to be negligible in a first order approximation. The functions $\underline{\pi}_0^-$ and $\underline{\pi}_{aq}^-$ are obtained in a similar way by adding the 'ghost' orbital to $\psi_0(1..N)$.

Inclusion of configuration interaction in the (N-1)- and (N+1)-electron systems leads to a mixing of these functions. This mixing can easily be calculated from the well-known formulas for the matrix elements for a closed-shell system [3]. In order to simplify the calculations, we shall neglect the influence of the charge in the σ-bond. Then the functions $\underline{\pi}_j^-$ after first order configuration interaction become

$$\underline{\pi}_0^- = \Phi_a + \sum_{p=1}^{a-1} \frac{\{h_{pa} + G_{pa} + \langle pa \Vert aa \rangle\}}{(E^A_{pa} - E_0)} \Phi_p - \sum_{q=a+1}^{m} \frac{\{h_{aq} + G_{aq} + \langle qa \Vert aa \rangle\}}{(E^S_{aq} - E_0^-)} \Phi_q$$

$$\underline{\pi}_{aq}^- = \frac{1}{\sqrt{2}} \Phi_q - \frac{1}{\sqrt{2}} \left[\frac{\{h_{aq} + G_{aq}\}}{(E^B_{aq} - E_0)} - \frac{2\{h_{aq} + G_{aq} + \langle qa \Vert aa \rangle\}}{(E^S_{aq} - E_0^-)} \right] \Phi_a$$

$$+ \frac{1}{\sqrt{2}} \sum_{p=1}^{a-1} \frac{\{h_{pq} + G_{pq} + \langle pa \Vert qa \rangle - 1/2 \langle pa \Vert aq \rangle\}}{(E^C_{pq} - E_0)} \Phi_p + \frac{3\sqrt{2}}{4} \sum_{p=1}^{a-1} \frac{\langle pa \Vert aq \rangle}{(E^D_{pq} - E_0)} \Phi_p + \qquad 3.7$$

$$-\frac{1}{\sqrt{2}}\sum_{\substack{s=a+1\\ s\neq q}}^{m}\frac{\{h_{qs}+G_{qs}+\langle qa\|sa\rangle+\langle qa\|as\rangle\}}{(E^{S}_{as}-E^{S}_{aq})}\Phi_s \qquad \text{for singlet } \Phi_a \rightarrow \Phi_q$$

$$\pi^{-}_{aq}=\frac{1}{\sqrt{2}}\Phi_q+\frac{1}{\sqrt{2}}\frac{\{h_{aq}+G_{aq}\}}{(E^{B}_{aq}-E_0)}\Phi_a+\frac{1}{\sqrt{2}}\sum_{p=1}^{a-1}\frac{\{h_{pq}+G_{pq}+\langle pa\|qa\rangle-1/2\langle pa\|aq\rangle\}}{(E^{C}_{pq}-E_0)}\Phi_p$$

$$-\frac{\sqrt{2}}{4}\sum_{p=1}^{a-1}\frac{\langle pa\|aq\rangle}{(E^{D}_{pq}-E_0)}\Phi_p-\frac{1}{\sqrt{2}}\sum_{\substack{s=a+1\\ s\neq q}}^{m}\frac{\{h_{qs}+G_{qs}+\langle qa\|sa\rangle-\langle qa\|as\rangle\}}{(E^{T}_{as}-E^{T}_{aq})}\Phi_s$$

$$\text{for triplet } \Phi_a \rightarrow \Phi_q$$

where E_0^{-}, E^{S}_{aq} and E^{T}_{aq} are the energies of the ground state and the $\Phi_a \rightarrow \Phi_q$ singlet and triplet excited states of the (N+1)-electron system.

For the functions π^{+}_{j} similar formulas can be derived.

The spin density distribution $\rho^{\pi}(1,2)$

By application of 2.19 or 2.20, $\rho^{\pi}(1,2)$ appears to be

$$\rho^{\pi}(1,2)=\Phi_a(1)\Phi_a(2)+2\sum_{p=1}^{a-1}\frac{\{h_{pa}+G_{pa}+\langle pa\|aa\rangle\}}{(E^{A}_{pa}-E_0)}\frac{1}{2}\{\Phi_a(1)\Phi_p(2)+\Phi_p(1)\Phi_a(2)\}$$

$$-2\sum_{q=a+1}^{m}\frac{\{h_{aq}+G_{aq}\}}{(E^{B}_{aq}-E_0)}\frac{1}{2}\{\Phi_a(1)\Phi_q(2)+\Phi_q(1)\Phi_a(2)\} \qquad 3.8$$

$$+2\sum_{p=1}^{a-1}\sum_{q=a+1}^{m}\frac{\langle pa\|aq\rangle}{(E^{D}_{pq}-E_0)}\frac{1}{2}\{\Phi_p(1)\Phi_q(2)+\Phi_q(1)\Phi_p(2)\}$$

Usually $\rho^{\pi}(1,2)$ is written in terms of an atomic orbital spin density matrix:

$$\rho^{\pi}(1,2)=\sum_{\alpha}\rho^{\pi}_{\alpha\alpha}f_{\alpha}(1)f_{\alpha}(2)+\sum_{(\alpha\beta)}\rho^{\pi}_{\alpha\beta}\{f_{\alpha}(1)f_{\beta}(2)+f_{\beta}(1)f_{\alpha}(2)\}$$

where $\rho^{\pi}_{\alpha\alpha}$, the spin density in atomic orbital f_{α}, is

$$\rho^{\pi}_{\alpha\alpha} = c^2_{a\alpha} + 2 \sum_{p=1}^{a-1} \frac{\{h_{pa} + G_{pa} + \langle pa\|aa\rangle\}}{(E^A_{pa} - E_0)} c_{a\alpha} c_{p\alpha} - 2 \sum_{q=a+1}^{m} \frac{\{h_{aq} + G_{aq}\}}{(E^B_{aq} - E_0)} c_{a\alpha} c_{q\alpha}$$

$$+ 2 \sum_{p=1}^{a-1} \sum_{q=a+1}^{m} \frac{\langle pa\|aq\rangle}{(E^D_{pq} - E_0)} c_{p\alpha} c_{q\alpha} \qquad 3.9$$

This formula for $\rho^{\pi}_{\alpha\alpha}$ has first been derived by Hoytink [4].

$\rho^{\pi}_{\alpha\beta}$ might be called the overlap (or bond) spin density

$$\rho^{\pi}_{\alpha\beta} = c_{a\alpha} c_{a\beta} + 2 \sum_{p=1}^{a-1} \frac{\{h_{pa} + G_{pa} + \langle pa\|aa\rangle\}}{(E^A_{pa} - E_0)} \frac{1}{2} \{c_{a\alpha} c_{p\beta} + c_{p\alpha} c_{a\beta}\} - 2 \sum_{q=a+1}^{m} \frac{\{h_{aq} + G_{aq}\}}{(E^B_{aq} - E_0)}$$

$$\times \frac{1}{2} \{c_{a\alpha} c_{q\beta} + c_{q\alpha} c_{a\beta}\} + 2 \sum_{p=1}^{a-1} \sum_{q=a+1}^{m} \frac{\langle pa\|aq\rangle}{(E^D_{pq} - E_0)} \frac{1}{2} \{c_{p\alpha} c_{q\beta} + c_{q\alpha} c_{p\beta}\} \qquad 3.10$$

3. Approximate expressions for the spin density distribution

For molecular orbitals calculated according to Longuet-Higgins and Pople's method [1] equation 3.9 becomes

$$\rho^{\pi}_{\alpha\alpha} = c^2_{a\alpha} + \sum_{p=1}^{a-1} \frac{\langle pa\|aa\rangle}{(E^A_{pa} - E_0)} c_{a\alpha} c_{p\alpha} + \sum_{q=a+1}^{m} \frac{\langle qa\|aa\rangle}{(E^B_{aq} - E_0)} c_{a\alpha} c_{q\alpha}$$

$$+ 2 \sum_{p=1}^{a-1} \sum_{q=a+1}^{m} \frac{\langle pa\|aq\rangle}{(E^D_{pq} - E_0)} c_{p\alpha} c_{q\alpha} \qquad 3.11$$

From 3.10 a similar expression for the overlap spin densities can be derived. On neglect of differential overlap and replacement of the excitation energies by the differences in orbital energy, $\rho^{\pi}_{\alpha\alpha}$ and $\rho^{\pi}_{\alpha\beta}$ become

$$\rho^{\pi}_{\alpha\alpha} = c^2_{a\alpha} - \frac{1}{2} \sum_{\mu} \pi_{\alpha\mu} \gamma_{\mu\mu} c^2_{a\mu} - \frac{1}{2} \sum_{(\mu\nu)} \pi_{\alpha,\mu\nu} \gamma_{\mu\nu} c_{a\mu} c_{a\nu}$$

$$\rho^{\pi}_{\alpha\beta} = c_{a\alpha} c_{a\beta} - \frac{1}{2} \sum_{\mu} \pi_{\alpha\beta,\mu} \gamma_{\mu\mu} c^2_{a\mu} - \frac{1}{2} \sum_{(\mu\nu)} \pi_{\alpha\beta,\mu\nu} \gamma_{\mu\nu} c_{a\mu} c_{a\nu} \qquad 3.12$$

where $\gamma_{\mu\nu} = \langle\mu\nu\|\mu\nu\rangle$. $\pi_{\alpha\mu}$, $\pi_{\alpha,\mu\nu}$, $\pi_{\alpha\beta,\mu}$ and $\pi_{\alpha\beta,\mu\nu}$ are quantities introduced by Coulson and Longuet-Higgins [5, 6]. For systems of an odd number of electrons they are defined by

$$\pi_{\alpha\mu} = -4 \sum_{j=1}^{a-1} \sum_{k=a+1}^{m} \frac{c_{j\alpha}c_{k\alpha}c_{j\mu}c_{k\mu}}{(\epsilon_k-\epsilon_j)} - 2 \sum_{j=1}^{a-1} \frac{c_{j\alpha}c_{a\alpha}c_{j\mu}c_{a\mu}}{(\epsilon_a-\epsilon_j)}$$

$$-2 \sum_{k=a+1}^{m} \frac{c_{k\alpha}c_{a\alpha}c_{k\mu}c_{a\mu}}{(\epsilon_k-\epsilon_a)} \qquad \text{(atom-atom polarizability)} \quad 3.13a$$

$$\pi_{\alpha,\mu\nu} = -4 \sum_{j=1}^{a-1} \sum_{k=a+1}^{m} \frac{c_{k\alpha}c_{j\alpha}\{c_{j\mu}c_{k\nu}+c_{k\mu}c_{j\nu}\}}{(\epsilon_k-\epsilon_j)} - 2 \sum_{j=1}^{a-1} \frac{c_{a\alpha}c_{j\alpha}\{c_{j\mu}c_{a\nu}+c_{a\mu}c_{j\nu}\}}{(\epsilon_a-\epsilon_j)}$$

$$-2 \sum_{k=a+1}^{m} \frac{c_{a\alpha}c_{k\alpha}\{c_{k\mu}c_{a\nu}+c_{a\mu}c_{k\nu}\}}{(\epsilon_k-\epsilon_a)} \qquad \text{(atom-bond polarizability)} \quad 3.13b$$

$$\pi_{\alpha\beta,\mu} = \frac{1}{2}\pi_{\mu,\alpha\beta} \qquad \text{(bond-atom polarizability)} \quad 3.13c$$

$$\pi_{\alpha\beta,\mu\nu} = -2 \sum_{j=1}^{a-1} \sum_{k=a+1}^{m} \frac{\{c_{j\alpha}c_{k\beta}+c_{k\alpha}c_{j\beta}\}\{c_{j\mu}c_{k\nu}+c_{k\mu}c_{j\nu}\}}{(\epsilon_k-\epsilon_j)} \qquad 3.13d$$

$$- \sum_{j=1}^{a-1} \frac{\{c_{j\alpha}c_{a\beta}+c_{a\alpha}c_{j\beta}\}\{c_{j\mu}c_{a\nu}+c_{a\mu}c_{j\nu}\}}{(\epsilon_a-\epsilon_j)} - \sum_{k=a+1}^{m} \frac{\{c_{k\alpha}c_{a\beta}+c_{a\alpha}c_{k\beta}\}\{c_{k\mu}c_{a\nu}+c_{a\mu}c_{k\nu}\}}{(\epsilon_k-\epsilon_a)}$$

$$\text{(bond-bond polarizability)}$$

For molecular orbitals calculated according to Roothaan's method [2], the second and third term of 3.11 have to be omitted. It is then also possible to use 3.12 provided the polarizabilities are defined by the first term of 3.13 only.

For calculations of the spin density distribution in radical-ions from the self consistent field orbitals of the neutral molecule the polarizabilities of the neutral molecule have to be substituted in 3.12. These can be obtained from 3.13 by considering the first term only and taking j to be the orbitals which are occupied in the neutral molecule and k to be the unoccupied orbitals.

It can easily be shown that for alternant hydrocarbons $\pi_{\alpha,\mu\nu} = 0$ if μ and ν

do not belong to the same set. The contribution of the third term in $\rho^{\pi}_{\alpha\alpha}$ will therefore be small and is usually neglected. The value of $\rho^{\pi}_{\alpha\beta}$ is especially important for α and β nearest neighbours. In this case the second term vanishes; the third term will be considered for μ and ν nearest neighbours only. Assuming $\gamma_{\mu\mu}$ and $\gamma_{\mu\nu}$ to be independent of μ and ν and introducing

$$\lambda_1 = -\frac{1}{2}\,\frac{\gamma_{\mu\mu}}{\beta}$$

$$\lambda_2 = -\frac{1}{2}\,\frac{\gamma_{\mu\nu}}{\beta}$$

we obtain from 3.12

$$\rho^{\pi}_{\alpha\alpha} = c^2_{a\alpha} + \lambda_1 \sum_{\mu} \pi_{\alpha\mu}\, c^2_{a\mu}$$

$$\rho^{\pi}_{\alpha\beta} = c_{a\alpha}\, c_{a\beta} + \lambda_2 \sum_{(\mu\nu)} \pi_{\alpha\beta,\mu\nu}\, c_{a\mu}\, c_{a\nu} \qquad 3.14$$

where $\pi_{\alpha\mu}$ and $\pi_{\alpha\beta,\mu\nu}$ are expressed in units $1/\beta$.

The formula for $\rho^{\pi}_{\alpha\alpha}$ has first been derived by McLachlan [7] from an approximated unrestricted Hartree-Fock wave function.

It is usually assumed that these formulas can also be used for Hückel-orbitals. In these calculations the Hückel-orbitals must be regarded as an approximation of self consistent field orbitals according to Longuet-Higgins and Pople for neutral radicals and as an approximation of the self consistent field orbitals for the neutral molecule in the case of radical-ions.

According to the pairing principle [8] simple relations must exist between the spin densities in positive and negative ions of alternant hydrocarbons. From the pairing properties of the molecular orbitals it can easily be shown that

$$(\rho^{\pi}_{\alpha\alpha})_{\text{positive ion}} = (\rho^{\pi}_{\alpha\alpha})_{\text{negative ion}}$$

$$(\rho^{\pi}_{\alpha\beta})_{\text{positive ion}} = -(\rho^{\pi}_{\alpha\beta})_{\text{negative ion}} \qquad 3.15$$

whereas for neutral alternant radicals

$$\rho^{\pi}_{\alpha\beta} = 0 \qquad 3.16$$

For the functions π_j^+ and π_j^- an approximation similar to 3.14 can be used. In chapter II it has been shown that in the spin density in the σ-bonds these functions appear in terms of the type

$$\sum_j \frac{\ldots|\pi_j\rangle\langle\pi_j|\ldots}{\ldots+\Delta E_j+\ldots}$$

In the approximations used above the singlet and triplet excitation energies for an excitation $\Phi_a \to \Phi_q$ in the (N+1)-electron system can be written $\epsilon_q - \epsilon_a$ and $\epsilon_q - \epsilon_a - 2\langle qa\|aq\rangle$ respectively. After substitution the terms for corresponding singlets and triplets can be added together. Then a formula is obtained in which the same approximation for the exchange integrals can be introduced as has been used in 3.14. This has been applied for the calculations of α-alkyl proton splittings in chapter IV.

C. COMPARISON OF SOME APPROXIMATION METHODS

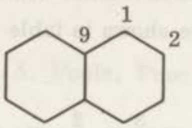
In order to investigate the reliability of the simplified formulas 3.14, we have calculated the values of $\rho^{\pi}_{\alpha\alpha}$ for naphtalene anion and benzyl according to several approximation methods.

Naphtalene anion

The spin density in naphtalene anion (which, in our approximation, is equal to the one in the cation) has been calculated according to the following methods:

1. Configuration interaction with all singly excited states starting with the self consistent field orbitals of the neutral molecule.
2. In a second calculation we have included the doubly excited states which, in terms of differences in orbital energy, have the same excitation energy as one of the singly excited states.
3. First order configuration interaction starting with the self consistent field orbitals for the neutral molecule (equation 3.9).
4. McLachlan's formula 3.14 applied to Hückel-orbitals. The constant λ_1 has been given the usual value of 1.2.
5. Hückel approximation without configuration interaction.

The resulting spin densities are collected in table 3.1.



	1	2	3	4	5
ρ^{π}_{11}	0.232	0.232	0.222	0.229	0.181
ρ^{π}_{22}	0.040	0.041	0.049	0.043	0.069
ρ^{π}_{99}	-0.045	-0.044	-0.041	-0.044	0

Table 3.1. Calculated spin densities in naphtalene anion

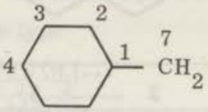
From previously published calculations it appears that for ions of alternant hydrocarbons the spin densities calculated according to McLachlan's formula are in very good agreement with the ones obtained from first order configuration interaction. From our results it seems quite reasonable to assume that McLachlan's formula is also a good approximation of a calculation in which configuration interaction is taken into account by diagonalization of the Hamiltonian matrix. It is not quite clear if this will also be true for non-alternant hydrocarbons. It is usually assumed that in this case McLachlan's formula is less correct but calculations on fluoranthene and acenaphtalene according to McLachlan's formula or with first order configuration interaction do not give largely different results (see references 7 and 9).

Benzyl

The spin density in benzyl has been calculated from self consistent field orbitals obtained according to Roothaan's method and from Hückel-orbitals in the following approximations:

1. Configuration interaction with all singly excited states starting with self consistent field orbitals.
2. First order configuration interaction starting with self consistent field orbitals.
3. McLachlan's formula applied to self consistent field orbitals (see text after equation 3.13).

4. Mc Lachlan's formula applied to Hückel-orbitals.
The resulting spin densities are shown in table 3.2.



	1	2	3	4
ρ^{π}_{11}	-0.101	-0.092	-0.096	-0.123
ρ^{π}_{22}	0.183	0.123	0.121	0.164
ρ^{π}_{33}	-0.065	-0.039	-0.031	-0.075
ρ^{π}_{44}	0.160	0.084	0.077	0.137
ρ^{π}_{77}	0.706	0.848	0.842	0.810

Table 3.2. Calculated spin densities in benzyl

From the spin densities given in table 3.2 (which are in good agreement with values given by Carrington and Smith [10]) it appears that Mc Lachlan's formula applied to self consistent field orbitals, calculated according to Roothaan, is in good agreement with first order configuration interaction. In this case, however, the agreement with the complete calculation is much less satisfactory. In fact, Mc Lachlan's formula applied to Hückel-orbitals is a much better approximation of the complete calculation. As Hückel-orbitals can be regarded as an approximation of self consistent field orbitals according to Longuet-Higgins and Pople, this could mean that these orbitals are superior to the ones obtained according to Roothaan's method.

From the calculations on naphtalene anion and on benzyl we may conclude that for ions of alternant hydrocarbons and for neutral alternant radicals equation 3.14 applied to Hückel-orbitals is a good approximation of spin densities obtained from configuration interaction methods. This formula will therefore be used in all further calculations.

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CHAPTER IV

THE CALCULATION OF PROTON SPLITTINGS

In chapter II formulas have been derived for the spin density in the σ-bonds of a π-electron radical. In this chapter we shall discuss the application of these formulas in the calculation of the splitting constants of protons in the nodal plane of the π-electron system and of α- and β-protons of alkyl substituents.

A. THE WAVE FUNCTIONS FOR THE σ-BONDS

1. General formulas

As in many theoretical discussions we assume that σ-bonds can be described in a sufficiently accurate way with wave functions which are calculated in a basis of two atomic orbitals. Then, molecular orbitals can be chosen such that the best wave functions for the one- and three-electron systems consist of one Slater determinant. In general, the sets of molecular orbitals for the one- and three-electron systems are different e.g. by differences in the coefficients of the atomic orbitals and by differences in the effective nuclear charges for the atomic orbitals. Writing the bonding and antibonding orbitals Φ_{σ_1}, $\Phi^*_{\sigma_1}$ and Φ_{σ_3}, $\Phi^*_{\sigma_3}$ for the one- and three-electron system respectively, we obtain from the formulas given in section III.A for the functions introduced in chapter II

$$\sigma(1) = \Phi_{\sigma_1}(1) \qquad 4.1$$

$$\sigma_1(1,2,3) = \sqrt{\frac{2}{3}}\,\{\Phi_{\sigma_3}(1)\Phi_{\sigma_3}(2)\Phi^*_{\sigma_3}(3) - \frac{1}{2}\Phi_{\sigma_3}(1)\Phi^*_{\sigma_3}(2)\Phi_{\sigma_3}(3) - \frac{1}{2}\Phi^*_{\sigma_3}(1)\Phi_{\sigma_3}(2)\Phi_{\sigma_3}(3)\} \qquad 4.2$$

$$\sigma_2(1,2,3) = \frac{1}{\sqrt{2}}\,\{\Phi^*_{\sigma_3}(1)\Phi_{\sigma_3}(2)\Phi_{\sigma_3}(3) - \Phi_{\sigma_3}(1)\Phi^*_{\sigma_3}(2)\Phi_{\sigma_3}(3)\}$$

The singlet ground state wave function for the two-electron system is a linear combination of the three possible singlet functions

$$^0\sigma(1,2) = \mu\,\Phi_{\sigma_2}(1)\Phi_{\sigma_2}(2) + \frac{\lambda}{\sqrt{2}}\{\Phi_{\sigma_2}(1)\Phi^*_{\sigma_2}(2) + \Phi^*_{\sigma_2}(1)\Phi_{\sigma_2}(2)\} + \nu\,\Phi^*_{\sigma_2}(1)\Phi^*_{\sigma_2}(2) \qquad 4.3$$

In addition there is only one possible triplet function

$$^1\sigma(1,2) = \frac{1}{\sqrt{2}}\{\Phi_{\sigma_{2'}}(1)\Phi^*_{\sigma_{2'}}(2) - \Phi^*_{\sigma_{2'}}(1)\Phi_{\sigma_{2'}}(2)\} \qquad 4.4$$

The molecular orbitals for the singlet and triplet functions may be different, e.g. by differences in the effective nuclear charges for the atomic orbitals.

In a molecular orbital approximation without configuration interaction the coefficients in 4.3 are μ=1, $\lambda = \nu$=0 whereas, when the coefficients of the atomic orbitals in Φ_σ are equal, the covalent valence bond wave function can be obtained by substitution of

$$\mu = -\nu = \frac{1}{\sqrt{2}}, \qquad \lambda = 0$$

if the overlap is neglected and substitution of

$$\mu = \frac{(1+S)}{\sqrt{(2+2S^2)}}, \qquad \nu = -\frac{(1-S)}{\sqrt{(2+2S^2)}}, \qquad \lambda = 0$$

if the overlap is included.

It is always possible to choose molecular orbitals in such a way that $\lambda = 0$ in the exact wave function for the ground state. For a symmetric σ-bond the

coefficients of the atomic orbitals in these molecular orbitals are equal to the coefficients in the molecular orbitals for the one- and three-electron system. For bonds having a small polarity, as is usually assumed to be the case for all normal σ-bonds, it seems quite reasonable to suppose that the coefficients in the molecular orbitals for the one- and three-electron system can be set equal to the coefficients in the molecular orbitals for the two-electron system for which $\lambda = 0$. Because this assumption greatly simplifies the calculations, we shall use this approximation in most applications.
If we assume the molecular orbitals in 4.1 until 4.4 to be identical, then we obtain on substitution in 2.11, 2.12, 2.16 and 2.18

$$\underline{\sigma}_S^{+} = \mu\,\Phi_\sigma + \frac{\lambda}{\sqrt{2}}\,\Phi^*_\sigma \qquad \underline{\sigma}_S^{-} = \mu\,\Phi^*_\sigma - \frac{\lambda}{\sqrt{2}}\,\Phi_\sigma$$

$$\underline{\sigma}_T^{+} = \frac{1}{\sqrt{2}}\,\Phi^*_\sigma \qquad \underline{\sigma}_T^{-} = -\frac{1}{\sqrt{2}}\,\Phi_\sigma \tag{4.5}$$

$$\rho_1^{\sigma}(1,2) = \Phi_\sigma(1)\Phi_\sigma(2)$$

$$\rho_3^{\sigma}(1,2) = \Phi^*_\sigma(1)\Phi^*_\sigma(2) \tag{4.6}$$

$$\rho_{ST}^{\sigma}(1,2) = \frac{(\nu-\mu)}{\sqrt{2}}\left\{\Phi_\sigma(1)\Phi^*_\sigma(2) + \Phi^*_\sigma(1)\Phi_\sigma(2)\right\} + \lambda\left\{\Phi_\sigma(1)\Phi_\sigma(2) - \Phi^*_\sigma(1)\Phi^*_\sigma(2)\right\}$$

where $\lambda = 0$ in most applications.

When we assume that the molecular orbitals for the one-, two- and three-electron systems are different because of differences in the effective nuclear charges for the atomic orbitals, then the factors μ, λ and ν in 4.5 and 4.6 must be multiplied by overlap integrals such as $\langle \Phi_{\sigma_1} | \Phi_{\sigma_2} \rangle$. In practice, however, these integrals can be set equal to 1. The error introduced in this way is very small, e.g. the overlap integral between hydrogen 1s-orbitals with effective nuclear charges of 1.0 and 1.2 is 0.98.

2. The influence of a change in the π-electron system

In section C.1 of chapter II it has been remarked that the wave functions for the σ-bonds are assumed to be calculated in the presence of the π-electron system (and, of course, of all other σ-bonds). Therefore the wave functions for the σ-bonds are dependent on the charge and spin density distribution in the π-electron system according to equations 2.26 and 2.27. In the following we shall calculate the influence of a change $\Delta Q^{\pi}(1,2)$ and $\Delta\rho^{\pi}(1,2)$ on the wave functions for the σ-bonds with first order perturbation theory. In this calculation we assume that the atomic orbitals in the perturbed and unperturbed wave functions are identical. The molecular orbitals are chosen such that $\lambda = 0$ in the wave function for the unperturbed ground state:

$$\psi_1 = \mu\ \Phi_\sigma(1)\Phi_\sigma(2) + \nu\ \Phi^*_\sigma(1)\Phi^*_\sigma(2)$$

The perturbation causes a mixing of the wave functions for the excited states with ψ_1. The wave functions for the excited states are assumed to be

$$\psi_2 = \nu\ \Phi_\sigma(1)\Phi_\sigma(2) - \mu\ \Phi^*_\sigma(1)\Phi^*_\sigma(2)$$

$$\psi_3 = \frac{1}{\sqrt{2}}\{\Phi_\sigma(1)\Phi^*_\sigma(2) + \Phi^*_\sigma(1)\Phi_\sigma(2)\}$$

These wave functions are exactly correct for a symmetric σ-bond such as a C-C bond in benzene. For C-H bonds this will not be true but in a first order calculation the errors introduced in this way will be small.

The matrix elements of the perturbation operator are calculated from 2.26 to be

$$\langle\psi_1|H'|\psi_1\rangle = \sum_\alpha\sum_\beta \Delta q^{\pi}_{\alpha\beta}\{2\mu^2\langle\sigma\alpha\|\sigma\beta\rangle - \mu^2\langle\sigma\alpha\|\beta\sigma\rangle + 2\nu^2\langle\sigma^*\alpha\|\sigma^*\beta\rangle - \nu^2\langle\sigma^*\alpha\|\beta\sigma^*\rangle\}$$

$$\langle\psi_1|H'|\psi_2\rangle = \sum_\alpha\sum_\beta \Delta q^{\pi}_{\alpha\beta}\,\mu\nu\{2\langle\sigma\alpha\|\sigma\beta\rangle - \langle\sigma\alpha\|\beta\sigma\rangle - 2\langle\sigma^*\alpha\|\sigma^*\beta\rangle + \langle\sigma^*\alpha\|\beta\sigma^*\rangle\}$$

$$\langle\psi_1|H'|\psi_3\rangle = \sum_\alpha\sum_\beta \Delta q^{\pi}_{\alpha\beta}\frac{(\mu+\nu)}{\sqrt{2}}\{2\langle\sigma\alpha\|\sigma^*\beta\rangle - \langle\sigma\alpha\|\beta\sigma^*\rangle\}$$

where $\Delta Q^{\pi}(1,2)$ is written in terms of the charge-density bond-order matrix $q^{\pi}_{\alpha\beta}$. From 2.27 the first order correction in the energy of the triplet state appears to be

$$\langle{}^1\sigma(1,2)|H'|{}^1\sigma(1,2)\rangle = \sum_\alpha\sum_\beta \Delta q^{\pi}_{\alpha\beta}\{\langle\sigma\alpha\|\sigma\beta\rangle - \frac{1}{2}\langle\sigma\alpha\|\beta\sigma\rangle + \langle\sigma^*\alpha\|\sigma^*\beta\rangle - \frac{1}{2}\langle\sigma^*\alpha\|\beta\sigma^*\rangle\}$$

$$+ \sum_\alpha\sum_\beta \Delta\rho^{\pi}_{\alpha\beta}\{\langle\sigma\alpha\|\beta\sigma\rangle + \langle\sigma^*\alpha\|\beta\sigma^*\rangle\}$$

After substitution of the matrix elements in the first order formula

$$\psi_1' = \psi_1 - \sum_{j=2,3} \frac{\langle \psi_1 | H' | \psi_j \rangle}{(E_j - E_1)} \psi_j$$

the coefficients in the singlet ground state wave function become

$$\mu' = \mu - \frac{\mu\nu^2}{(E_2-E_1)} \sum_\alpha \sum_\beta \Delta q^\pi_{\alpha\beta} \{2 \langle \sigma\alpha \| \sigma\beta \rangle - \langle \sigma\alpha \| \beta\sigma \rangle - 2 \langle \sigma^*\alpha \| \sigma^*\beta \rangle + \langle \sigma^*\alpha \| \beta\sigma^* \rangle \}$$

$$\lambda' = - \frac{(\mu+\nu)}{(E_3-E_1)\sqrt{2}} \sum_\alpha \sum_\beta \Delta q^\pi_{\alpha\beta} \{2 \langle \sigma\alpha \| \sigma^*\beta \rangle - \langle \sigma\alpha \| \beta\sigma^* \rangle \}$$

$$\nu' = \nu + \frac{\mu^2\nu}{(E_2-E_1)} \sum_\alpha \sum_\beta \Delta q^\pi_{\alpha\beta} \{2 \langle \sigma\alpha \| \sigma\beta \rangle - \langle \sigma\alpha \| \beta\sigma \rangle - 2 \langle \sigma^*\alpha \| \sigma^*\beta \rangle + \langle \sigma^*\alpha \| \beta\sigma^* \rangle \}$$

from which we obtain on substitution in 4.6

$$(\rho^\sigma_{ST}(1,2))' = \frac{(\nu-\mu)}{\sqrt{2}} \{\Phi_\sigma(1)\Phi^*_\sigma(2) + \Phi^*_\sigma(1)\Phi_\sigma(2)\}$$

$$+ \frac{(\mu+\nu)}{\sqrt{2}} \sum_\alpha \sum_\beta \Delta q^\pi_{\alpha\beta} \left[\frac{\mu\nu}{(E_2-E_1)} \{2 \langle \sigma\alpha \| \sigma\beta \rangle - \langle \sigma\alpha \| \beta\sigma \rangle - 2 \langle \sigma^*\alpha \| \sigma^*\beta \rangle \right.$$

$$+ \langle \sigma^*\alpha \| \beta\sigma^* \rangle \} \{\Phi_\sigma(1)\Phi^*_\sigma(2) + \Phi^*_\sigma(1)\Phi_\sigma(2)\} \qquad 4.7$$

$$\left. - \frac{1}{(E_3-E_1)} \{2 \langle \sigma\alpha \| \sigma^*\beta \rangle - \langle \sigma\alpha \| \beta\sigma^* \rangle \} \{\Phi_\sigma(1)\Phi_\sigma(2) - \Phi^*_\sigma(1)\Phi^*_\sigma(2)\} \right]$$

The excitation energy of the triplet state becomes

$$(\Delta E^T_\sigma)' = \Delta E^T_\sigma + \frac{(\nu^2-\mu^2)}{2} \sum_\alpha \sum_\beta \Delta q^\pi_{\alpha\beta} \{2 \langle \sigma\alpha \| \sigma\beta \rangle - \langle \sigma\alpha \| \beta\sigma \rangle - 2 \langle \sigma^*\alpha \| \sigma^*\beta \rangle + \langle \sigma^*\alpha \| \beta\sigma^* \rangle \}$$

$$+ \sum_\alpha \sum_\beta \Delta \rho^\pi_{\alpha\beta} \{ \langle \sigma\alpha \| \beta\sigma \rangle - \langle \sigma^*\alpha \| \beta\sigma^* \rangle \} \qquad 4.8$$

B. PROTONS IN THE NODAL PLANE

The spin density in σ-bonds in the nodal plane of a π-electron radical is given by equation 2.28. Writing the spin density distribution in the π-electron system in terms of the atomic orbital spin density matrix, we obtain on substitution of 4.6 (with $\lambda = 0$)

$$\rho^{\sigma}(1,2) = \frac{2(\nu-\mu)^2}{\Delta E^T_{\sigma}} \sum_{\alpha} \sum_{\beta} \rho^{\pi}_{\alpha\beta} \langle \sigma\alpha \| \beta\sigma^* \rangle \frac{1}{2} \{ \Phi_{\sigma}(1)\Phi^*_{\sigma}(2) + \Phi^*_{\sigma}(1)\Phi_{\sigma}(2) \} \qquad 4.9$$

In the calculation of splitting constants of protons bonded to unsaturated carbon atoms usually only the terms arising from the spin density $\rho^{\pi}_{\alpha\alpha}$ on the carbon atom C_{α} to which the proton is bonded are considered. In this approximation $\rho^{\sigma}(1,2)$ becomes

$$\rho^{\sigma}_{\alpha}(1,2) = \frac{2(\nu-\mu)^2}{\Delta E^T_{\sigma}} \langle \sigma\alpha \| \alpha\sigma^* \rangle \frac{1}{2} \{ \Phi_{\sigma}(1)\Phi^*_{\sigma}(2) + \Phi^*_{\sigma}(1)\Phi_{\sigma}(2) \} \rho^{\pi}_{\alpha\alpha} \qquad 4.10$$

In order to obtain an impression which terms are important in 4.10 we assume

$$\Phi_{\sigma} = \frac{1}{\sqrt{N_{\sigma}}} \{ f_c + f_h \}$$

$$\Phi^*_{\sigma} = \frac{1}{\sqrt{N^*_{\sigma}}} \{ f_c - f_h \}$$

where f_c, f_h are the atomic orbitals and $\sqrt{N_{\sigma}}$, $\sqrt{N^*_{\sigma}}$ are the normalization constants. On substitution in 4.10 we obtain

$$\rho^{\sigma}_{\alpha}(1,2) = \frac{2(\nu-\mu)^2}{N_{\sigma} N^*_{\sigma} \Delta E^T_{\sigma}} \{ \langle \alpha c \| c\alpha \rangle - \langle \alpha h \| h\alpha \rangle \} \{ f_c(1)f_c(2) - f_h(1)f_h(2) \} \rho^{\pi}_{\alpha\alpha}$$

In the calculation of the proton splitting, which depends on the spin density at the nucleus, the contribution of the spin density in the carbon orbital is usually neglected. Usual (semi-empirical) values for the exchange integrals are, e.g. in a valence bond calculation with neglect of overlap [1]

$$\langle \alpha c \| c\alpha \rangle = 1.26 \text{ eV}$$
$$\langle \alpha h \| h\alpha \rangle = 0.79 \text{ eV}$$

From these figures it is clear that the interaction of f_α with the hydrogen orbital is very important and can not be neglected. On substitution of the integral values the spin density in the hydrogen orbital appears to be negative for positive values of $\rho^\pi_{\alpha\alpha}$. This is in agreement with experimental results [2].

If it is assumed that the properties of the C-H bond will be the same in different molecules, then the splitting constant a^H_α can be calculated from

$$a^H_\alpha = Q\,\rho^\pi_{\alpha\alpha} \tag{4.11}$$

where the coupling constant Q is about -28 gauss. 4.11 is usually called McConnell's formula [3,4].

A comparison of this formula with experimental results is very difficult because possible deviations might also be caused by errors in the calculated π-electron spin densities. Two problems in the calculation of proton splittings will be discussed in some detail:

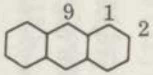
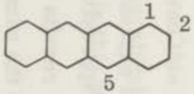
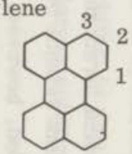
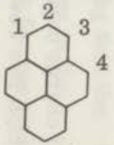
a. The differences between the splitting constants of positive and negative ions of alternant hydrocarbons.

b. The influence of configuration interaction in the π-electron system on the calculated splitting constants of ions of alternant hydrocarbons.

a. The differences between the splitting constants of positive and negative ions of alternant hydrocarbons

As has been discussed in chapter III (equation 3.15), the spin densities $\rho^\pi_{\alpha\alpha}$ in positive and negative ions of alternant hydrocarbons should be equal according to the pairing principle. Experimentally, however, the splitting constants appear to be different (see table 4.1). The experimental results are usually summarized by saying that the splitting constants are larger in the positive ion than in the negative ion but this is not completely correct because for some of the small splitting constants the reverse is found. It is very unlikely that the differences between positive and negative ions can be explained completely by differences in $\rho^\pi_{\alpha\alpha}$. If we assume, e.g. for the anthracene ions, that Q is a constant, then it follows from the experimental splitting constants that the difference in $\rho^\pi_{\alpha\alpha}$ for the carbon atoms C_{11} until C_{14} must be about 0.03. This seems to be almost impossible in view of the fact that $\rho^\pi_{\alpha\alpha}$ itself is 0.008 according to a Hückel approximation and -0.023 if first order configuration interaction is included. Moreover, Bolton and Fraenkel [8] have

Table 4.1. Splitting constants and spin densities in positive and negative ions of alternant hydrocarbons

		a^H cation ref. 5	a^H anion ref. 5	a^H averaged	ρ^π Hückel ref. 6	ρ^π Mc Lachlan $\lambda_1 = 1.17$ ref. 6	ρ^π first order conf. int. ref. 7	$-Q_{exp.}$ Hückel	$-Q_{exp.}$ Mc Lachlan	$-Q_{exp.}$ first order conf. int.
anthracene 	1	3.061	2.740	2.901	0.097	0.119	0.112	29.9	24.4	25.9
	2	1.379	1.509	1.444	0.048	0.031	0.040	30.1	46.6	36.1
	9	6.533	5.337	5.935	0.193	0.257	0.242	30.7	23.1	24.5
tetracene 	1	1.694	1.541	1.618	0.056	0.067	0.060	28.9	24.1	27.0
	2	1.030	1.162	1.096	0.034	0.022	0.020	32.2	49.8	54.8
	5	5.061	4.226	4.644	0.147	0.196	0.197	31.6	23.7	23.6
perylene 	1	3.054	3.043	3.049	0.083	0.106	0.102	36.7	28.8	29.9
	2	-0.446	-0.450	-0.448	0.013	-0.023	-0.018	----	19.5	24.9
	3	4.053	3.493	3.773	0.108	0.152	0.145	34.9	24.8	26.0
pyrene 	1	5.38	4.75	5.07	0.136	0.188	0.162	37.2	27.0	31.3
	2	-1.18	-1.09	-1.14	0.000	-0.053	-0.038	----	21.5	30.0
	4	2.12	2.08	2.10	0.087	0.093	0.085	24.1	22.6	24.7

shown that the differences in the ^{13}C splitting constants of the anthracene ions are much smaller than the differences in the proton splittings which, according to these authors, is most readily interpreted as implying that the pairing theorem is valid to a high degree of approximation.

In the literature two formulas have been proposed which give a difference in the proton splittings without a difference in the π-electron spin densities:

Colpa and Bolton's formula

Colpa and Bolton [9] and Higuchi [10] have discussed the influence of the charge density distribution in the π-electron system on the relation between a_α^H and $\rho_{\alpha\alpha}^\pi$ in a molecular orbital approximation. Their calculations can be repeated in a somewhat more general way by substitution of 4.7 and 4.8 in 2.28. When we restrict ourselves to terms in $\Delta q_{\alpha\alpha}^\pi$ and neglect terms in $\Delta\rho_{\alpha\alpha}^\pi$, which are equal for positive and negative ions, then we obtain instead of 4.10

$$\begin{aligned}
\rho_\alpha^\sigma(1,2) = {} & \frac{2(\nu-\mu)^2\langle\sigma\alpha\|\alpha\sigma^*\rangle}{\Delta E_\sigma^T}\frac{1}{2}\{\Phi_\sigma(1)\Phi_\sigma^*(2)+\Phi_\sigma^*(1)\Phi_\sigma(2)\}\ \rho_{\alpha\alpha}^\pi\Big[1 \\
& +\frac{(\nu^2-\mu^2)\,\Delta q_{\alpha\alpha}^\pi}{2}\{2\langle\sigma\alpha\|\sigma\alpha\rangle-\langle\sigma\alpha\|\alpha\sigma\rangle-2\langle\sigma^*\alpha\|\sigma^*\alpha\rangle+\langle\sigma^*\alpha\|\alpha\sigma^*\rangle\} \\
& \times\left\{\frac{4\mu\nu}{(\nu-\mu)^2(E_2-E_1)}-\frac{1}{\Delta E_\sigma^T}\right\}\Big] \qquad 4.12 \\
& -\frac{(\nu^2-\mu^2)\{2\langle\sigma\alpha\|\sigma^*\alpha\rangle-\langle\sigma\alpha\|\alpha\sigma^*\rangle\}}{(E_3-E_1)\Delta E_\sigma^T}\rho_{\alpha\alpha}^\pi\ \Delta q_{\alpha\alpha}^\pi\,[\langle\sigma\alpha\|\alpha\sigma^*\rangle \\
& \times\{\Phi_\sigma(1)\Phi_\sigma(2)-\Phi_\sigma^*(1)\Phi_\sigma^*(2)\}+\{\langle\sigma\alpha\|\alpha\sigma\rangle-\langle\sigma^*\alpha\|\alpha\sigma^*\rangle\} \\
& \times\frac{1}{2}\{\Phi_\sigma(1)\Phi_\sigma^*(2)+\Phi_\sigma^*(1)\Phi_\sigma(2)\}]
\end{aligned}$$

All charge dependent terms in this expression are proportional to $(\nu+\mu)$ so they vanish in a covalent valence bond approximation with neglect of overlap. If the overlap is included, however, the results from a molecular orbital and a valence bond calculation will have the same order of magnitude. From Higuchi's calculations we should conclude that the charge dependent terms are not negligible.

The resulting splitting constants, however, are larger for negative ions than for positive ions which is not in agreement with the experiments.

In our opinion the charge effect is much more complicated than is assumed in Colpa and Bolton's and Higuchi's papers (and in the derivation of 4.12). The magnitude of this effect is dependent on the shift of charge in the C-H bond caused by the charge in the $2p_z$-orbital. According to Higuchi's calculation this shift is about 0.2 electron per unit change of charge in the $2p_z$-orbital (from Colpa and Bolton's figures the same order of magnitude can be calculated). If we assume this to be correct, then we should, in many cases, expect about the same shift in the C-C bonds, e.g. for the C_9-C_{11} and C_9-C_{14} bonds in the anthracene ions where the charge on C_9 is much larger than the charge on C_{11} and C_{14}. Then, in view of the large magnitude of the shift, the Coulomb interaction between the σ-bonds would considerably reduce the magnitude of the calculated effect for the proton bonded to C_9. On the other hand, no shift is expected in the C_2-C_3 bond for reasons of symmetry whereas in the C_1-C_2 bond a shift of charge from C_1 to C_2 is expected because the charge on C_1 is larger than the charge on C_2. Therefore the charge effect for the proton bonded to C_2 is not reduced by the interaction between the σ-bonds and will be more important than the effect for the proton bonded to C_9. This might explain the fact that the splitting of the proton bonded to C_2 is larger in the negative ion than in the positive ion but this conclusion must await further investigations.

Due to a sign error, Colpa and Bolton assumed that the charge dependent terms discussed above should give larger splittings for positive ions. Instead of McConnell's formula they therefore proposed

$$a_\alpha^H = (Q + K\,\epsilon_{\alpha\alpha}^\pi)\,\rho_{\alpha\alpha}^\pi \qquad 4.13$$

$$\text{where } \epsilon_{\alpha\alpha}^\pi = 1 - q_{\alpha\alpha}^\pi$$

In a later paper Bolton [11] has derived this formula by assuming that the effective nuclear charge for the carbon atomic orbitals is smaller in the negative ion than in the positive ion. In this way larger splittings for positive ions are obtained [11,12].

Giacometti, Nordio and Pavan's formula

Giacometti, Nordio and Pavan [13] ascribed the differences between positive and negative ions to the overlap spin densities $\rho^{\pi}_{\alpha\beta}$ which are opposite for positive and negative ions for C_{α} and C_{β} nearest neighbours (see chapter III). They therefore proposed

$$a^{H}_{\alpha} = Q_1 \rho^{\pi}_{\alpha\alpha} + \sum_{\beta} Q_2 \rho^{\pi}_{\alpha\beta} \qquad 4.14$$

It can easily be shown from the secular equations that in a Hückel approximation 4.14 can also be written

$$a^{H}_{\alpha} = (Q_1 + m_a Q_2)\, c^2_{a\alpha} \qquad 4.15$$

where m_a is the coefficient of the resonance integral in the energy of the singly occupied orbital Φ_a. In a Hückel approximation the splitting constants will therefore be larger for positive ions than for negative ions whereas the coupling constant Q in 4.11 is a constant within one radical-ion. If configuration interaction is included, however, 4.15 is not correct. It is difficult to see whether it is possible that in some cases configuration interaction should give larger splitting constants for negative ions. Because this could explain the difference e.g. for the 2-position in the anthracene ions, we have calculated $(\rho^{\pi}_{12} + \rho^{\pi}_{23})$ in the anthracene positive ion according to 3.14 from Hückel-orbitals. The inclusion of configuration interaction yielded a smaller value for $(\rho^{\pi}_{12} + \rho^{\pi}_{23})$ than is obtained from the coefficients in the singly occupied orbital but the correction was too small to explain the experimental differences for the 2-position.

Besides the charge dependent terms and the overlap spin densities several other effects might influence the difference between positive and negative ions. The e.s.r. spectra of these ions are measured in strongly different solvents; negative ions in solvents such as dimethoxyethane and positive ions in sulfuric acid or dichloromethane-$SbCl_5$. It is therefore not impossible that solvent effects are of importance.

In all mechanisms discussed before it is assumed that, apart from the effects studied, the σ-bonds in positive and negative ions have equal properties. However, differences e.g. in the bond lengths could easily cause differences in the splitting constants. The theoretical values for $\langle \alpha h \| h \alpha \rangle$ for C-H bond lengths of 1.09 and 1.11 Å are 0.71 and 0.68 eV respectively. From the figures given before it can be seen that, though the difference between these two values is small, it yields a difference in the splitting constants of 5 to 10%. One might of course consider this to be negligible but the experimental differences are not very much larger.

From comparisons of 4.11, 4.13 and 4.14 with experimental splittings it has been concluded that 4.13 and 4.14 predict splitting constants equally well [7,14,15]. Bloor, Gilson and Daykin [7] even conclude that the extra terms in 4.13 and 4.14 do not improve the agreement with the experiments obtained from 4.11. Their conclusions have been criticized by Bolton [16,17].

For a further study of the differences between positive and negative ions it would be of importance to know more about the ^{13}C splittings. A correct interpretation of the differences in the proton splittings must also explain why the differences in the ^{13}C splittings in the anthracene ions are much smaller. It is difficult to see how Bolton's explanation of the differences in the proton splittings can be in accordance with the observed differences in the ^{13}C splittings. The influence of the overlap spin densities, however, may be different for H and ^{13}C splittings (compare e.g. the influence of the overlap spin densities on nitrogen splittings as discussed by Henning [18,19]). At present, however, the theory of ^{13}C splittings [1] is insufficiently developed to draw reliable conclusions from the experimental observations.

b. The influence of configuration interaction in the π-electron system on the calculated splitting constants of ions of alternant hydrocarbons

Besides the differences between positive and negative ions, a second problem in the calculation of the splitting constants of ions of alternant hydrocarbons has been discussed in several papers. For the negative ion of naphtalene the spin densities obtained from a Hückel calculation show a better agreement with the experimental splittings than spin densities obtained from more accurate methods [20]. According to Colpa and Bolton [9] this could be due to the effects causing the differences between positive and negative ions but, when we assume that these effects are opposite for these ions, we can exclude this possibility by comparing the theoretical results with the averaged splittings. The experimental Q-values in table 4.1 are calculated from these averaged splittings and from spin densities obtained from several approximation methods. In a Hückel approximation no negative spin densities can be obtained but for atoms having a positive spin density the experimental Q-values show smaller deviations from a constant value than Q-values obtained from more accurate calculations.

The reason for this discrepancy, which occurs especially at the 2-position in the anthracene and tetracene ions, is not clear. According to Schug, Brown and Karplus [21, 22] a valence bond approximation should give better results but their calculations are of a very approximate nature and it is easily possible that an improvement would give the same difficulties as are encountered in the molecular orbital theory. These authors suggest that parameter changes in the molecular orbital calculation which cause a reduction of the q_α/q_β ratio in the naphtalene ions might improve the agreement with the experimental splittings. It must be noted, however, that this is only correct for parameter changes which do not alter the alternant character of the neutral hydrocarbon, i.e. variations in the β-values. If we assume β to be proportional to the overlap, then a calculation for the naphtalene anion based on the bond lengths in naphtalene does not show a significant improvement in the agreement with the experimental splittings. A variation of the α-value for atoms bonded to three other carbons has a negligible effect on the spin density distribution because these atoms are in a nodal plane of the singly occupied orbital. For the other atoms a change in the α-value which reduces the q_α/q_β ratio leads to an increase of the ρ_α/ρ_β ratio whereas the opposite change is opposite to the variations which are usually accepted, e.g. in ω-technique calculations [23].

From these considerations it is clear that it is at present impossible to predict splitting constants very accurately. On the other hand, in view of the crude approximations in even the most accurate calculations, the agreement with the experimental splittings is surprisingly good.

C. α-PROTONS OF ALKYL SUBSTITUENTS

In the calculation of the spin density on the α-hydrogen atoms of alkyl substituents in π-electron radicals the most important terms will be caused by the direct interaction of the C-H bond with the π-electron system. Besides, terms will occur in which the spin density is transferred via another σ-bond of the substituent. The latter terms are assumed to be negligible. Consequently

the spin density will be calculated according to equation 2.32.
In the following we shall first discuss the question whether it is possible to calculate the spin density from the first order term 2.30 only. After this the complete formula 2.32 will be considered and finally some remarks will be made about the question spin polarization versus charge transfer and about the influence of the substituent on the spin density distribution in the π-electron system.

1. The first order term 2.30

On neglect of the charge transfer wave functions, the spin density in the C-H bond depends on the first order term 2.30 only. This type of approximation has been used by McLachlan [24] in his valence bond discussion of the splitting constants of the protons of methyl substituents. In this calculation the usual assumption has been made that, due to the σ-π overlap, the exchange integrals between σ- and π-orbitals are negative. A positive spin density on the carbon atom to which the substituent is bonded then leads to a positive spin density on the hydrogen atom. This is in agreement with the experimental observations [25]. According to McLachlan the magnitude of the calculated splitting also agrees with the experiments. On closer inspection, however, it appears that the first order term 2.30 is not sufficient for an explanation of the observed splittings:

a. In McLachlan's calculation the interaction of the π-electron wave function with the hydrogen orbital is completely neglected. In the preceding section it has been shown that this is certainly not correct for protons directly bonded to the unsaturated system. For methyl protons the π-H interaction is probably even more important because the difference between the distances from the carbon and hydrogen orbitals to the π-electron functions is relatively smaller than in the former case. Therefore the inclusion of the π-H interaction should considerably reduce the proton splittings calculated by McLachlan.

b. From 2.30 we should conclude that a formula similar to McConnell's formula 4.11 is valid e.g. for the protons of freely rotating methyl substituents. As will be shown later, this is not in agreement with the experimental e.s.r. spectra e.g. of the ions of methyl substituted alternant hydrocarbons and of methyl substituted triphenylmethyl radicals.

c. In the derivation of the contribution of the charge transfer wave functions in 2.32 the overlap of the σ and π wave functions has been neglected. It can easily be shown that on inclusion of the overlap a first order charge transfer term is obtained which has a magnitude comparable to the value obtained from 2.30.

2. Evaluation of the complete formula 2.32

It is important to note that the overlap has been neglected in the derivation of the charge transfer contribution in 2.32. As has been remarked above, the inclusion of overlap leads to a first order term comparable to 2.30. Because a calculation without neglect of overlap is very complicated, we shall assume that the σ and π wave functions have been orthogonalized. Consequently we shall also assume that the exchange integrals in the first order term 2.30 are positive. Then the spin density in the hydrogen orbital due to this term has a negligibly small negative value. For α-alkyl protons the value of the π-electron wave functions at the proton will be small so the first order charge transfer contributions in 2.32 are also neglected.

After expansion of the functions $\underline{\pi}_j^+$ and $\underline{\pi}_j^-$ in atomic orbitals, the Hamiltonian matrix elements with the σ-functions are calculated by neglecting all terms except those involving the $2p_z$-orbital f_α of the carbon atom C_α to which the substituent is bonded. The interaction of f_α with the σ-functions is assumed to vary as the cosine of the angle θ between the plane of the C-H bond and the C_α-C_{alkyl} bond and the plane of the z-axis of f_α and the C_α-C_{alkyl} bond. Equation 2.32 then becomes

$$\rho_\alpha^\sigma(1,2) = \cos^2\theta \Bigg[\sum_j \delta_j (\underline{c}_{j\alpha}^+)^2 \left\{ \frac{\mu^2 \beta^2_{\alpha\sigma^*} \Phi^*_\sigma(1)\Phi^*_\sigma(2)}{(I_\pi - E_\sigma + \Delta E_j^+ + C_{j\sigma})^2} + \frac{2\mu(\nu-\mu)\beta_{\alpha\sigma}\beta_{\alpha\sigma^*}}{(I_\pi - E_\sigma + \Delta E_j^+ + C_{j\sigma})\Delta E_\sigma^T} \right.$$

$$\left. \times \frac{1}{2}\{\Phi_\sigma(1)\Phi^*_\sigma(2) + \Phi^*_\sigma(1)\Phi_\sigma(2)\} \right\} \qquad 4.16$$

$$+ \sum_j \delta_j (\underline{c}_{j\alpha}^-)^2 \left\{ \frac{\mu^2 \beta^2_{\alpha\sigma} \Phi_\sigma(1)\Phi_\sigma(2)}{(I_\sigma - E_\pi + \Delta E_j^- + C_{\sigma j})^2} + \frac{2\mu(\nu-\mu)\beta_{\alpha\sigma}\beta_{\alpha\sigma^*}}{(I_\sigma - E_\pi + \Delta E_j^- + C_{\sigma j})\Delta E_\sigma^T} \right.$$

$$\left. \times \frac{1}{2}\{\Phi_\sigma(1)\Phi^*_\sigma(2) + \Phi^*_\sigma(1)\Phi_\sigma(2)\} \right\} \Bigg]$$

where $$\left.\begin{array}{l} \beta_{\alpha\sigma} = \langle f_\alpha | H | \Phi_\sigma \rangle \\ \beta_{\alpha\sigma^*} = \langle f_\alpha | H | \Phi^*_\sigma \rangle \end{array}\right\} \text{ for } \theta = 0$$

$\underline{c}^+_{j\alpha}$, $\underline{c}^-_{j\alpha}$ are the coefficients of f_α in $\underline{\pi}^+_{j\alpha}$ and $\underline{\pi}^-_{j\alpha}$ respectively.

In the calculation of the splitting constants it is in general necessary to average $\rho^\sigma_\alpha(1,2)$ over all possible orientations of the C-H bond. When we assume that the energy terms in the denominator are independent of the orientation, then $\rho^\sigma_\alpha(1,2)$ can be averaged by taking the averaged value of $\cos^2\theta$. For a freely rotating methyl substituent $\overline{\cos^2\theta} = 1/2$ but for other substituents the averaging is more difficult, e.g. for ethyl substituents it has been observed in several radicals that the α-hydrogen splitting is about 50% of the splitting constant of the protons in a corresponding methyl substituent. This is usually interpreted as being caused by a preferred orientation of the ethyl-group such that $\overline{\cos^2\theta}$ for the two C-H bonds has its minimum value of 1/4 which means that $\theta = \pm 60^\circ$ or $\pm 120^\circ$ (see e.g. ref. 26).

In the following we shall discuss some general properties of equation 4.16. After this some simplified approximation methods will be considered.

a. The influence of differences in the excitation energies

If for a number of radicals the ionization energies, the electron affinities and the correction terms in the Coulomb energies are nearly equal and the contribution of the terms for which $j \neq 0$ is small, then it follows from 2.19 and 2.20 that McConnell's formula 4.11 should be valid e.g. for the protons of freely rotating methyl substituents in these radicals. In this case the coupling constant Q has a positive value but the magnitude of Q will be different for different series of radicals. An example of a series of radicals for which McConnell's formula is valid is the series of symmetrically substituted dimethylnaphtalene anions [27, 28, 29]. In general, however, McConnell's formula will not be valid for methyl protons. Important deviations are expected for radicals where configuration interaction can not be neglected in the calculation of the π-electron spin density distribution, e.g. methyl substituted triphenylmethyl radicals, and in comparisons of radicals having a large difference in the energy terms in the denominator, e.g. positive and negative ions of methyl substituted alternant hydrocarbons. These two examples will be discussed in more detail.

Methyl substituted neutral alternant radicals

From the formulas given in section B.2 of chapter III it follows that the functions $\underline{\pi}_j^+$ and $\underline{\pi}_j^-$ for $j \neq 0$ are closely related to the configuration interaction terms in the π-electron wave functions. Then, according to 4.16, the configuration interaction terms in the π-electron spin density distribution will have an influence on the spin density in the σ-bond which is different from the influence of the π-electron spin density distribution before configuration interaction (i.e. the distribution in the singly occupied orbital). This effect is clearly demonstrated by the e.s.r. spectra of methyl substituted triphenylmethyl radicals. As will be shown in chapter V, the π-electron spin density distribution in unsubstituted, mono- and tri-para-substituted and mono-meta-substituted triphenylmethyl is almost equal. In the spin density on the para position the contribution of the singly occupied orbital is the most important one whereas the spin density on the meta position depends on configuration interaction terms only. Therefore we should expect from 4.16 that the meta- and para-methyl proton splittings correspond to different Q-values. This is in agreement with the observed ratios of the methyl proton splittings and the corresponding ring proton splittings in the unsubstituted radical (table 4.2).

	a^H_{ring} unsubstituted	a^H_{methyl}	$a^H_{\text{methyl}}/a^H_{\text{ring}}$
para (from mono-para)	2.80	2.97	1.06
para (from tri-para)	2.80	2.93	1.05
meta (from mono-meta)	1.13	0.84	0.74

Table 4.2. Methyl proton splittings (gauss) of substituted triphenylmethyl radicals

Positive and negative ions of methyl substituted alternant hydrocarbons

It is usually assumed that a methyl substituent is an electron-donor in a neutral molecule. Because the electron-donating properties will be more important in positive than in negative ions, we should expect that methyl proton splittings are larger in positive than in negative ions. This conclusion can not be derived from 4.16 in a general way but it is certainly more probable than the opposite possibility. Bolton, Carrington and Mc Lachlan [30] and Colpa and de Boer [31] have shown that, indeed, α-alkyl proton splittings are larger in positive than in negative ions (see table 4. 3.).

	positive ion	negative ion
9,10-dimethylanthracene [30]	8. 00	3. 88
9-methylanthracene [30]	7. 79	4. 27
pyracene [31]	12. 80	6. 58

Table 4. 3. α-alkyl proton splittings of ions of substituted alternant hydrocarbons

It must be noted that the observed differences can not be explained with an inductive effect. Calculations show that this should cause a much smaller difference between positive and negative ions. Moreover, the inductive effect leads in many cases to a larger splitting in the negative ion, e. g. in pyracene.

The possibility that the effects, which cause the differences between the ring proton splittings in the unsubstituted ions, are also of importance can not be excluded. However, these effects are not well understood so a correction is impossible. Moreover, the differences in the α-alkyl proton splittings are much larger than the differences in the ring proton splittings so the neglect of these effects seems to be reasonable.

b. Comparison of the spin densities in the carbon and hydrogen orbitals of the C-H bond

In their discussion of α-alkyl proton splittings Colpa and de Boer [31] have compared Mulliken's hyperconjugation model and the pseudo-hetero-atom approximation (these methods will be discussed later) by calculation of the ratio of the spin densities in the carbon and hydrogen orbitals of the C-H bond. The magnitude of this ratio is strongly dependent on the choice of the parameters in 4.16.
In order to illustrate this, we consider a radical for which the configuration interaction terms in the π-electron spin density distribution can be neglected so only terms for $j = 0$ are taken into account. In a molecular orbital approximation for the C-H bond is $\mu=1$ and $\nu=0$ whereas the excitation energies can be approximated as

$$
\begin{aligned}
I_{\pi}-E_{\sigma}+C_{0\sigma} &= \epsilon_{\sigma *}-\epsilon_{a}\\
I_{\sigma}-E_{\pi}+C_{\sigma 0} &= \epsilon_{a}-\epsilon_{\sigma}\\
\Delta E_{\sigma}^{T} &= \epsilon_{\sigma *}-\epsilon_{\sigma}
\end{aligned}
$$

where ϵ_{σ}, $\epsilon_{\sigma *}$ and ϵ_{a} are the orbital energies of the bonding and antibonding σ-orbital and the singly occupied π-orbital respectively. From these figures it is clear that in this approximation

$$\Delta E_{\sigma}^{T} = I_{\pi} - E_{\sigma} + C_{0\sigma} + I_{\sigma} - E_{\pi} + C_{\sigma 0}$$

On substitution in 4.16 $\rho_{\alpha}^{\sigma}(1,1)$ for a freely rotating methyl substituent becomes

$$\rho_{\alpha}^{\sigma}(1,1) = \frac{1}{2} c_{a\alpha}^{2} \left[\left\{ \frac{\beta_{\alpha\sigma *} c_{\sigma * c}}{(\epsilon_{\sigma *}-\epsilon_{a})} - \frac{\beta_{\alpha\sigma} c_{\sigma c}}{(\epsilon_{a}-\epsilon_{\sigma})} \right\} f_{c}(1) + \left\{ \frac{\beta_{\alpha\sigma *} c_{\sigma * h}}{(\epsilon_{\sigma *}-\epsilon_{a})} - \frac{\beta_{\alpha\sigma} c_{\sigma h}}{(\epsilon_{a}-\epsilon_{\sigma})} \right\} f_{h}(1) \right]^{2} \tag{4.17}$$

From the usual assumption that the polarity of a C-H bond is small it follows that $c_{\sigma c} \approx c_{\sigma h}$ and $c_{\sigma * c} \approx -c_{\sigma * h}$. $c_{\sigma * h}$ is taken to be negative; the other coefficients are positive. If we assume $|\beta_{\alpha c}| > |\beta_{\alpha h}|$, e.g. from the overlap integrals for Slater orbitals [32]

$$S_{\alpha c} = 0.157 \cos\theta$$

$$S_{\alpha h} = 0.082 \cos\theta$$

then $\beta_{\alpha\sigma}$ and $\beta_{\alpha\sigma *}$ will be negative. It follows that the spin density in the hydrogen orbital depends on the sum of two positive terms whereas the spin density in the carbon orbital depends on the difference of these terms. Therefore the spin density in the carbon orbital will have a value somewhere between zero and a value in the neighbourhood of the spin density in the hydrogen orbital. In a better approximation for the C-H bond ν will be negative so

$$\mu(\mu-\nu) > \mu^{2}$$

Besides, it seems reasonable to assume

$$\Delta E_{\sigma}^{T} < I_{\pi} - E_{\sigma} + C_{0\sigma} + I_{\sigma} - E_{\pi} + C_{\sigma 0}$$

If this is taken into account, the ratio of the spin densities in the carbon and hydrogen orbitals becomes smaller than the value obtained from 4.17. It might even be possible that the spin density in the carbon orbital is negative.

From these considerations it is clear that for a correct choice of the parameters in 4.16 the spin density in the carbon orbital is of equal importance as the spin density in the hydrogen orbital. From e.s.r. spectra, however, only the spin density in the hydrogen orbital can be obtained. Therefore the choice of a set of parameters, which allows a reliable prediction of the spin density in the carbon orbital, is very difficult.

c. Simplified approximation methods.

The splitting constants of α-alkyl protons are usually calculated in a molecular orbital approximation for the complete system of π-electrons and σ-bond. Two different methods have been used in the literature, the pseudo-hetero-atom approximation and Mulliken's hyperconjugation model. The calculations are carried out by a diagonalization of the Hückel or s.c.f. matrix or by application of perturbation theory. These two procedures yield comparable results (see e.g. reference 33).

The pseudo-hetero-atom approximation

In the pseudo-hetero-atom approximation the wave functions in which an electron is transferred to the σ-bond are completely neglected. This is achieved by replacing the methyl group by one pseudo-atomic orbital of π-symmetry which contributes two electrons in the ground state of the molecule. A charge transfer to the methyl group then becomes impossible. In this approximation equation 4.16 reduces to

$$\rho_{\alpha}^{\sigma}(1,2) = \overline{\cos^2\theta} \sum_j \delta_j (\underline{c}_{j\alpha}^-)^2 \frac{\mu^2 \beta_{\alpha\sigma}^2 \Phi_\sigma(1)\Phi_\sigma(2)}{(I_\sigma - E_\pi + \Delta E_j^- + C_{\sigma j})^2} \qquad 4.18$$

Bolton, Carrington and McLachlan [30] have used this model in a discussion of the e.s.r. spectra of the ions of 9- and 9,10-methyl substituted anthracenes. Their parameters were calculated from the Coulson-Crawford parameters [34] for the hyperconjugation model. In this way a qualitative description of the methyl proton splittings could be obtained but the absolute magnitude of the calculated splittings is too small [31] whereas the ratio of the splittings in the positive and negative ion is too large. For these reasons Colpa and Bolton [31] rejected the pseudo-hetero-atom approximation.

We have tried to obtain a better agreement with the observed splittings by parameter changes. From calculations in which we assumed $\mu^2=1$ and neglected terms for $j \neq 0$ and the correction terms in the Coulomb energy, we obtained an 'experimental' value $\beta_{\alpha\sigma} \approx 1.25\beta_0$ where β_0 is the value of the resonance integral in π-electron calculations. By substitution of the overlap integrals given in the preceding section in the usual formula $\beta = 4S\beta_0$ we obtained on neglect of the overlap in the σ-bond $\beta_{\alpha\sigma} = 0.7\beta_0$ which is much smaller than the 'experimental' value. So, 4.18 is not sufficient for a calculation of the splitting constants.

Mulliken's hyperconjugation model

The hyperconjugation model [35, 36] is essentially a molecular orbital calculation for the complete system of π-electrons and methyl substituent. This calculation is simplified by replacing the original atomic orbitals by linear combinations. Because of the trigonal symmetry of the methyl group, both the three carbon orbitals and the three hydrogen orbitals of the C-H bonds can be combined to one totally symmetric orbital and one degenerate pair of orbitals. For the latter the combinations are chosen which are symmetric and antisymmetric with respect to the nodal plane of the π-electron system. In this way the three C-H bonds can be replaced by two pseudo-σ-bonds and one pseudo-π-bond. In the calculations only the pseudo-π-bond is considered because, for reasons of symmetry, the pseudo-σ-bonds do not mix with the π-electron wave functions. An essential point in the hyperconjugation treatment is that this choice of pseudo-atomic orbitals is combined with a rather strong interaction between the C-H bonds. This leads to a higher energy for the pseudo-π-bond and one of the pseudo-σ-bonds whereas the energy of the totally symmetric pseudo-σ-bond is lowered with respect to the energy of the original C-H bonds.

In many hyperconjugation calculations a set of parameters proposed by Coulson and Crawford [34] has been used:

$S_{\alpha c'} = 0.19$ $\quad\beta_{\alpha c'} = 0.76\beta_0$ $\quad\alpha_{c'} = \alpha_0 - 0.1\beta_0$

$S_{\alpha h'} = 0$ $\quad\beta_{\alpha h'} = 0$ $\quad\alpha_{h'} = \alpha_0 - 0.5\beta_0$

$S_{c'h'} = 0.625$ $\quad\beta_{c'h'} = 2.5\beta_0$

where c' and h' represent the pseudo-π atomic orbitals for carbon and hydrogen respectively.

Colpa and de Boer [31] have used these parameters (except $S_{c'h'}$ and $\beta_{c'h'}$ which were chosen to be 0.5 and $2\beta_0$) in a calculation of the α-alkyl proton splittings of the ions of pyracene and acenaphtene and of cyclohexadienyl. A good agreement with the experimental splittings was obtained. As we have seen before, the pseudo-hetero-atom approximation could also give a good agreement with the experimental splittings but has been rejected because the necessary parameter values were assumed to be not very realistic. In our opinion this is also the case for the parameters used in the hyperconjugation model.

In the hyperconjugation model it is assumed that, due to the interaction between the C-H bonds, $|\alpha_{c'}| < |\alpha_0|$, $|\alpha_{h'}| < |\alpha_0|$ and $|\beta_{c'h'}| < |\beta_{ch}|$. If the interaction between the C-H bonds is neglected, then the calculated splittings would be larger for negative ions than for positive ions because both $|\alpha_c|$ and $|\alpha_h|$ are larger than $|\alpha_0|$. Moreover, the change in $\beta_{c'h'}$ would lead to a smaller averaged splitting. In view of the magnitude of the calculated splittings, it is therefore clear that in the hyperconjugation model the splitting constants are strongly dependent on the interaction between the C-H bonds: It is difficult to give an exact value of the magnitude of this interaction because this also depends on parameter values for an isolated C-H bond. In a crude estimate, however, the interaction between the bonding orbitals of the C-H bonds is about half the interaction within a bond. Because this value seems to be very large, we shall discuss the interaction between the C-H bonds in some more detail.

The ground state wave function for a system of N π-electrons and two σ-bonds A and B, which are symmetrically located with respect to the nodal plane of the π-electron system, can be written

$$\psi_1 = \mathscr{A}\pi(1..N)\,{}^0\sigma_A(N+1, N+2)\,{}^0\sigma_B(N+3, N+4)\ \chi_1(1..N+4)$$

The σ→π charge transfer wave functions are

$$\psi_2 = \mathscr{A}\pi(1..N, N+2)\sigma_A(N+1)\,{}^0\sigma_B(N+3, N+4)\ \chi_2(1..N+4)$$

$$\psi_3 = \mathscr{A}\pi(1..N, N+4)\,{}^0\sigma_A(N+1, N+2)\sigma_B(N+3)\ \chi_3(1..N+4)$$

The interaction between the σ-bonds is introduced via the mixing of ψ_2 and ψ_3. This mixing leads to a change in the charge transfer excitation energy which is equal to

$$\langle \underline{\sigma}_{AS}^{+}|H|\underline{\sigma}_{BS}^{+}\rangle = \mu^{2} h_{ab}$$

where a and b represent the bonding orbitals Φ_{σ} as introduced in equation 4.3 for A and B respectively (this change in the charge transfer excitation energy corresponds to the lifting of the energy of the pseudo-π orbital in the hyperconjugation model). The function ${}^{0}\sigma(1,2)$ in 4.3 is the best possible one of this particular form. In calculations on the hydrogen molecule a variation of the effective nuclear charge for the hydrogen orbitals leads to $Z_H = 1.2$ instead of $Z_H = 1$ (see e.g. table XVIII-1 in reference 37). It is often assumed that this value should also give a better wave function for C-H bonds. In the same way it seems reasonable to suppose that the effective nuclear charge for the carbon orbital is larger than the value for the $2p_z$-orbitals. Due to this contraction of the atomic orbitals the interaction between the σ-bonds will be smaller than is assumed in the hyperconjugation model, even if we take $\mu^2 = 1$.

From these considerations it will be clear that the explanation of the differences between the α-alkyl proton splittings in positive and negative ions according to the hyperconjugation model is not correct.

A much simpler explanation is obtained on introduction of the π-H interaction which is neglected in the hyperconjugation model. For Slater orbitals $S_{\alpha c} \approx 2S_{\alpha h}$ so, on neglect of the overlap within the σ-bond, $\beta_{\alpha\sigma} \approx 3\beta_{\alpha\sigma^*}$. This difference in the β-values causes a stronger mixing with the $\sigma \rightarrow \pi$ charge transfer wave functions than with the $\pi \rightarrow \sigma$ charge transfer wave functions which leads to larger splitting constants in the positive ion. (if the overlap within the σ-bond is not neglected $\beta_{\alpha\sigma^*}$ will be nearly equal to $\beta_{\alpha\sigma}$ but then $(I_\pi - E_\sigma) > (I_\sigma - E_\pi)$ which has the same effect). It is of course not certain that the interaction between the σ-bonds is completely negligible, therefore I_σ and E_σ in 4.16 must be regarded as semi-empirical parameters for a C-H bond in a substituent instead of the values for an isolated C-H bond. For a methyl substituent I_σ can be set equal to the ionization energy of methane but, in view of the fact that the ground state of the methane anion will be totally symmetric, E_σ must be regarded as the second electron affinity of methane. The semi-empirical parameters may be different for different alkyl substituents. It has been observed in some cases (see e.g. reference 38) that the α-alkyl proton splitting of an ethyl substituent in a positive ion is smaller than the minimum value of half the corresponding methyl proton splitting. This may be due to the interaction between the σ-bonds of the substituent in which case I_π and E_σ must be given other values than for a methyl substituent.

One might argue that the contraction of the σ-electron wave functions also leads to a smaller interaction between the σ-bond and the π-electron system. This effect, however, is compensated by the proportionality of the splitting constant with Z_H^3. In order to illustrate this we have calculated $S_{\alpha h}^2 Z_H^3$. For $Z_H = 1$, $S_{\alpha h}^2 Z_H^3 = 0.0067$ whereas for $Z_H = 1.2$ the even slightly larger value of 0.0085 was obtained.

A semi-empirical formula for α-alkyl proton splittings

From the assumption $|\beta_{\pi\sigma}| > |\beta_{\pi\sigma^*}|$ it follows that in equation 4.16 the first term can be neglected with respect to the third term. If the overlap in the σ-bond is neglected, then the second and fourth terms will have about the same magnitude. However, as has been remarked above, the inclusion of overlap leads to $\beta_{\pi\sigma} \approx \beta_{\pi\sigma^*}$ and $(I_\pi - E_\sigma) > (I_\sigma - E_\pi)$. Therefore, we also neglect the second term. Then we obtain from 4.16 for the splitting constant of α-alkyl protons

$$a_\alpha^H = \overline{\cos^2\theta} \sum_j \delta_j (\underline{c}_{j\alpha}^-)^2 \left\{ \frac{A_1}{(I_\sigma - E_\pi + \Delta E_j^-)^2} + \frac{A_2}{(I_\sigma - E_\pi + \Delta E_j^-)} \right\} \qquad 4.19$$

where A_1 and A_2 are constants and the terms $C_{\sigma j}$ have been neglected.
For a calculation of the splitting constants three parameters are needed. For methyl protons we have tried the formula

$$a_\alpha^H = \sum_j \delta_j (\underline{c}_{j\alpha}^-)^2 \left\{ \frac{60}{(2-\epsilon_0-\Delta\epsilon_j^-)^2} + \frac{40}{(2-\epsilon_0-\Delta\epsilon_j^-)} \right\} \qquad 4.20$$

where $\underline{c}_{j\alpha}^-$ is calculated as discussed in chapter III and ϵ_0 and $\Delta\epsilon_j^-$ are the orbital energy of the singly occupied orbital and the excitation energy of the negative ion in units β_0.
For methylene protons as in pyracene and in acenaphtene $\overline{\cos^2\theta} = 3/4$ instead of 1/2. For these protons 4.20 must be multiplied by 1.5. For methylene substituents bonded to two unsaturated carbon atoms α and β, $\underline{c}_{j\alpha}^-$ must be replaced by $(\underline{c}_{j\alpha}^- + \underline{c}_{j\beta}^-)$. This is important for molecules such as cyclohexadienyl and cycloheptatriene anion.

In this way we have calculated the α-alkyl proton splitting constants for a number of radicals. The results are given in table 4.4. The terms for $j \neq 0$ have been neglected for all radicals except diphenyl-m-tolylmethyl and cycloheptatriene anion where the terms for $j = 0$ do not contribute.

In the case of the cycloheptatriene anion our result differs essentially from the splitting constant obtained by application of McLachlan's formula 3.14 to molecular orbitals calculated according to the hyperconjugation model. According to Levy an Myers [39] the latter method yields a small negative splitting constant whereas in our approximation a positive splitting constant is obtained. The influence of the substituent on the spin density distribution in the π-electron system has been included by introduction of an inductive effect of $-0.3\beta_0$ (see section C.4).

	experimental	equation 4.20
9-methylanthracene cation [30]	7.79	8.2
anion [30]	4.27	5.2
9,10-dimethylanthracene cation [30]	8.00	9.2
anion [30]	3.88	4.2
pyracene cation [31]	12.80	12.2
anion [31]	6.58	6.2
acenaphtene anion [31]	7.53	6.7
1-methylnaphtalene anion [40]	3.86	4.0
2-methylnaphtalene anion [40]	1.81	1.27
diphenyl-p-tolylmethyl	2.93	2.4 2)
diphenyl-m-tolylmethyl	0.84	0.87 1) 2)
tri-p-tolylaminium ion	3.89	3.9 2) 4)
di-p-tolylnitrogen [41]	4.70	6.0 3) 4)
cyclohexadienyl [31]	47.7	60. 5)
cycloheptatriene anion [39]	2.16	4.3 1)

1) Terms for $j \neq 0$ included

2) Phenyl rings 30° rotated out of the plane of the three central bonds

3) Calculated for the planar radical

4) Nitrogen parameters: $\alpha_N = \alpha_0 + 1.5\beta_0$; $\beta_{CN} = \beta_{CC}$

5) In view of the large spin density on the methylene protons it might be better to renormalize the spin density. The calculated splitting then reduces to about 56 gauss.

Table 4.4. α-alkyl proton splittings (gauss) calculated according to equation 4.20

3. Spin polarization versus charge transfer

In several papers the question has been discussed whether the spin density on α-alkyl protons is caused by spin polarization or by charge transfer effects. In most of these papers, however, different definitions of spin polarization have been used.

From the correspondence between the equations 2.28 and 2.30 it seems reasonable to define spin polarization for α-alkyl protons as the first order mixing leading to 2.30. This definition has been used by Bolton, Carrington and McLachlan [30]. As we have shown before, this term might give a small contribution in calculations in which the overlap between σ- and π-orbitals is included but 2.30 alone is insufficient to explain the splitting constants of α-alkyl protons. Because Bolton, Carrington and McLachlan accepted McLachlan's valence bond calculation of 2.30, which leads to a non-negligible contribution, they have used the experimentally observed differences between positive and negative ions as an argument for the importance of charge transfer effects. In other papers [39, 42] it has been argued that the influence of charge transfer effects can be investigated by a measurement of the e.s.r. spectra of compounds such as cyclobutenyl and cycloheptatriene anion where the methylene protons are in a nodal plane of the singly occupied orbital. For these molecules charge transfer will have a very small influence on the splitting of the methylene protons whereas a spin polarization formula $a^H = Q(\rho_\alpha + \rho_\beta)$, where α and β are the two atoms to which the methylene group is bonded, predicts a large splitting. In cycloheptatriene anion a small splitting is observed [39], which has been considered as a proof of the charge transfer mechanism. This, however, is not correct because a spin polarization mechanism should also lead to a small splitting. From equation 2.30 it follows that the spin polarization contribution depends on

$$\langle \ldots \pi_a \sigma |H| \ldots \sigma^* \pi_a \rangle = c_{a\alpha}^2 \langle \ldots \alpha\sigma |H| \ldots \sigma^*\alpha \rangle + c_{a\alpha} c_{a\beta} \{ \langle \ldots \alpha\sigma |H| \ldots \sigma^*\beta \rangle + \langle \ldots \beta\sigma |H| \ldots \sigma^*\alpha \rangle \} + c_{a\beta}^2 \langle \ldots \beta\sigma |H| \ldots \sigma^*\beta \rangle$$

where the spin density in the π-electron system is approximated as the electron distribution in the singly occupied orbital Φ_a. The formula $a^H = Q(\rho_\alpha + \rho_\beta)$ is based on the neglect of the integrals $\langle \ldots \alpha\sigma |H| \ldots \sigma^*\beta \rangle$ and $\langle \ldots \beta\sigma |H| \ldots \sigma^*\alpha \rangle$. This is certainly correct for orthogonal π- and σ-orbitals. However, the spin density on α-alkyl protons is known to be positive for positive π-electron spin densities. Therefore the overlap terms within the exchange integrals can not be neglected and the exchange integrals will be negative. In this case the four integrals will have about the same value so for radicals where $c_{a\alpha} = - c_{a\beta}$ spin polarization also predicts a very small splitting.

Colpa and de Boer [31] define spin polarization as the interaction of the π-electron system with the pseudo-σ bonds of the hyperconjugation model. In this case spin polarization yields a very small splitting (the corresponding term for ring protons is always neglected). In a discussion which compares two possible mechanisms this definition does not give a reasonable alternative for charge transfer effects because a spin polarization of the pseudo-π bond is neglected. Moreover, a splitting in pseudo-π and pseudo-σ bonds can only be correct in molecular orbital calculations. Therefore this definition can not be used in a general discussion.

In Lazdins and Karplus' definition [33] the second order terms in equation 2.32 which are dependent on the triplet state of the C-H bond are considered as spin polarization terms. From our derivation of equation 4.17 it is obvious that in this case a large part of the charge transfer terms is called spin polarization even when the charge transfer terms are calculated in the hyperconjugation approximation. Therefore it is incorrect to conclude from Lazdins and Karplus' discussion that charge transfer effects can only explain about 50% of the experimental splitting constants (in a later paper with Colpa and de Boer [43] Lazdins and Karplus have corrected their original conclusion). If one adopts equation 4.20, it might be possible to consider the first term as the spin density obtained from a pseudo-hetero-atom approximation and the second term as the spin polarization contribution as defined by Lazdins and Karplus. This, however, is somewhat dangerous because a clear separation into two non-overlapping terms is only possible when the $\pi \rightarrow \sigma$ charge transfer terms are completely neglected.

4. The influence of the substituent on the spin density distribution in the π-electron system

The influence of substituents on the wave functions for the π-electron system is usually discussed in terms of inductive and conjugative effects. An inductive effect is introduced by a change $\delta_{\mu} \beta_0$ in the α-value for the carbon atom(s) C_{μ} to which the substituent is bonded. This change causes a mixing of the molecular orbitals for the unsubstituted system. In first order we obtain

$$\phi_i' = \phi_i - \sum_{j\neq i}\sum_{\mu} \frac{c_{i\mu}\, c_{j\mu}\, \delta_{\mu}\, \beta_0}{(\epsilon_j - \epsilon_i)}\, \phi_j$$

$$\epsilon_i' = \epsilon_i + \sum_{\mu} c_{j\mu}^2\, \delta_{\mu}\, \beta_0$$

For simplicity we consider a radical where the electron distribution in the singly occupied orbital is a good approximation of the spin density distribution in the π-electron system. Then the spin density in the $2p_z$-orbital of carbon atom C becomes

$$(c'_{a\nu})^2 = c_{a\nu}^2 - 2 \sum_{j\neq a}\sum_{\mu} \frac{c_{a\mu}\, c_{j\mu}\, c_{a\nu}\, c_{j\nu}\, \delta_{\mu}\, \beta_0}{(\epsilon_j - \epsilon_a)}$$

A conjugative effect causes in first order a mixing of π- and σ-electron wave functions whereas in second order a mixing of the π-electron wave functions via the σ-functions is obtained. When we assume that the wave functions for the σ-bonds are calculated in a molecular orbital approximation, then the molecular orbitals for the perturbed π-electron system become

$$\phi_i' = \phi_i - \sum_r \sum_\mu \frac{c_{i\mu}\, \beta_{\mu r}\, \phi_\sigma^r}{(\epsilon_\sigma^r - \epsilon_i)} + \sum_{j\neq i}\sum_\mu \sum_r \frac{c_{i\mu}\, c_{j\mu}\, \beta_{\mu r}^2\, \phi_j}{(\epsilon_\sigma^r - \epsilon_i)(\epsilon_j - \epsilon_i)}$$

$$- \frac{1}{2} \sum_r \sum_\mu \frac{c_{i\mu}^2\, \beta_{\mu r}^2\, \phi_i}{(\epsilon_\sigma^r - \epsilon_i)^2}$$

The orbital energy is

$$\epsilon_i' = \epsilon_i - \sum_r \sum_\mu \frac{c_{i\mu}^2\, \beta_{\mu r}^2}{(\epsilon_\sigma^r - \epsilon_i)^2}$$

where r enumerates the σ-orbitals.

The spin density in the perturbed system becomes

$$(c'_{a\nu})^2 = c_{a\nu}^2 \left\{ 1 - \sum_r \sum_\mu \frac{c_{a\mu}^2\, \beta_{\mu r}^2}{(\epsilon_\sigma^r - \epsilon_a)^2} \right\} + 2 \sum_r \sum_\mu \sum_{j\neq a} \frac{c_{a\mu}\, c_{j\mu}\, c_{a\nu}\, c_{j\nu}\, \beta_{\mu r}^2}{(\epsilon_\sigma^r - \epsilon_a)(\epsilon_j - \epsilon_a)}$$

The coefficient of $c_{a\nu}^{2}$ in this formula assures the normalization of the spin density. As has been remarked by Bolton, Carrington and McLachlan [30], the remaining terms can also be obtained from the formula for an inductive effect by substitution of

$$\delta_{\mu} = -\sum_{r} \frac{\beta_{\mu r}^{2}}{(\epsilon_{\sigma}^{r}-\epsilon_{a})\beta_{0}}$$

In the hyperconjugation model

$$\frac{\beta_{\mu,-r}^{2}}{(\epsilon_{\sigma}^{-r}-\epsilon_{a})} \approx -\frac{\beta_{\mu r}^{2}}{(\epsilon_{\sigma}^{r}-\epsilon_{a})}$$

where (-r) represents the antibonding σ-orbital which corresponds to the bonding orbital Φ_{σ}^{r}. As has been remarked by de Waard [28] this means that in the hyperconjugation model the influence of the substituent on the spin density distribution in the π-electron system is negligibly small.

If we assume, as before, that $|\beta_{\mu r}| > |\beta_{\mu,-r}|$, then the mixing via the antibonding orbitals can be neglected. For methyl substituents the mixing via the three bonding orbitals can be replaced by the mixing via one linear combination of π-symmetry. So, the influence of the substituent on the π-electron spin density distribution can be calculated in the pseudo-hetero-atom approximation. From equation 4.20 it is obvious that in this approximation the energy of the σ-orbital is $\alpha_{0} + 2\beta_{0}$. If we assume $Z_{H} = 1.2$, then it follows from 4.20 that $\beta_{\mu\sigma}$ will be 0.6 to 0.65β_{0}. On substitution of these values it appears that for naphtalene anions these parameters correspond to an inductive effect of -0.15 to -0.20β_{0}. For the ring proton splittings of dimethyl substituted naphtalene anions a good agreement is obtained with an inductive effect of -0.3β_{0} [27,28,29], so to the pseudo-hetero-atom parameters an inductive effect of -0.10 to -0.15β_{0} must be added. For naphtalene cations this combination of parameters corresponds to an inductive effect of -0.4β_{0}. For calculations of spin density distributions the difference between the pseudo-hetero-atom approximation and an inductive-effect-calculation will therefore be small.
In our calculations in section C.2 we have used an inductive effect only because in this case a smaller number of parameters is needed.

D. β-PROTONS OF ALKYL SUBSTITUENTS

For σ-bonds having a weak interaction with the π-electron system the coupling via other σ-bonds might also be of importance. Therefore the spin density in these bonds can not be calculated from equation 2. 32 but a more general formula is needed which also contains the interaction via other σ-bonds. In equation 2. 36 we have included the interaction via one σ-bond A. The derivation of a more general formula is practically impossible therefore we assume that 2. 36 may be generalized by summing over all possible σ-bonds A. Even in this case a reasonable calculation of the spin density is very difficult because, as can easily be shown, the different terms in 2. 36 may give both positive and negative contributions in the final spin density on the proton. Moreover, the averaging of the spin density over all possible orientations of the C-H bond is much more complicated than for α-alkyl protons. These problems are clearly demonstrated by the measurements of de Boer and MacLean [40] and of Hausser, Brunner and Jochims [44] (table 4. 5), which show that the splitting constants of β-alkyl protons may have positive and negative values without a difference in the sign of the π-electron spin density on the carbon atom to which the substituent is bonded.

	Splitting constant (milligauss) of protons in position			
	α	β	γ	δ
naphtalene anions [40]				
1-CH_3	+ 3860			
1-C_2H_5	+ 3280	- 74		
1-C_3H_7	+ 2670	- 212	+ 64	
1-C_4H_9	+ 2800	- 155	+ 45	+ 35
2-CH_3	+ 1810			
2-C_2H_5	+ 1130	+ 32		
2-C_3H_7	+ 1080	$\leqslant 2$	+ 27	
2-C_4H_9	+ 1050	---	--	+ 20
di-t-butylnitroxide [44]		- 107		
2, 4, 6-tri-t. butylphenoxyl [44] (protons of 2- and 6-substituents)		+ 72		

Table 4. 5. Splitting constants of alkyl protons

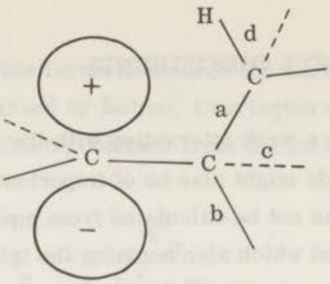


Fig. 4.1. Numbering of σ-bonds in alkyl substituents

Due to this difference in sign it is rather dangerous to neglect one of the terms in 2.36. In a first approximation, however, it seems reasonable to neglect all terms depending on $(I_A - E_B)$ or $(I_B - E_A)$. Equation 2.36 then reduces to the terms K(1, 2) and N(1, 2).

In the evaluation of K(1, 2), which may be called the spin polarization contribution, we assume that all terms except the spin polarization due to the spin density in the neighbouring C-C bond a (see fig. 4.1) can be neglected. Consequently

$$K(1,2) = \frac{\int \rho^{a}(1,2)\, H\, \rho^{d}_{ST}(1,2)\, d\tau_1\, d\tau_2}{\Delta E^{T}_{d}}\, \rho^{d}_{ST}(1,2)$$

From the orthogonality of the hybrid orbitals on one atom and the sign of the spin density in bond a it follows that the spin density on the proton due to K(1, 2) is negative for a positive value of the π-electron spin density on the carbon atom to which the substituent is bonded. Because the spin density in a varies as $\cos^2\theta$, K(1, 2) will also be proportional to $\cos^2\theta$.

In N(1, 2) we neglect the π→a charge transfer wave functions as before. The π→d terms, however, are not negligible because it might easily be possible that for some orientations of the C-H bond $|\beta_{\pi\sigma^*}| > |\beta_{\pi\sigma}|$. Consequently N(1, 2) can be calculated by replacing $\underline{\pi}_j^+$ and $\underline{\pi}_j^-$ in equation 2.32 by

$$\underline{\pi}_j^+ \quad \text{and} \quad \underline{\pi}_j^- + \sum_{A=a,b,c} \frac{\langle \underline{\pi}_j^- |H| \underline{A}_S^+ \rangle\, \underline{A}_S^+}{(I_A - E_\pi + \Delta E_j^- + C_{Aj})}$$

respectively. An actual calculation, however, is very difficult. The direct interaction of bond d with the π-electron system is not negligible. When we consider this term only, then for many orientations of the C-H bond the same difficulties are encountered as in the calculation of the spin density in the carbon orbital of α-CH bonds because now $|\beta_{\pi h}| > |\beta_{\pi c}|$. Moreover, in the calculation of the interaction with the π-electron system a restriction to the $2p_z$-orbital of the carbon atom, to which the substituent is bonded, is highly questionable. Finally it must be noted that for a conformation, in which bond a is in the nodal plane of the π-electron system, the direct interaction and the coupling via bond b and bond c do not vanish so, even for freely rotating substituents, the contribution of N(1, 2) is not proportional to $\cos^2\theta$.

If we assume that the contribution from N(1, 2) is positive and has a smaller variation with θ than K(1, 2), then we should conclude that the contribution of the negative terms becomes more important when bond a is lifted out of the nodal plane of the π-electrons. It is easy to show that a smaller probability of a conformation where bond a is in the nodal plane leads to a smaller averaged splitting of the α-alkyl protons. Therefore we should expect that a smaller value of the α-alkyl proton splitting is coupled with a more negative value of the β-alkyl proton splitting. This is in agreement with the observed variations of the splitting constants of 1-alkyl substituents in naphtalene anions (see table 4. 5). In the same way the difference in sign between the β-proton splittings of 1- and 2-alkyl substituents can be attributed to the steric interference of a 1-alkyl substituent with the proton at C_8 which makes one of the two conformations, where bond a is in the nodal plane, very unlikely. On the other hand, from this interpretation we should expect a relatively larger splitting of the α-protons of the 2-alkyl substituents which is not in agreement with the experimental values.

From these considerations it will be clear that a reliable calculation of β-proton splittings is at present practically impossible. It might be, however, that a reasonable approximation becomes possible when more experimental values of β-alkyl proton splittings are known. Especially a knowledge of the sign of these splittings will be of importance.

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CHAPTER V

ELECTRON SPIN RESONANCE OF TRIPHENYLMETHYL AND RELATED COMPOUNDS

A. INTRODUCTION

Triphenylmethyl, the first known free radical [1], was one of the first radicals being studied by electron spin resonance [2]. The most important result from these early investigations was the serious discrepancy between the observed hyperfine structure and spin densities obtained from the simple molecular orbital theory. This problem could be solved by a valence bond approximation [3,4] and by molecular orbital calculations including configuration interaction [5,6] from which a negative spin density in the $2p_z$-orbital of the meta carbon atoms was obtained.

A further study of triphenylmethyl radicals is interesting for several reasons:

1. As has been discussed in chapter IV, the splitting constants of positive and negative ions of alternant hydrocarbons are different. These differences are usually ascribed to effects which are opposite for positive and negative ions and vanish in neutral alternant radicals. From these theories one should therefore expect that McConnell's formula 4.11 is accurately valid for neutral alternant radicals. This has never been proved to be correct.

2. As will be shown later, the influence of substituents on the spin density distribution in the π-electron system of neutral alternant radicals is small. These radicals are therefore very well suited for a study of the propagation of spin density into the substituent. A second advantage of neutral alternant radicals

in these investigations is the occurrence of negative spin densities in the π-electron system; the propagation of a negative spin density can not be calculated with simple molecular orbital theory.

3. Finally it may be hoped that the e.s.r. spectra of substituted triphenylmethyl radicals give important information about the influence of substituents on the sterical structure.

Despite the large number of investigations on triphenylmethyl itself, relatively little is known about the e.s.r. spectra of substituted triphenylmethyl radicals. In our laboratory Lupinski [7] has measured the e.s.r. spectra of some of these compounds but at that time the technique of obtaining highly resolved spectra was insufficiently developed to obtain reliable sets of splitting constants. In later papers some spectra have been published (see table 5.1) but only Sinclair [8] has discussed the e.s.r. spectra of a larger series of (halogen-) substituted radicals.

In section B of this chapter we shall discuss the measurement and interpretation of the e.s.r. spectra of a number of phenyl-, alkyl-, chlorine- and methoxyl-substituted radicals. A theoretical discussion of the resulting splitting constants is presented in section C. In section D the e.s.r. spectra of 'biradicals' related to triphenylmethyl will be considered.

B. MEASUREMENT AND INTERPRETATION OF THE E.S.R. SPECTRA

1. Preparation of the radicals

The triarylmethyl radicals were prepared from the corresponding triarylmethanols according to

$$\mathrm{Ar_3C\text{-}OH} \xrightarrow{\mathrm{CH_3COCl}} \mathrm{Ar_3C\text{-}Cl} \xrightarrow{\mathrm{Ag}} \mathrm{Ar_3C^{\cdot}} \rightleftarrows \mathrm{(Ar_3C)_2}$$

Tri-p-biphenylylmethanol, tris(p-tert.butylphenyl)methanol, tris(p-ethylphenyl)-methanol and 9-mesitylfluorenol were obtained from the department of physical chemistry to which they were given by Prof. Theilacker. The other triarylmethanols were available at the laboratory or were prepared from substituted benzophenones or benzoic acids by Grignard methods [13].

In the preparation of the chloromethanes the alcohols were boiled with acetylchloride for one hour. In many cases the chloromethane was not isolated but a solution in acetylchloride was prepared from a few milligrams of the alcohol, transferred to apparatus B (see below) and converted into the radical.

The radicals were prepared in vacuum (10^{-5} torr) in toluene solution.

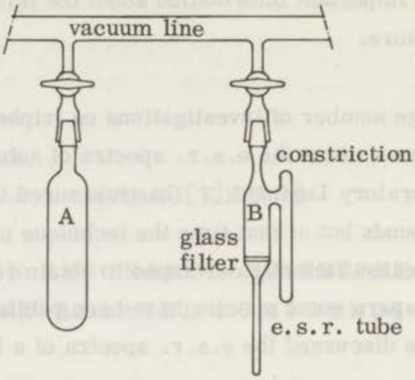


Fig. 5.1. Apparatus for the preparation of radical solutions

Toluene (Merck, p.a.) was dried on molecular seeves, refluxed on sodium for one hour and transferred to the storage vessel A (fig. 5.1). After dissolving some triphenylchloromethane, nitrogen was passed through and some silver (B.D.H. silver precipitated) was added. The storage vessel was connected to the vacuum line and the toluene was thoroughly degassed by freezing and melting. The dissolved radical removes the last traces of impurities. The solvent can be used as long as the colour of the radical is visible.

The radicals were prepared in apparatus B (fig. 5.1). After introduction of 2 mg of the chloromethane and 100 mg of silver B was connected to the vacuum line. In order to remove traces of acetylchloride and water as much as possible, B was evacuated for several hours. By cooling B with liquid nitrogen a few ml of the solvent were distilled from A after which B was sealed off at the constriction. The radicals were prepared by shaking for 10 to 15 minutes.

2. The measurement of the e.s.r. spectra

The e.s.r. spectra were taken on a super-heterodyne spectrometer equipped with a Varian 12-inch magnet. The principles of this apparatus have been described by Lupinski [7] but later on important improvements were introduced by Horsman [14]. At the time of most of our measurements no reliable method for the measurement of differences in magnetic field was present in the laboratory. Therefore the spectra were calibrated by comparison with the spectrum of triphenylmethyl for which the splitting constants were taken from the literature [15,16]. In order to obtain a correct calibration, the central parts of the spectrum of triphenylmethyl and of the spectrum which has to be calibrated were measured several times in exactly the same way (including the past history of the magnet). From later measurements of the magnetic field we obtained splitting constants for triphenylmethyl which are slightly different from the values reported in the literature. All spectra were recalibrated with these new values except the spectra for tris(p-chlorophenyl)-methyl and diphenyl(p-chlorophenyl)methyl which were calibrated directly from measurements of the magnetic field.

The e.s.r. spectra were measured on solutions in the e.s.r. tube of apparatus B (fig. 5.1). In order to obtain highly resolved spectra of sufficient intensity, the concentration of the solutions was varied by distillation of solvent from the side tube of B. The final concentrations are not known but are probably of the order of 10^{-5} to 10^{-4} Mol/l.

In several papers [15,16,17] it is assumed that highly resolved spectra of triarylmethyl radicals can only be obtained at temperatures of -20 to -50°C. The observed effect of temperature on the line width is caused by the fact that in these investigations the radical concentration at room temperature was too large to obtain a high resolution. At lower temperatures the concentration will be less because of the smaller dissociation of the dimer (for a recent discussion of the structure of the dimer of triphenylmethyl see reference 18). We have observed that by dilution the line width in the spectrum of triphenylmethyl can be reduced to about 25 milligauss. This value remains unaltered on cooling to about -25°C which is in agreement with the observed temperature-independence of the line width in the spectrum of tris(p-nitrophenyl)methyl [9]. The spectra discussed in this chapter are measured at room temperature.

3. The e.s.r. spectra and their interpretation

For most of the radicals, we have studied, highly resolved e.s.r. spectra could be obtained. As usual we have tried to analyse these spectra by trial and error. From the observed spectrum and other data, e.g. the splitting constants of similar radicals, a set of splitting constants was assumed and the corresponding derivative spectrum was calculated with a computer program. When the agreement with the observed spectrum was considered to be insufficient. then the calculation was repeated with a new set of splitting constants. For radicals having a small number of different splitting constants the computed spectrum is almost identical to the observed one. An example has been given in fig. 5.18. For radicals with a large number of splitting constants each line in the observed spectrum is a superposition of a large number of lines. Therefore the form of the spectrum and the intensity of the individual lines can only

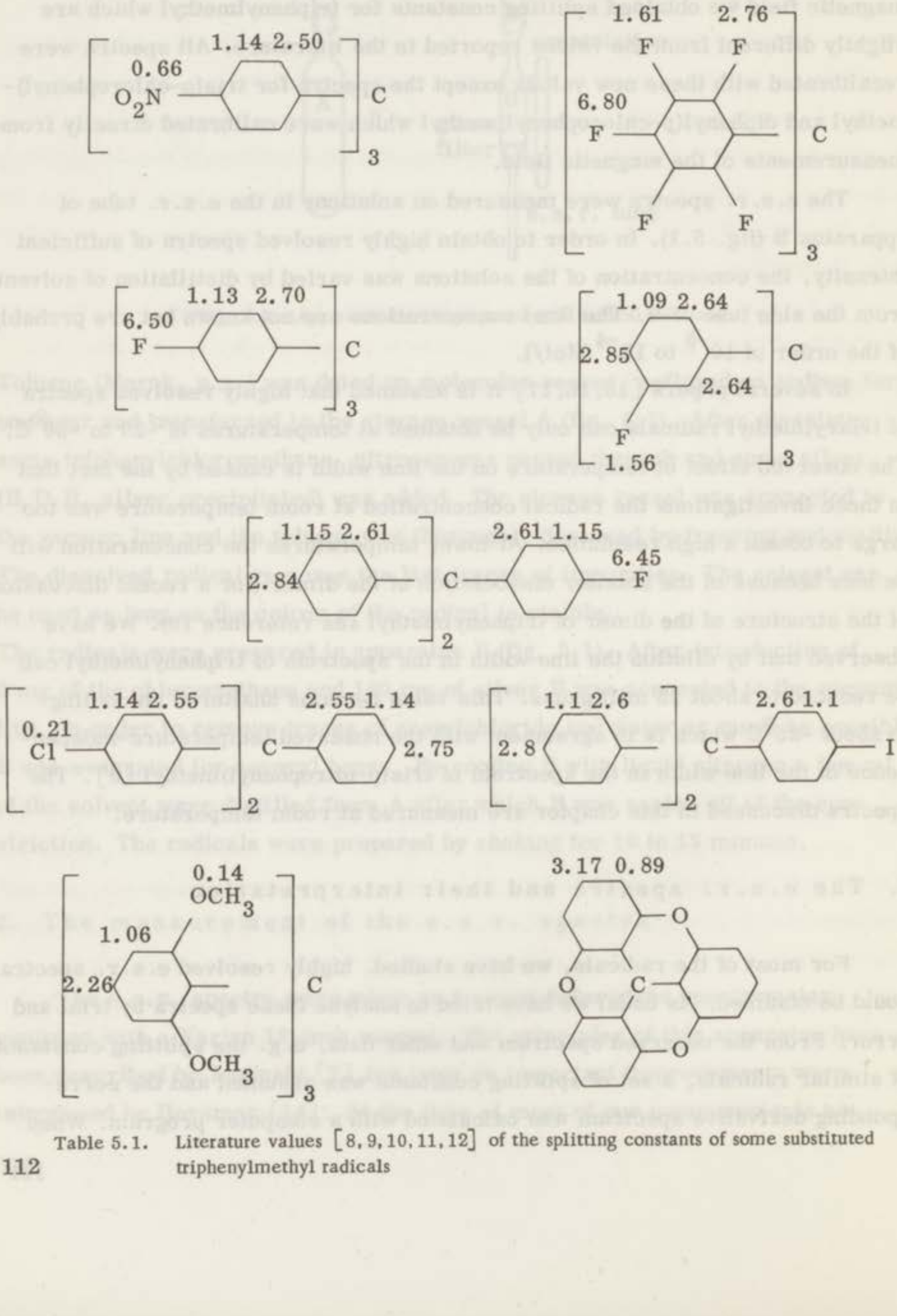


Table 5.1. Literature values [8, 9, 10, 11, 12] of the splitting constants of some substituted triphenylmethyl radicals

be reproduced exactly with very accurate values of the splitting constants. In practice this means that an exact reproduction is unfeasible. An example of a computed spectrum, which we assumed to be in agreement with the observed one, is given in fig. 5.4. In this case the final interpretation of the spectrum is based both on the computed spectrum and on the splitting constants of similar radicals so, in our opinion, the final set of splitting constants is correct. In a more general case, however, it is not certain that other sets of splitting constants can be excluded. For phenyl(p-methoxyphenyl)-p-biphenylylmethyl we could obtain two different sets of splitting constants for which the computed spectrum shows a clear resemblance with the observed one (fig. 5.19). One of the two possibilities seems to be in slightly better agreement with the observed spectrum but the differences are too small to allow of a definite conclusion.

The possible error in the final splitting constants is estimated to be 1% for values larger than 2 gauss whereas smaller splittings will be somewhat less accurate. In table 5.1 we have collected some literature values for other triphenylmethyl radicals.

In the following the interpretation of the e.s.r. spectra will be discussed in more detail.

Triphenylmethyl

A completely resolved spectrum for triphenylmethyl (fig. 5.2) has first been obtained by Chesnut and Sloan [15]. According to these authors the splitting constants are 2.77, 2.53 and 1.11 gauss for para, ortho and meta protons respectively. From ENDOR measurements Hyde [19] obtained values which are 3 to 4% larger. Our values:

are between these two results. The usual assignment of the splitting constants for ortho and meta protons is based on theoretical arguments. A clear experimental proof is obtained by comparison with the splitting constants of ortho- and meta-substituted radicals.

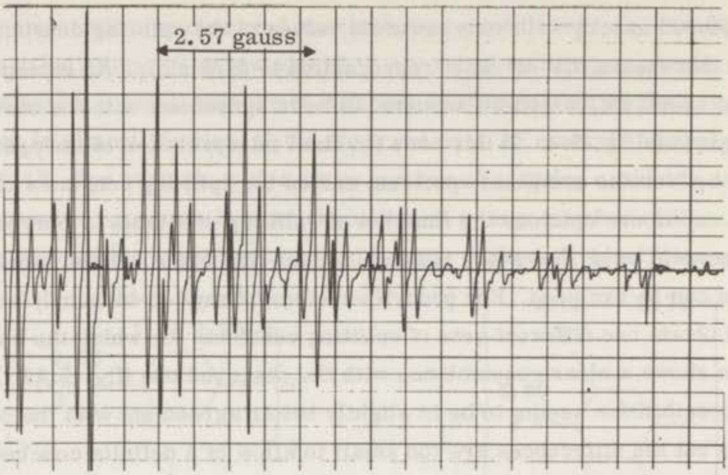
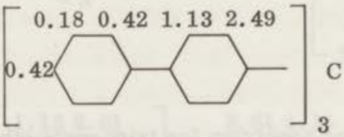


Fig. 5.2. E.s.r. spectrum of triphenylmethyl (high-field half)

Tri-p-biphenylylmethyl and diphenyl-p-biphenylylmethyl

The splitting constants of tri-p-biphenylylmethyl:



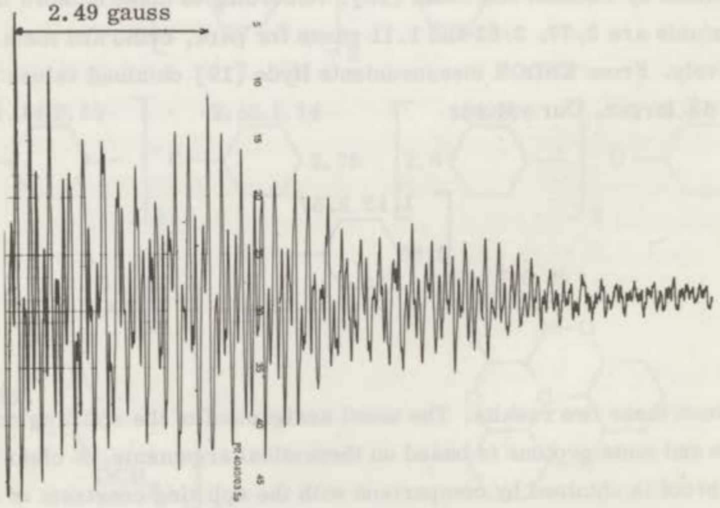


Fig. 5.3. E.s.r. spectrum of tri-p-biphenylylmethyl (high-field half)

are easily found from the observed spectrum (fig. 5.3). The assignment of the splitting constants has been made from the assumption that the spin density distribution in the different rings of this radical is analogous to the distribution in the rings of triphenylmethyl.

In the spectrum of diphenyl-p-biphenylylmethyl (fig. 5.4) a large number of lines with a relatively small difference in intensity is observed. In general it is very difficult to analyse this type of spectrum without a further knowledge of the spin density distribution. In this case, however, we may assume that the

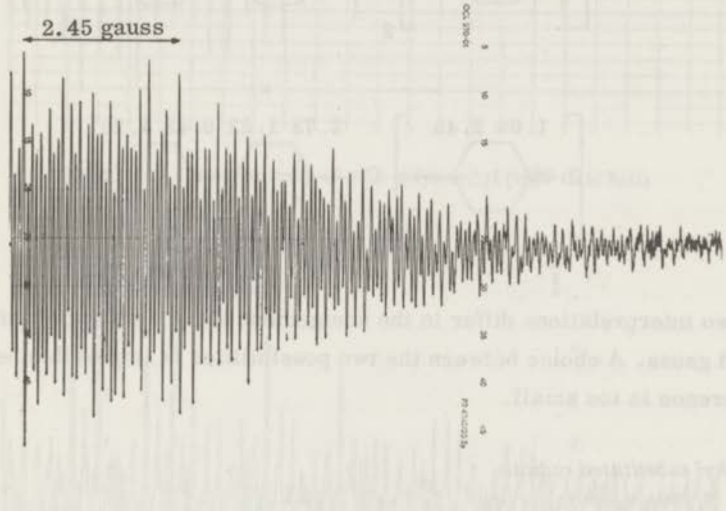
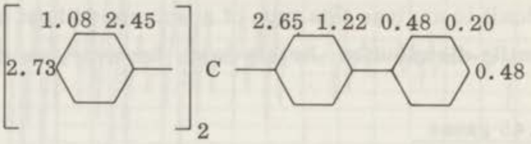
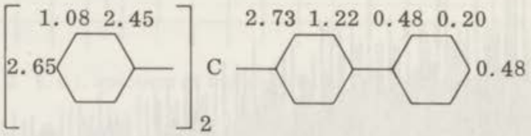


Fig. 5.4. Experimental and calculated e.s.r. spectra of diphenyl-p-biphenylylmethyl (high-field half)

splitting constants will not differ very much from those in triphenylmethyl and tri-p-biphenylylmethyl. After several less successful estimations a good agreement between calculated and observed spectrum was obtained with a set of splitting constants which can be interpreted in two different ways:

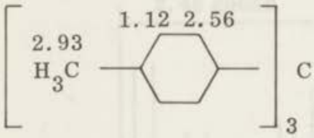


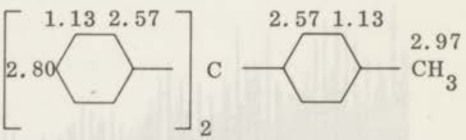


These two interpretations differ in the assignment of the splitting constants 2.65 and 2.73 gauss. A choice between the two possibilities is impossible because the difference is too small.

Para-methyl substituted radicals

The splitting constants of tri-p-tolylmethyl and diphenyl-p-tolylmethyl:





can easily be found from the observed spectra (figs. 5.5 and 5.6). Our values for diphenyl-p-tolylmethyl are about 2% smaller than the values given by Sinclair [8].

In order to compare the splitting constants of the methyl protons we have also measured the e.s.r. spectrum of tri-p-tolylaminium ion (fig. 5.7). In this spectrum the line width is not a constant. The calculation of the spectrum from assumed splitting constants has therefore been carried out with a variant of the usual program. In this calculation we assumed that the line width depends on the magnetic quantum number of the nitrogen nucleus. Van Willigen [20] has observed the same asymmetry in the spectrum of the triphenylaminium

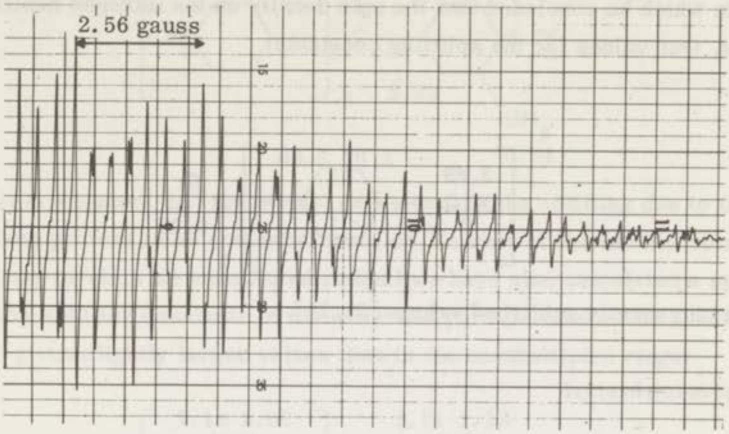


Fig. 5.5. E.s.r. spectrum of tri-p-tolylmethyl (high-field half)

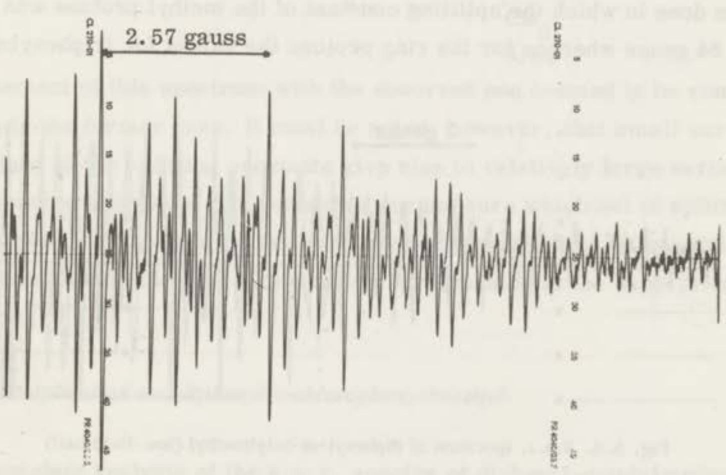


Fig. 5.6. E.s.r. spectrum of diphenyl-p-tolylmethyl (high-field half)

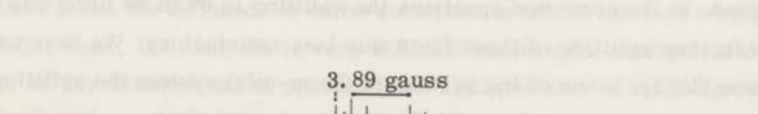
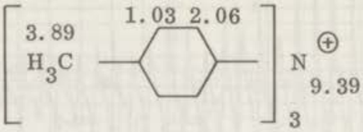


Fig. 5.7. E.s.r. spectrum of tri-p-tolylaminium ion

ion from which he concluded that the spin density on the nitrogen nucleus is positive. Our values for the splitting constants:



agree with recently published values [21,22].

Diphenyl-m-tolylmethyl

In the e.s.r. spectrum of diphenyl-m-tolylmethyl (fig. 5.8) 80 to 90 lines are observed each consisting of a number of closely spaced lines. A calculation has been done in which the splitting constant of the methyl protons was taken to be 0.84 gauss whereas for the ring protons the values for triphenylmethyl were used. In the computed spectrum the splitting in 80 to 90 lines was observed but the further splitting of these lines was less satisfactory. We have assumed therefore that for some of the protons of the m-tolyl system the splitting constant is slightly different from the value for the unsubstituted rings. In a first series of calculations part of the ortho and para protons of the substituted ring were given somewhat smaller splitting constants than in the unsubstituted rings. In these calculations the best agreement with the observed spectrum was obtained with the set of splitting constants:

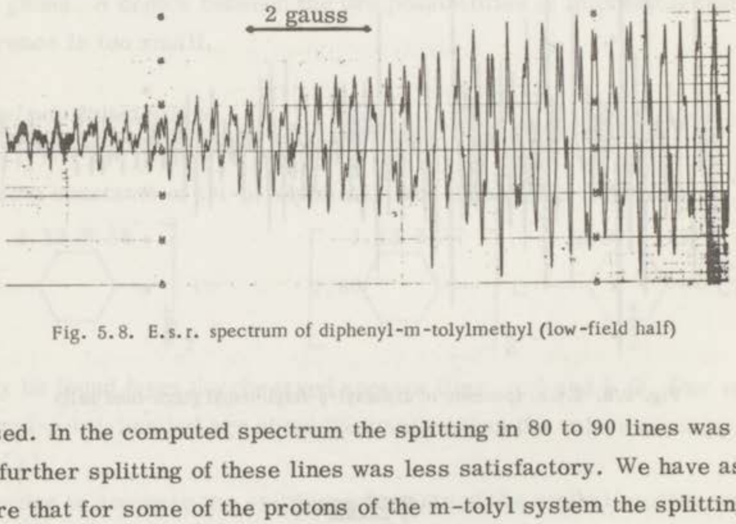
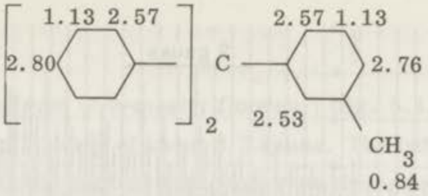
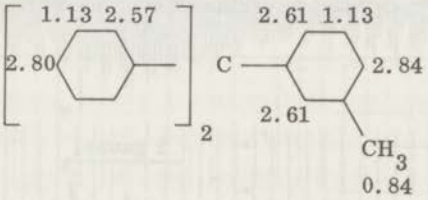


Fig. 5.8. E.s.r. spectrum of diphenyl-m-tolylmethyl (low-field half)



in which it is assumed that the methyl group causes the splitting due to the neighbouring protons to be somewhat smaller. In view of the results obtained for the mono-m-chlorine substituted radical we have also calculated a spectrum in which the splitting constants of the ortho and para protons of the substituted ring were given slightly larger values than in the unsubstituted rings:



The agreement of this spectrum with the observed one seemed to be somewhat less than in the former case. It must be noted, however, that small variations in the values of the splitting constants give rise to relatively large variations in the computed spectrum. Therefore we are not sure which set of splitting constants must be regarded as the correct one. It might even be possible that other combinations also give a reasonable agreement with the experimental spectrum.

Diphenyl-o-tolylmethyl and diphenyl(o-chlorophenyl)methyl

A complete analysis of the e.s.r. spectra of diphenyl-o-tolylmethyl (fig. 5.9) and diphenyl(o-chlorophenyl)methyl (fig. 5.10) should give important information about the influence of ortho substituents on the sterical configuration. On the other hand, the analysis is very difficult because the configuration is unknown. In our calculations of spectra from assumed sets of splitting constants some resemblance with the observed spectra was obtained but the differences were too large for a correct analysis (Sinclair's attempts [8] to analyse the spectrum of diphenyl(o-fluorophenyl)methyl were also not successful). Because many distances between intense lines in both spectra are nearly equal, it seems to be probable that the splitting constants have about the same value which means that the radicals have about the same structure but further conclusions

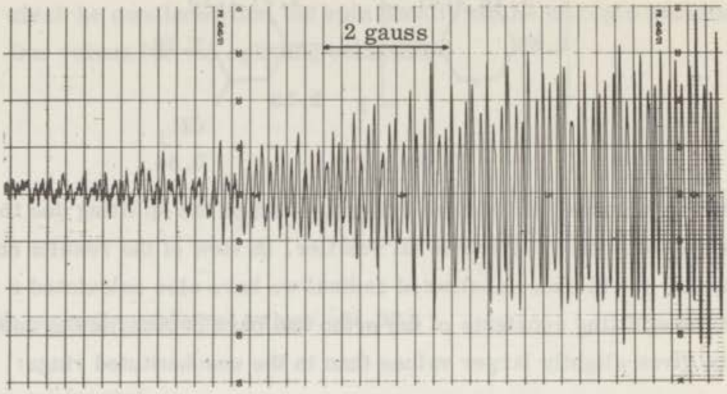


Fig. 5.9. E.s.r. spectrum of diphenyl-o-tolylmethyl (low-field half)

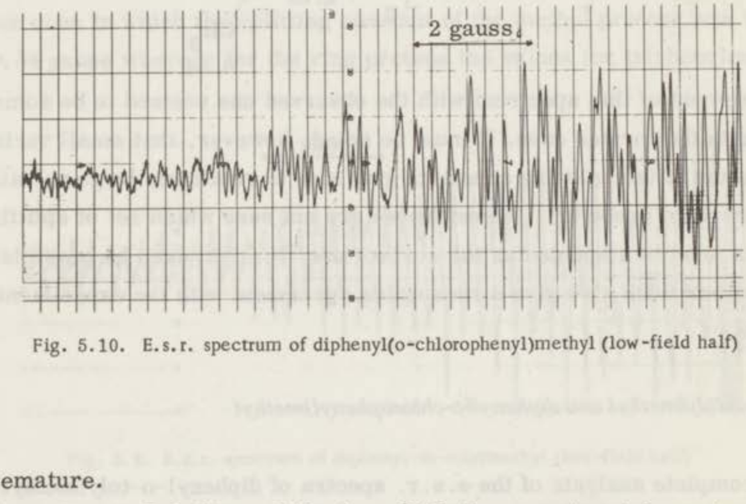


Fig. 5.10. E.s.r. spectrum of diphenyl(o-chlorophenyl)methyl (low-field half)

are premature.

According to Judeikis and Kivelson [17] the experimental spectrum of diphenyl-o-tolylmethyl can be approximated with a spectrum calculated from a combination of the splitting constants of triphenylmethyl with a methyl proton splitting of 2.2 gauss. In view of our spectrum, which is much better resolved, this interpretation seems to be unlikely. Sinclair [8] has shown that the spectrum of diphenyl-o-tolylmethyl is temperature-dependent. This may be ascribed to a hindered rotation of the methyl group or to a mixture of two radicals having a different structure.

9-mesitylfluorenyl

The e.s.r. spectrum of 9-mesitylfluorenyl (fig. 5.11) consists of five groups of lines with a spacing of about 3.5 gauss. The outer groups have about the same structure as the central group whereas the second and fourth groups may be regarded as a superposition of two groups having the same structure as the central and outer groups. This means that there are two different splitting constants of about 3.5 gauss caused by two sets of two protons. The remaining five splitting constants determine the structure of the groups. From the structure of the groups we should conclude that most of these five splitting constants are simple multiples of a common value but the fact that even the two larger splitting constants could not be determined with certainty hampered a further analysis of the spectrum.

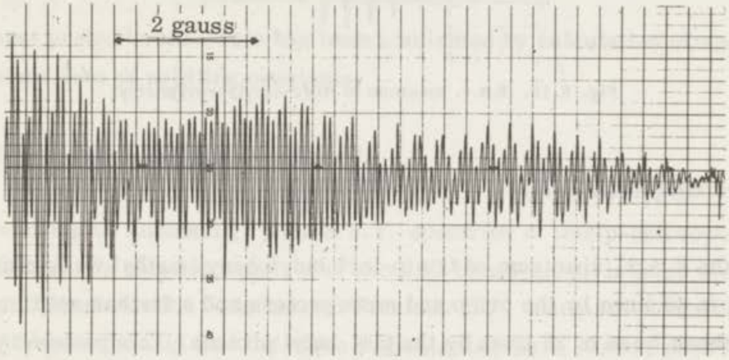


Fig. 5.11. E.s.r. spectrum of 9-mesitylfluorenyl (high-field half)

Tris(o-ethylphenyl)methyl

In the measurement of the spectrum of tris(o-ethylphenyl)methyl no further resolution could be obtained than a splitting in 15 to 17 broad lines (fig. 5.12). The total width of the spectrum is of the order of 20 to 25 gauss which is smaller than the total width for triphenylmethyl. This is in agreement with the expected larger rotation of the rings out of the plane of the three central bonds.

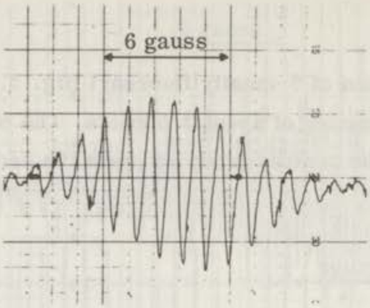


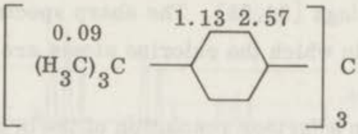
Fig. 5.12. E.s.r. spectrum of tris(o-ethylphenyl)methyl

Tris(p-tert.butylphenyl)methyl

In the e.s.r. spectrum of tris(p-tert.butylphenyl)methyl we expect a splitting in 49 lines by the ortho and meta protons and a further splitting of each of these lines in 28 lines by the tert.butyl protons. This pattern is clearly visible in the observed spectrum (fig. 5.13). The interpretation of this spectrum is somewhat hampered by the strong overlapping of the groups of lines. It is therefore not easy to determine the splitting constants of the ortho and meta protons within one tert.butyl proton splitting (see also tris(p-methoxyphenyl)-methyl). From the position of the groups of lines in the wings of the spectrum

Fig. 5.13. E.s.r. spectrum of tris(p-tert.butylphenyl)methyl (high-field half)

it appeared that the set of splitting constants:



is the most probable one. This has been confirmed by calculation of spectra for different sets of splitting constants.

*Para- and meta-chlorine substituted radicals *)*

According to Lupinski [7] the e.s.r. spectrum of tris(p-chlorophenyl)-methyl in benzene solution consists of about 13 broad lines. In later measurements in toluene solution Judeikis and Kivelson [17] could not obtain a further splitting despite the fact that the other radicals they have studied show a much better resolution. This was ascribed to unresolved hyperfine splittings and quadrupole moment effects arising from the two chlorine isotopes.

In our measurements in toluene solution the same results were obtained after short reaction times. A prolonged reaction with silver leads to a gradual change in the spectrum. Finally a sharp spectrum (fig. 5.14) is obtained having a hyperfine structure which is easily interpreted as being caused by two sets

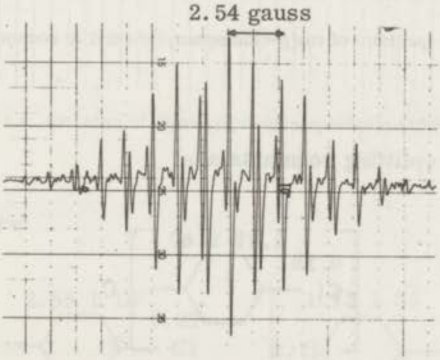


Fig. 5.14. E.s.r. spectrum of the reaction product of tris(p-chlorophenyl)chloromethane with silver after long reaction times

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*) The e.s.r. spectra of the chlorine substituted radicals have been published in reference 23.

of six equivalent protons with splitting constants of 2.54 and 1.14 gauss. It is well known that the prolonged reaction with silver leads to a removal of the chlorine atoms in the rings [24,25]. The sharp spectrum must therefore be attributed to a radical in which the chlorine atoms are replaced by (substituted) triphenylmethyl groups.

In acetone solution a further resolution of the broad spectrum could be obtained after short reaction times (fig. 5.15), probably because of the lower viscosity of the solvent. This spectrum clearly shows a splitting due to the chlorine atoms. The splitting constants are:

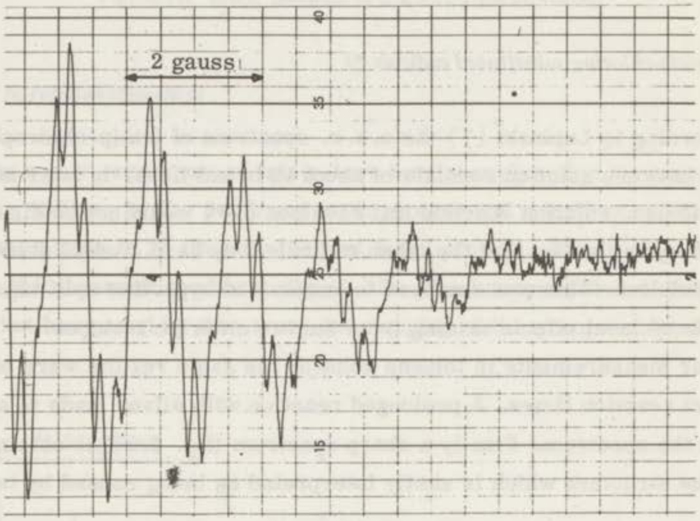
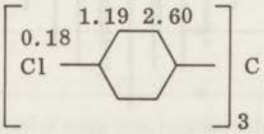


Fig. 5.15. E.s.r. spectrum of tris(p-chlorophenyl)methyl in acetone (high-field half)



In the computed spectrum the influence of both chlorine isotopes has been included. The line width was estimated to be 150 milligauss.

The spectra obtained for diphenyl(p-chlorophenyl)methyl (fig. 5.16) and diphenyl(m-chlorophenyl)methyl (fig. 5.17) could easily be interpreted. The

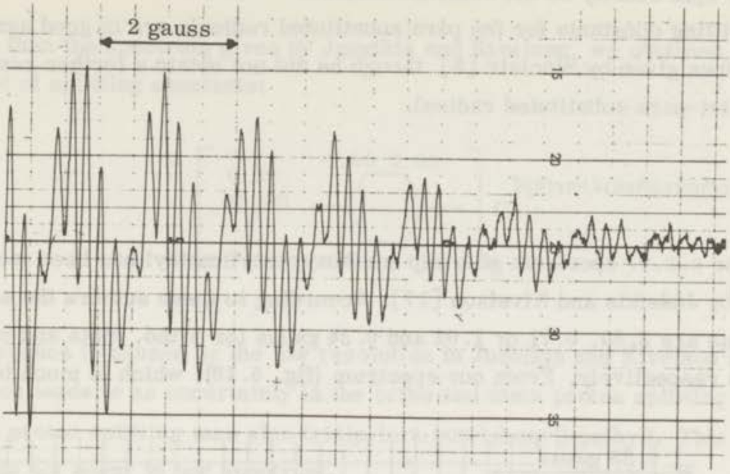


Fig. 5.16. E.s.r. spectrum of diphenyl(p-chlorophenyl)methyl (high-field half)

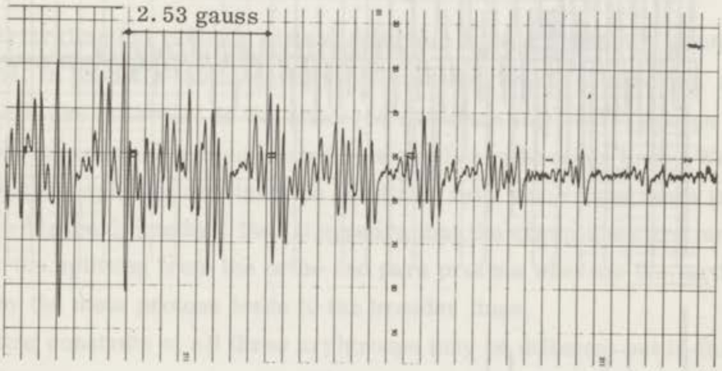
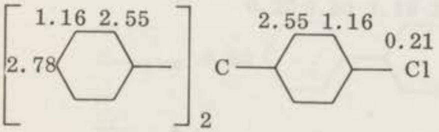
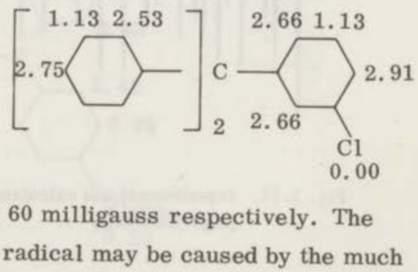


Fig. 5.17. E.s.r. spectrum of diphenyl(m-chlorophenyl)methyl (high-field half)

splitting constants are:





The line width in these spectra are 120 and 60 milligauss respectively. The smaller line width for the meta substituted radical may be caused by the much

smaller spin density on the chlorine nucleus.
The splitting constants for the para substituted radicals are in good agreement with values given by Sinclair [8] though he did not obtain a further resolution for the tri-para substituted radical.

Tris(p-methoxyphenyl)methyl

The e.s.r. spectrum of tris(p-methoxyphenyl)methyl has been measured before by Judeikis and Kivelson [17]. According to these authors the splitting constants are 2.89, 0.71 or 1.02 and 0.34 gauss for ortho, meta and methoxyl protons respectively. From our spectrum (fig. 5.18), which is much better

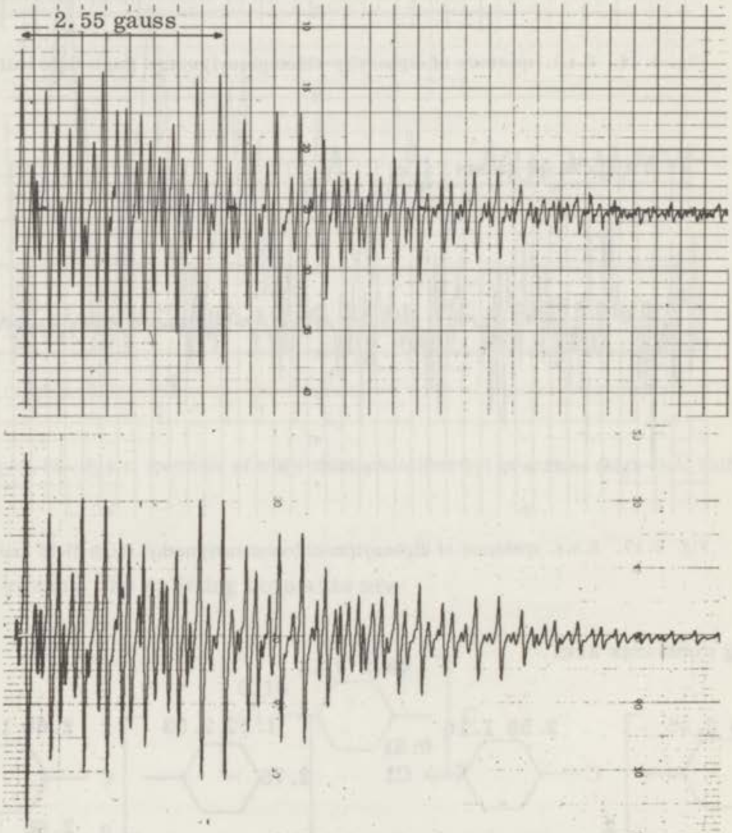
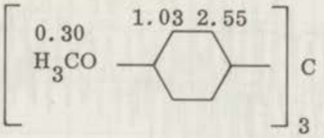


Fig. 5.18. Experimental and calculated e.s.r. spectra of tris(p-methoxyphenyl)methyl. (high-field half)

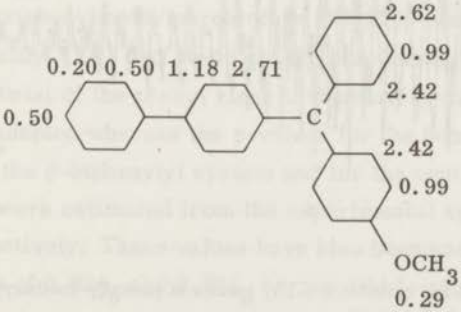
resolved than the spectrum given by Judeikis and Kivelson, we obtained a different set of splitting constants:



This difference is caused by the low resolution in Judeikis and Kivelson's spectrum which leads to an uncertainty in the ortho and meta proton splitting of one methoxyl proton splitting (see also tris(p-tert.butylphenyl)methyl). This uncertainty does not occur in our spectrum.

Phenyl(p-methoxyphenyl)-p-biphenylylmethyl

All triarylmethyl radicals discussed before have at least two identical arylgroups. In phenyl(p-methoxyphenyl)-p-biphenylylmethyl, however, all three groups are different. In the observed spectrum (fig. 5.19) groups of sharp lines occur which are separated by a number of broader lines. When we assume that the splitting constants do not differ very much from those in diphenyl-p-biphenylylmethyl, then it appears that the sharp lines are mainly caused by the splitting from the ortho and para protons whereas the further splitting by the meta protons leads to the broader lines.
The splitting constants of all three arylgroups may be different but in this case we should expect an even more complicated spectrum. Therefore we have performed a calculation in which the splitting constants of the ortho and meta protons of the phenyl and p-methoxyphenyl groups were set equal:



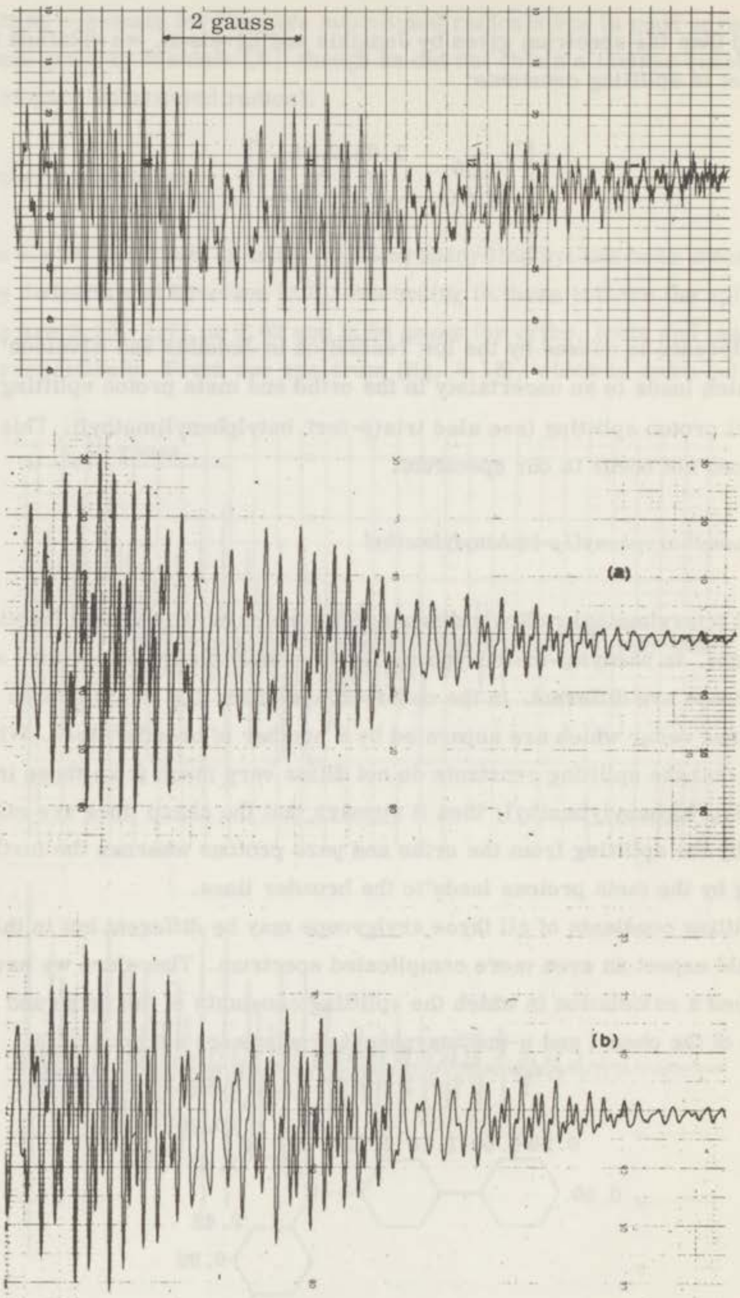
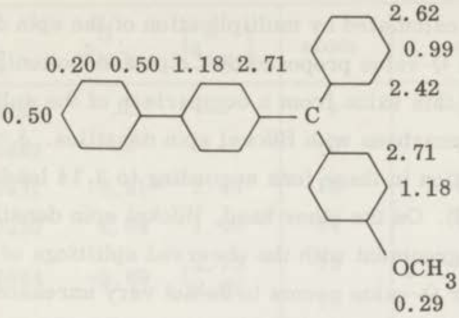


Fig. 5.19. Experimental and calculated e.s.r. spectra of phenyl(p-methoxyphenyl)-p-biphenylylmethyl (high-field half)

(fig. 5.19a) and one in which the ortho and meta protons of the p-methoxyphenyl and p-biphenylyl groups were given the same splitting constant:



(fig. 5.19b). Both spectra show a clear resemblance with the experimental one. A definite choice is therefore impossible although fig. 5.19b seems to be in slightly better agreement with the observed spectrum.

C. THEORETICAL DISCUSSION

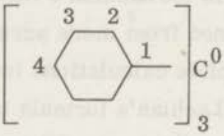
1. Unsubstituted radicals

In chapter III it has been shown that spin densities calculated from Hückel molecular orbitals according to McLachlan's formula 3.14 are a good approximation of spin densities obtained from more accurate configuration interaction methods. Because more complete calculations for large radicals are practically impossible, we have used McLachlan's formula in all calculations of spin densities discussed in this chapter. The constant λ_1 has been given the value 1.2.

In the calculation for triphenylmethyl the phenyl rings were assumed to be 30^o rotated out of the plane of the three central bonds which corresponds to a β-value of $0.866\beta_0$. Comparable experimental values for the angle of twist are 31^o in solid triphenylmethylperchlorate [26,27], about 30^o in solid tris-(p-nitrophenyl)methyl [28] and 40-45^o in triphenylmethyl in the gas phase [29]. For the angle of twist of the phenyl rings in diphenyl-p-biphenylylmethyl the same value was adopted whereas the β-values for the bond between the central carbon atom and the p-biphenylyl system and for the central bond of the p-biphenylyl system were estimated from the experimental splittings to be $0.92\beta_0$ and $0.82\beta_0$ respectively. These values have also been used for tri-p-biphenylylmethyl. β-values of $0.92\beta_0$ and $0.82\beta_0$ correspond to angles of twist of 23^o and 35^o respectively but, of course, differences in β-values may also be caused by differences in bond lengths.

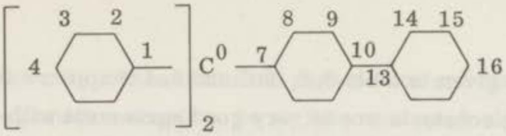
The resulting spin densities are collected in tables 5.2, 5.3 and 5.4. The splitting constants were calculated by multiplication of the spin densities by -31.2 gauss which is the Q-value proposed by Colpa and Bolton [30]. Colpa and Bolton have deduced this value from a comparison of the splitting constants of ions of alternant hydrocarbons with Hückel spin densities. A calculation of the spin density distribution in these ions according to 3.14 leads to a smaller Q-value (see chapter III). On the other hand, Hückel spin densities show in several cases a better agreement with the observed splittings of ions of alternant hydrocarbons so our Q-value seems to be not very unreasonable. Moreover, according to Andersen [29] the C-H bond length in triphenylmethyl is 1.11 Å. From this rather large value we should also expect a somewhat larger Q-value than for normal C-H bonds.

In order to compare the calculated splitting constants with those obtained for a radical having a more rigid structure, we have also calculated the splitting constants of phenalenyl (table 5.5). The signs of the splitting constants in this radical are known from measurements in a liquid crystal [31, 32].



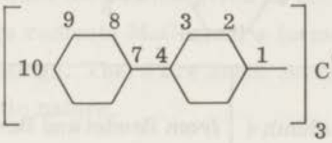
atom	ρ_{calc}	a^H_{calc}	$\lvert a^H_{exp} \rvert$
0	0.5210	--	--
1	-0.0494	--	--
2	0.0963	-3.00	2.57
3	-0.0359	1.12	1.13
4	0.0881	-2.75	2.80

Table 5.2. Calculated and experimental splitting constants in triphenylmethyl



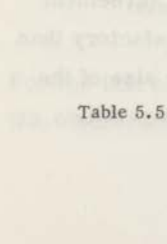
atom	ρ_{calc}	a^H_{calc}	$\lvert a^H_{exp} \rvert$	atom	ρ_{calc}	a^H_{calc}	$\lvert a^H_{exp} \rvert$
0	0.4954	--	--	9	-0.0386	1.21	1.22
1	-0.0449	--	--	10	0.0887	--	--
2	0.0931	-2.91	2.45	13	-0.0105	--	--
3	-0.0335	1.04	1.08	14	0.0143	-0.45	0.48
4	0.0864	-2.69	{2.73 2.65	15	-0.0066	0.21	0.20
				16	0.0123	-0.38	0.48
7	-0.0524	--	--				
8	0.1034	-3.23	{2.65 2.73				

Table 5.3. Calculated and experimental splitting constants in diphenyl-p-biphenylylmethyl



atom	ρ_{calc}	a^H_{calc}	$\lvert a^H_{exp} \rvert$	atom	ρ_{calc}	a^H_{calc}	$\lvert a^H_{exp} \rvert$
0	0.4103	--	--	7	-0.0084	--	--
1	-0.0438	--	--	8	0.0148	-0.46	0.42
2	0.0985	-3.07	2.49	9	-0.0058	0.18	0.18
3	-0.0337	1.05	1.13	10	0.0135	-0.42	0.42
4	0.0876	--	--				

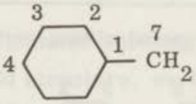
Table 5.4. Calculated and experimental splitting constants in tri-p-biphenylylmethyl



atom	ρ_{calc}	a^H_{calc}	a^H_{exp} ref. 31,32,33
0	0.0059	--	--
1	-0.0534	--	--
2	0.2282	-7.12	-6.29
3	-0.0715	2.23	1.81

Table 5.5. Calculated and experimental splitting constants in phenalenyl

From the figures given in table 5.2, 5.3 and 5.4 it appears that most of the calculated splitting constants are in very good agreement with the experimental ones. There is one important exception, however. All calculated ortho proton splittings are about 20% too large. A deviation of the ortho protons is not unexpected because the interaction with the neighbouring ring might be of importance whereas the spin density on the proton due to the interaction with the central carbon atom (directly and via the σ-bonds) is comparable to the spin density on the β-protons of alkyl substituents and may therefore have a non-negligible value. On the other hand, the same deviation is observed in the benzyl radical where these terms do not occur or are assumed to be much smaller (see table 5.6).



atom	from table 3.2 column 4		from Baudet and Berthier [34]		$\lvert a^H_{exp} \rvert$ [35]
	ρ_{calc}	a^H_{calc}	ρ_{calc}	a^H_{calc}	
1	-0.123	--	-0.103	--	--
2	0.164	- 5.12	0.200	- 6.24	5.14
3	-0.075	2.34	-0.089	2.78	1.75
4	0.137	- 4.27	0.208	- 6.49	6.14
7	0.810	-25.27	0.673	-21.00	16.35

Table 5.6. Calculated and experimental splitting constants in benzyl

As far as we know, Baudet and Berthier's calculation of the benzyl radical [34] is the only one which predicts the para proton splitting to be larger than the ortho proton splitting but even in this case the calculated ratio $\rho_{para}/\rho_{ortho} = 1.04$ is much smaller than the observed ratio a^H_{para}/a^H_{ortho}. The agreement between calculated and observed splittings for benzyl is less satisfactory than for the triphenylmethyl radicals. This may be due to the smaller size of the radical. If we assume that benzyl and triphenylmethyl show a comparable deviation in the ratio of the ortho and para proton splittings, then the only reasonable explanation seems to be an inaccurate calculation of the spin density for atoms in the neighbourhood of atoms having a very large spin density.

The calculated splitting constants for phenalenyl are about 15% too large but the ratio of the calculated splittings agrees with the experimental one. It is of course possible to obtain a better correspondence with the calculations for triphenylmethyl derivatives by a variation of the angles of twist but then an angle much smaller than 30° is needed which is very unlikely in view of the experimental values. The errors in the ortho para ratio can also be ascribed to incorrect calculations of the spin densities on the meta and para position because the ortho proton splittings in the triarylmethyl radicals correspond to the same Q-value as is obtained from the experimental splittings in phenalenyl. In this case an explanation of the deviation of the meta and para proton splittings becomes very difficult.

The conclusions from the results given in the tables can be summarized by saying that for large radicals McConnell's formula is in good agreement with the observed splittings. There are some unexplained deviations but these are of a very systematic nature.

2. Substituted radicals

From the splitting constants of the substituted triphenylmethyl radicals it appears that for meta and para substituted radicals the influence of the substituent on the splitting constants of the ring protons is small. From this it may be concluded that the influence of the substituent on both the spin density distribution in the π-electron system and the sterical structure of the radical is small. This small influence is also reflected by the known ^{13}C splitting constants of the central carbon atom:

triphenylmethyl	26 gauss [4,16]
	23.0 gauss [11]
tris(p-fluorophenyl)methyl	24.5 gauss [8]
tris(p-methoxyphenyl)methyl	22.9 gauss [8]
tris(o,o'-dimethoxyphenyl)methyl	26.2 gauss [11]

For the last compound the splitting constant is larger than in triphenylmethyl (23.0 according to the same author) because of the smaller interaction with the rings caused by the larger angle of twist.

The small influence of the substituent on the spin density distribution is easily understood. As has been shown in section C.4 of chapter IV, the squares of the coefficients of the atomic orbital in the singly occupied molecular orbitals become on introduction of a substituent having an inductive effect $\delta_\mu \beta_0$:

$$(c'_{a\nu})^2 = c_{a\nu}^2 - 2 \sum_{j \neq a} \frac{c_{a\mu} c_{j\mu} c_{a\nu} c_{j\nu} \delta_\mu \beta_0}{(\epsilon_j - \epsilon_a)}$$

whereas a conjugative effect leads to

$$(c'_{a\nu})^2 = c_{a\nu}^2 \left\{ 1 - \sum_r \frac{c_{a\mu}^2 \beta_{\mu r}^2}{(\epsilon_\sigma^r - \epsilon_a)^2} \right\} + 2 \sum_{j \neq a} \sum_r \frac{c_{a\mu} c_{j\mu} c_{a\nu} c_{j\nu} \beta_{\mu r}^2}{(\epsilon_\sigma^r - \epsilon_a)(\epsilon_j - \epsilon_a)}$$

It can easily be shown from the pairing principle that in both formulas the correction terms (except the renormalization correction in the latter formula) vanish for neutral alternant radicals. In McLachlan's formula 3.14 the influence of configuration interaction is calculated via the atom-atom polarizabilities. These quantities are known to predict substituent effects in a rather accurate way. Therefore we may assume that they are relatively independent on small changes in the π-electron system. Then the spin density distribution in neutral alternant radicals is unchanged in first order (for an inductive effect this can be shown to be exactly correct).

From this it follows that substituents will only change the spin density distribution when they cause a change in the sterical configuration. Meta and para substituents do not increase the steric interaction between the aryl systems so in this case we expect that differences between substituted and unsubstituted rings depend on differences in the bond orders for the central C-C bonds. These differences will be larger for para than for meta substituents. It is highly remarkable, therefore, that we have only observed a difference between substituted and unsubstituted rings in the mono-meta-chlorine substituted radical (and possibly in the mono-meta-methyl substituted one). In the mono-para-chlorine substituted radical no effect is observed but this may be due to the large line width whereas the small chlorine splitting might also obscure small differences between splitting constants. However, the fact that no differences are observed in the mono-para-methyl and -fluorine substituted radicals seems to exclude an explanation via the bond orders.

The only reasonable explanation then seems to be a difference in the averaged angle of twist due to the difference in the moments of inertia of substituted and unsubstituted rings. For a symmetric potential well the averaged angle of twist is independent of the moment of inertia but for an asymmetric potential well there may be an observable effect when the difference in the zero-point vibrational energies is sufficiently large. We have made a very crude estimation of this effect by assuming that for angles of twist larger than $\pi/6$ radians the potential energy is

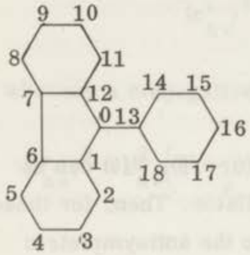
$$V(\theta) = V_0 \sin^2 \tfrac{3}{2}(\theta - \pi/6)$$

whereas $V = \infty$ for $\theta \leqslant \pi/6$. For small positive values of $(\theta - \pi/6)$, $V(\theta)$ can be approximated as the potential energy of an harmonic oscillator. Then, for these values of θ the (unnormalized) wave functions are equal to the antisymmetric wave functions for the harmonic oscillator whereas the wave functions vanish for $\theta \leqslant \pi/6$. It is easy to show that the averaged value of $(\theta - \pi/6)$ for the zero-point vibration becomes

$$\overline{(\theta - \pi/6)} = \frac{2}{\pi} \sqrt[4]{\frac{h^2}{18 I V_0}}$$

where I is the moment of inertia of the aryl system. Assuming V_0 to be 10 kcal/Mol we obtain about half the observed difference in the splitting constants of the unsubstituted and mono-m-chlorine substituted rings. After inclusion of the thermal mixing of the excited vibrational levels the calculated value reduces to about one quarter of the observed one. Though this result is rather small when compared with the experiments, our calculation certainly shows that the influence of differences in the moments of inertia may be of importance but more experimental values of splitting constants of meta substituted radicals are required for a final conclusion about the interpretation of the observed differences.

The e.s.r. spectra of ortho substituted triphenylmethyl radicals could not be analysed so conclusions about the structure of these radicals are impossible. For 9-mesitylfluorenyl, however, some conclusions are possible. From the e.s.r. spectrum of this radical it appeared that there are two large splitting constants of about 3.5 gauss caused by two sets of two equivalent protons. All other protons occurring an even number of times have much smaller splitting constants. A comparison with calculated spin densities in the phenylfluorenyl radical (table 5.7) shows that this distribution of splitting constants is only possible for large angles of twist of the mesityl system. This agrees with the expected structure of 9-mesitylfluorenyl.



atom	calculated spin densities for an angle of twist	
	0^o	60^o
0	0.3916	0.4869
1	-0.0325	-0.0452
2	0.0995	0.1166
3	-0.0164	-0.0220
4	0.0882	0.1014
5	-0.0053	-0.0072
6	0.0806	0.0947
13	-0.0436	-0.0199
14	0.1013	0.0276
15	-0.0373	-0.0120
16	0.0953	0.0242

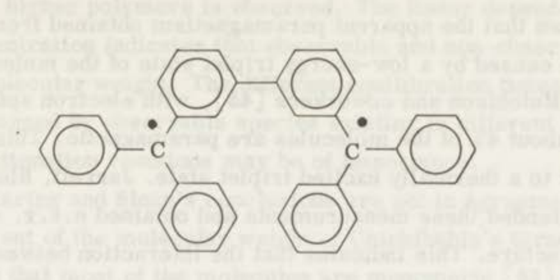
Table 5.7. Calculated spin densities in 9-phenylfluorenyl

Besides the splittings of the ring protons we have also observed splittings due to substituent groups.

The splitting constants of protons of alkyl substituents have been discussed in detail in chapter IV. Much less is known about the splitting constants of chlorine and methoxyl substituents. It is only a few years ago that chlorine splittings have been observed for the first time. For fluorine splittings it has been suggested that they depend on both the spin density on the neighbouring carbon atom and the spin density in the $2p_z$-orbital of the fluorine atom and probably also on the overlap π-electron spin density in the C-F bond (see e.g. reference 36). From the correspondence between fluorine and chlorine splittings in substituted triphenylmethyl radicals it seems reasonable to suppose that the same holds for chlorine splittings. The splitting constants of the methoxyl protons in tris(p-methoxyphenyl)methyl have been discussed by Rabold and coworkers [37].

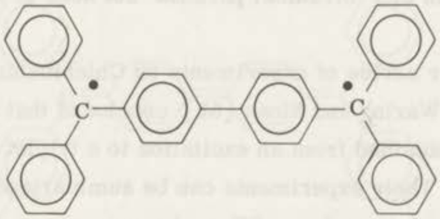
D. CHICHIBABIN'S BIRADICAL

Shortly after the discovery of triphenylmethyl attempts have been made to obtain biradicals by linking two triphenylmethyl radicals together. A typical example of a biradical is

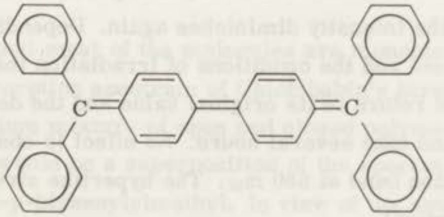


For this compound (Schlenk's biradical [38]), which strongly resembles triphenylmethyl, no normal structures can be written with all electrons paired. In the molecular orbital theory the biradical character is caused by the occurrence of two non-bonding orbitals, each containing one electron.

A much more difficult problem is offered by Chichibabin's biradical [39]:



This compound has an intense violet colour and is highly reactive e.g. with respect to oxygen. Because of the high reactivity it has first been considered as a biradical. On the other hand it is also possible to write a quinoid structure



with all electrons paired from which we should conclude that the ground state is a singlet. This problem has in principle been solved by measurements of the magnetic susceptibility from which it appeared that Chichibabin's biradical is diamagnetic [40,41,42]. A different result was obtained from ortho-para-hydrogen conversion measurements [43] but in a more recent paper [44] it has been shown that the apparent paramagnetism obtained from these measurements can be caused by a low-energy triplet state of the molecule.

In 1952 Hutchison and coworkers [45], with electron spin resonance, showed that about 4% of the molecules are paramagnetic. This paramagnetism was ascribed to a thermally excited triplet state. Jarrett, Sloan and Vaughan [46] have extended these measurements and obtained e.s.r. spectra showing hyperfine structure. This indicates that the interaction between the two unpaired electrons is small. Further evidence for this small interaction was obtained by Reitz and Weissman [47] from measurements of biradicals where the two central carbon atoms of the triphenylmethyl halves were replaced by ^{13}C. On the other hand, the small fraction of paramagnetic molecules corresponds to a triplet excitation energy of about 2.5 kcal/Mol which indicates a much larger interaction between the unpaired electrons. Several attempts [48,49,50] have been made to explain this 'biradical paradox' but none of these seems to be conclusive.

From a further series of experiments on Chichibabin's biradical and related compounds Waring and Sloan [51] concluded that the paramagnetic molecules are not obtained from an excitation to a triplet state but from a chemical reaction. Their experiments can be summarized as follows:

1. Cooling of solutions from different temperatures to -100°C leads to different intensities of the e.s.r. signal.

2. The intensity of the e.s.r. signal of solutions in CS_2 for samples of constant volume varies linearly with concentration.

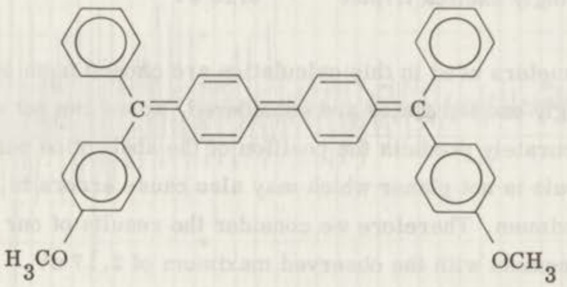
3. Irradiation at low temperatures (-90°C) with light of 420 mμ wave length leads to an enhancement of the e.s.r. signal intensity. Upon warming to room temperature the intensity diminishes again. Depending on the biradicalar compound, the solvent and the conditions of irradiation the e.s.r. signal intensity may or may not return to its original value and the decay may be immediate or it may be slow and take several hours. No effect is observed upon irradiation at the main absorption band at 580 mμ. The hyperfine structure before and after irradiation was identical.

4. After heating of solutions in toluene or CS_2 and cooling to room temperature the intensity of the e.s.r. signal is enhanced. This intensity diminishes slowly with characteristic times of many hours to a value somewhat less than the original intensity at room temperature. These non-equilibrium effects were not observed in benzene solutions.

From these experiments it was concluded that an equilibrium between open and closed dimers or higher polymers is observed. The linear dependence of signal intensity on concentration indicates that observable and non-observable species have the same molecular weight. The different equilibration times were interpreted as being caused by observable species existing in different forms whereas also disproportionation reactions may be of importance.

However, Waring and Sloan's conclusions are not in agreement with the recent measurement of the molecular weight of Chichibabin's biradical from which it appeared that most of the molecules are monomeric [52].

We have studied the 'biradical problem' by a calculation of the absorption maximum of Chichibabin's biradical in the visible region and by an attempt to analyse the e.s.r. spectra of Chichibabin's biradical and of the dimethoxy substituted derivative:



1. The absorption spectrum in the visible region

The conclusion that most of the molecules are monomeric can also be obtained from the absorption spectrum of Chichibabin's biradical. When the system is an equilibrium mixture of open and closed polymers, then the absorption spectrum would be a superposition of the spectra of benzene, biphenyl and diphenyl-p-biphenylylmethyl. In view of the small amount of paramagnetic molecules, the spectrum in the visible region would then consist of a weak broad band. In fact a very strong band is observed (λ_{max} = 574 mμ; log ε = 4.92 [53]). In view of the spectra of similar compounds such as diphenoquinone, it seems most reasonable to ascribe this band to the monomer molecule. We have calculated the first absorption band for the planar molecule in a Pariser-Parr type approximation [54, 55] from Hückel molecular orbitals. In the Hückel approximation there is a singly excited state at $-0.1472\beta_0$ and a doubly excited state at $-0.2944\beta_0$. After inclusion of the interaction between the electrons the excitation energies become

singly excited singlet	1.97 eV	oscillator strength 7.4
singly excited triplet	-0.84 eV	
doubly excited singlet	1.13 eV	

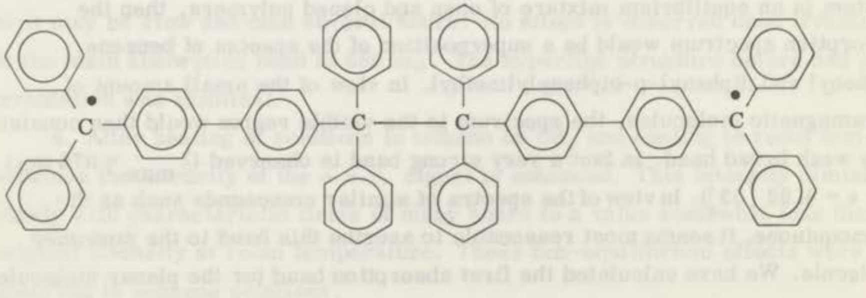
Because of the low excitation energy of the doubly excited state, there is a strong mixing of this state with the ground state. After inclusion of this mixing we obtain for the singly excited singlet and triplet states

singly excited singlet	2.91 eV	oscillator strength 0.8
singly excited triplet	0.10 eV	

The parameters used in this calculation are chosen from calculations where only singly excited states are considered, so we can not expect that this calculation accurately predicts the position of the absorption band. Moreover, the real molecule is not planar which may also cause errors in the calculated absorption maximum. Therefore we consider the results of our calculation to be in good agreement with the observed maximum of 2.17 eV.

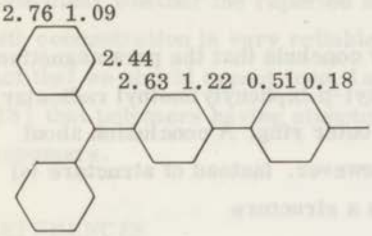
2. The e.s.r. spectra

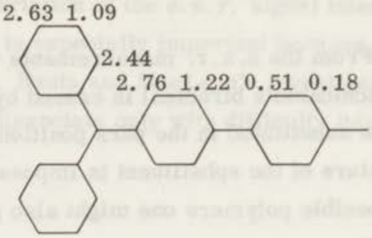
The e.s.r. spectrum of Chichibabin's biradical is given in figure 5.20. When the paramagnetic molecules are open polymers having a structure such as



(a)

then we should expect that the splitting constants are nearly equal to the ones obtained for diphenyl-p-biphenylylmethyl. This assumption is indeed in agreement with the observed spectrum which could be reproduced with a set of splitting constants which can be interpreted in two different ways:





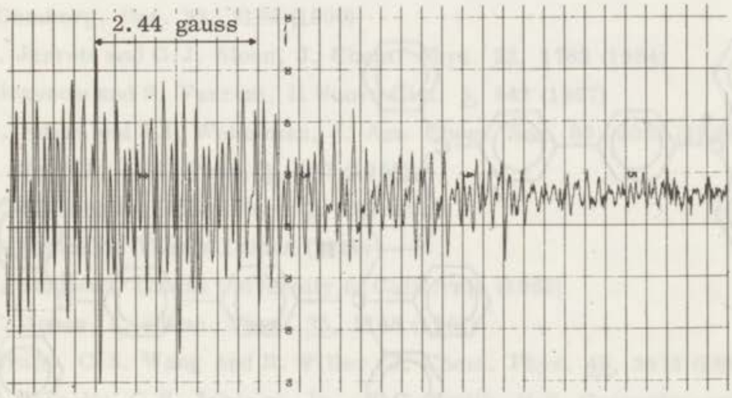


Fig. 5.20. E.s.r. spectrum of Chichibabin's biradical (high-field half)

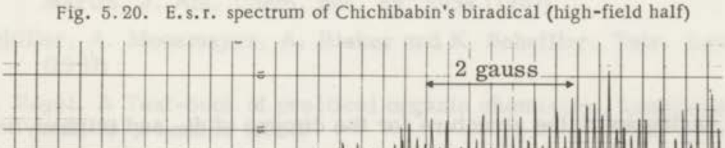
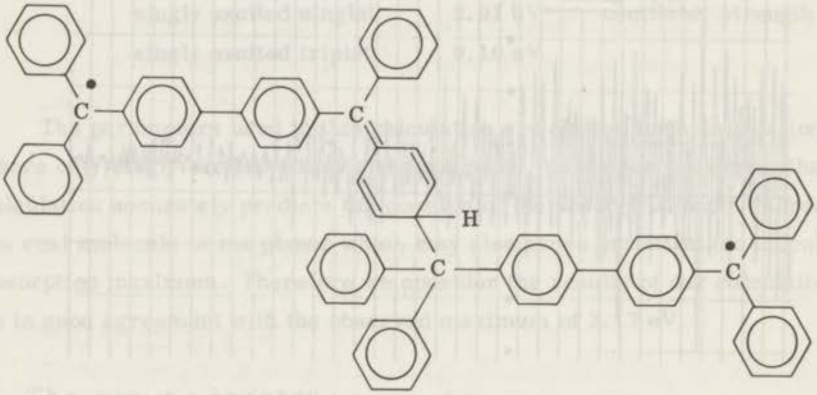


Fig. 5.21. E.s.r. spectrum of dimethoxy-substituted Chichibabin's biradical (low-field half)

In the e.s.r. spectrum (fig. 5.21) of the dimethoxy substituted derivative the small splittings obtained for phenyl(p-methoxyphenyl)-p-biphenylylmethyl could also be observed. Our attempts to obtain a complete analysis of this spectrum were not successful, however.

From the e.s.r. measurements we may conclude that the paramagnetism of Chichibabin's biradical is caused by diphenyl-p-biphenylylmethyl radicalar groups substituted in the para position of the outer ring. A conclusion about the nature of the substituent is impossible, however. Instead of structure (a) for possible polymers one might also propose a structure



(b)

which is analogous to the structure for the dimers of di- and triphenylmethyl radicals proposed by Lankamp, Nauta and MacLean [18]. Besides, we can not exclude the possible occurrence of radicals obtained from an incomplete removal of chlorine from the dichloride or from a disproportionation of one half of the molecule.

An explanation of the paramagnetism of Chichibabin's biradical with an impurity is unlikely in view of the influence of temperature on the e.s.r. signal intensity. On the other hand the conclusion that the paramagnetism is caused by polymer molecules is not in agreement with the concentration dependence of the e.s.r. signal.

In view of the long equilibration times mentioned by Waring and Sloan, it seems to be necessary to investigate the equilibration time after a change of concentration. Because this problem has not been discussed by these authors it is not quite clear whether the reported linear variation of the e.s.r. signal intensity with concentration is very reliable. This is especially important because of the fact that we should expect from Lankamp, Nauta and MacLean's investigations [18] that polymers having structure (a) dissociate only with difficulty into monomers.

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SUMMARY

The hyperfine structure in the e.s.r. spectra of organic radicals in solution yields valuable information about the electron distribution in these molecules. For most radicals, which have been studied up to now, the hyperfine structure is due to hydrogen or nitrogen nuclei. Besides, splittings have been observed due to ^{13}C, F, Cl, etc. In this thesis an extension of the theory of proton splittings in the e.s.r. spectra of π-electron radicals is presented. It has especially been developed to obtain a better insight in the mechanisms causing spin density in alkyl substituents. It is followed by a discussion of the often very intricate e.s.r. spectra of triphenylmethyl radicals.

The theoretical part of our investigations is described in chapters II, III and IV.

In chapter II formulas are derived, first for the spin density in σ-bonds for which the most important contribution is obtained from the direct interaction with the π-electron system, e.g. the C-H bonds of unsubstituted aromatic radicals and of methyl substituents, and thereafter for σ-bonds for which the coupling via other σ-bonds must also be considered, e.g. the C-H bonds of tert.butyl substituents. In the derivation of the formulas the zeroth order wave function for the ground state is chosen to be a combination of the best possible wave functions for the separated π- and σ-electron systems. This wave function is mixed with wave functions in which the σ-bond is excited to a triplet state and with wave functions in which an electron is transferred from the π-electron system to the σ-bond or vice versa. For σ-bonds for which the interaction with the π-electron system is weak, we have also considered wave functions in which an electron is transferred between two σ-bonds.

The calculation of the spin density distribution in the π-electron system is discussed in chapter III. The reliability of several possible approximation methods has been investigated by a comparison of calculated spin densities for the negative ion of naphtalene and for the benzyl radical with values obtained with more accurate methods. From this it appeared that spin densities calculated according to McLachlan's formula from Hückel molecular orbitals are a good approximation of spin densities obtained from a configuration interaction calculation with inclusion of all singly excited states. The substitution of self consistent field orbitals, calculated according to Roothaan's open-shell method, however, leads to rather erroneous spin densities.

The application of the formulas derived in chapter II in the calculation of proton splittings is discussed in chapter IV. This discussion is combined with a critical survey of the existing literature on the theory of the splitting constants of protons in π-electron radicals. A simplified formula for the splitting constants of methyl protons is proposed which is in good agreement with experimental splitting constants. The experimental values of splitting constants of β-alkyl protons appeared to be insufficient to allow of a simplified formula.

The e.s.r. spectra of triphenylmethyl radicals are discussed in chapter V. The most important conclusions from this part of our investigations are:

1. The ratio of the spin densities on the meta- and para-carbon atoms, calculated according to McLachlan's formula, is in very good agreement with the ratio of the experimental splitting constants. The calculated spin densities for the ortho-position, however, show a systematic deviation. A clear explanation of this discrepancy, which probably also occurs in the case of the benzyl radical, could not be obtained.
2. The influence of substituents on the spin density distribution in the π-electron system is very small unless the substituent causes a change in the sterical configuration of the radical. This could be explained from the alternant character of the unsubstituted radical.
3. Para-substituents do not alter the sterical configuration of the radical. In the case of the mono-meta-chlorine substituted radical, however, it appeared that the angle of twist out of the plane of the three central bonds is slightly smaller for the substituted ring than for the unsubstituted rings. According to a crude calculation this may be caused by the influence of the moment of inertia of the rings on the zero-point vibrations, but the agreement between this calculation and the experimental splitting constants was too unsatisfactory

to allow of a definite conclusion.

4. The e.s.r. spectra of ortho-substituted radicals could not be interpreted. In the case of 9-mesitylfluorenyl, however, the information obtained from the spectrum was sufficient to conclude that the angle of twist of the mesityl-group is very large.

5. The theory described in chapter IV is in agreement with the experimental splitting constants for the protons of para- and meta-methyl substituents.

In the last part of chapter V we have discussed the e.s.r. spectrum of Chichibabin's 'biradical'. The experimental splitting constants are in agreement with Waring and Sloan's suggestion that the paramagnetism is caused by polymeric molecules. From the absorption spectrum in the visible region and from the molecular weight, which has been measured by Hartmann and coworkers, it appears that most of the molecules in a solution of Chichibabin's biradical are monomeric. These data are not in agreement with the concentration-dependence of the e.s.r. signal intensity reported by Waring and Sloan. In view of the recent discussion by Lankamp, Nauta and MacLean of the structure of the dimer of triphenylmethyl, it seems to be necessary to repeat Waring and Sloan's measurements in order to obtain more accurate results.

SAMENVATTING

De hyperfijn structuur in de e.s.r. spectra van organische radicalen in oplossing levert belangrijke gegevens over de electronenverdeling in deze moleculen. Bij de meeste van de tot nu toe gemeten radicalen wordt de hyperfijn structuur veroorzaakt door waterstof- of stikstofkernen. Hiernaast zijn splitsingen waargenomen tengevolge van ^{13}C, F, Cl enz. In dit proefschrift wordt een uitbreiding gegeven van de theorie van de splitsingsconstanten van protonen in π-electron radicalen waarbij vooral getracht wordt een beter inzicht te krijgen in de wijze waarop de spindichtheid in alkyl substituenten veroorzaakt wordt. Dit wordt gevolgd door een bespreking van de dikwijls zeer ingewikkelde e.s.r. spectra van triphenylmethyl radicalen.

Het theoretisch gedeelte van het onderzoek is beschreven in de hoofdstukken II, III en IV.
In hoofdstuk II worden formules afgeleid voor de spindichtheid in σ-banden waarvoor de directe interactie met het π-electronensysteem de belangrijkste bijdrage levert, b.v. de C-H banden van ongesubstitueerde aromatische radicalen en van methyl substituenten, en voor σ-banden waarvoor ook rekening gehouden moet worden met de koppeling via andere σ-banden, b.v. de C-H banden van een tert. butyl substituent. In de afleiding van de formules wordt uitgegaan van een nulde orde golffunctie voor de grondtoestand die een combinatie is van de best mogelijke golffuncties voor de gescheiden π- en σ-systemen. Deze golffunctie wordt gemengd met golffuncties waarin de σ-band is aangeslagen naar een triplettoestand en met golffuncties waarin een electron is overgedragen van het π-electronensysteem naar de σ-band of omgekeerd. Voor σ-banden waarvoor de directe interactie met het π-electronensysteem zwak is, wordt ook rekening

gehouden met golffuncties waarin een electron is overgedragen tussen twee σ-banden.

De berekening van de spindichtheid in het π-electronensysteem wordt besproken in hoofdstuk III. De betrouwbaarheid van verschillende mogelijke benaderingsmethoden wordt nagegaan door een vergelijking van berekende spindichtheden voor het negatief ion van naftaleen en voor het benzyl radicaal met de resultaten van nauwkeuriger methoden. Hierbij bleek dat spindichtheden berekend volgens de formule van McLachlan uit Hückel 'molecular orbitals' in goede overeenstemming zijn met spindichtheden verkregen door configuratie interactie met alle enkel aangeslagen toestanden. Substitutie van 'molecular orbitals', berekend volgens de 'open-shell' methode van Roothaan, in de formule van McLachlan levert echter een minder juiste spindichtheidsverdeling.

In hoofdstuk IV worden de in hoofdstuk II afgeleide formules toegepast voor de berekening van de splitsingsconstanten van protonen. Dit wordt gecombineerd met een critisch overzicht van de bestaande literatuur. Een vereenvoudigde formule voor de splitsingsconstanten van methyl protonen wordt voorgesteld die in goede overeenstemming met experimentele splitsingsconstanten blijkt te zijn. De experimentele gegevens voor de β-protonen van alkyl substituenten blijken nog onvoldoende om een vereenvoudigde formule mogelijk te maken.

De e.s.r. spectra van triphenylmethyl radicalen worden besproken in hoofdstuk V. De voornaamste conclusies uit dit gedeelte van het onderzoek zijn:

1. De verhouding van de spindichtheden op de meta- en para-koolstof atomen, berekend volgens de formule van McLachlan, is in zeer goede overeenstemming met de gemeten splitsingsconstanten. Bij alle gemeten radicalen werd echter een systematische afwijking voor de ortho-protonen gevonden. Een duidelijke verklaring voor deze afwijking, die waarschijnlijk ook optreedt bij het benzyl radicaal, was nog niet mogelijk.
2. Substituenten hebben slechts een geringe invloed op de spindichtheidsverdeling in het π-electronensysteem, tenzij ze een verandering van de sterische configuratie van het radicaal veroorzaken. Dit kon verklaard worden uit het alternerende karakter van het ongesubstitueerde radicaal.
3. Para-substituenten hebben geen invloed op de sterische configuratie van het radicaal. Bij het mono-meta-chloor gesubstitueerde radicaal bleek echter dat de gesubstitueerde ring iets minder ver uit het vlak van de drie centrale C-C banden gedraaid is dan de ongesubstitueerde ringen. Volgens een ruwe berekening

kan dit veroorzaakt worden door de invloed van het traagheidsmoment van de ringen op de nulpunts-vibraties maar de overeenstemming tussen de berekening en de experimentele splitsingsconstanten was onvoldoende voor een definitieve conclusie.

4. De e.s.r. spectra van de ortho-gesubstitueerde radicalen konden niet geinterpreteerd worden. Uit het spectrum van 9-mesitylfluorenyl bleek echter wel dat de mesityl-groep ver uit vlak van de centrale banden gedraaid is.

5. De in de hoofdstukken II en IV besproken theorie is in overeenstemming met de gemeten splitsingsconstanten van de protonen van meta- en para-methyl substituenten.

In het laatste gedeelte van hoofdstuk V wordt het e.s.r. spectrum van Chichibabin's biradicaal besproken. De gevonden splitsingsconstanten zijn in overeenstemming met Waring en Sloan's veronderstelling dat het paramagnetisme veroorzaakt wordt door polymeer-moleculen. Uit het absorptie-spectrum in het zichtbare gebied en uit het door Hartmann en zijn medewerkers gemeten molecuulgewicht blijkt dat de meeste moleculen in een oplossing van Chichibabin's biradicaal monomeer zijn. Deze gegevens zijn niet in overeenstemming met de door Waring en Sloan vermelde concentratie-afhankelijkheid van het paramagnetisme. Vooral in verband met de recente onderzoekingen van Lankamp, Nauta en MacLean naar de structuur van het dimeer van triphenylmethyl lijkt een herhaling van Waring en Sloan's experimenten noodzakelijk teneinde nauwkeuriger gegevens te verkrijgen.

STELLINGEN

I

De door Bailey en Golding gegeven discussie van de wijze waarop de spindichtheid in alkyl substituenten tot stand komt, is onvolledig en voor een gedeelte onjuist.

J.P.M. Bailey en R.M. Golding, Mol. Phys. 12, 49 (1967)
Dit proefschrift, hoofdstuk 2 en 4

II

De invloed van substituenten op het absorptiespectrum van het triphenylmethyl kation in het zichtbare gebied kan met een eenvoudig 'molecular orbital' model goed begrepen worden. Uit een dergelijke beschouwing blijkt onder andere dat, in tegenstelling tot de opvatting van Dallinga, Mackor en Verrijn Stuart en van Koutecky en Paldus, de invloed van de methyleengroep in de berekening van het absorptiespectrum van het 9-anthracenium ion niet verwaarloosd kan worden.

A.A. Verrijn Stuart en E.L. Mackor, J. Chem. Phys. 27, 826 (1957)
G. Dallinga, E.L. Mackor en A.A. Verrijn Stuart, Mol. Phys. 1, 123 (1958)
J. Koutecky en J. Paldus, Coll. Czech. Chem. Comm. 28, 1483 (1963)

III

Bij de keuze van parameters in 'valence bond' berekeningen met ionogene structuren wordt in het algemeen te weinig rekening gehouden met de aard van de integralen die in deze benadering voorkomen.

D.P. Craig, Proc. Roy. Soc. (London) A200, 390 (1950)
M. Simonetta, J. Chim. Phys. 49, 68 (1952)
J.C. Schug, T.H. Brown en M. Karplus, J. Chem. Phys. 35, 1873 (1961)
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IV

Het door Gomberg en Cone gegeven mechanisme van de reactie van para-halogeen gesubstitueerde triphenylmethyl radicalen met zilver verdient de voorkeur boven het door Beynon en Bowden gegeven reactieverloop.

M. Gomberg en L.H. Cone, Ber. 39, 3274 (1906)
K.I. Beynon en S.T. Bowden, J. Chem. Soc. 4257 (1957)
H. Lankamp, W.Th. Nauta en C. MacLean, Tetr. Letters 249 (1968)

V

Bij het toepassen van de regel van Woodward en Hoffmann voor sigmatrope reacties dient men met de volgende punten rekening te houden:

1. Het is niet juist om, in navolging van Woodward en Hoffmann, de 'transition state' opgebouwd te denken uit een π-electronensysteem met een oneven aantal electronen en een waterstofatoom. Dit kan voor fotochemische reacties tot onjuiste conclusies leiden.
2. Voor monocyclische verbindingen zoals cycloheptatrieen is een conclusie, uitsluitend op grond van de symmetrie van de 'molecular orbitals', niet mogelijk.

R.B. Woodward en R. Hoffmann, J. Am. Chem. Soc. 87, 2511 (1965)
L.B. Jones en V.K. Jones, J. Am. Chem. Soc. 89, 1880 (1967)
A.G. Anastassiou, Chem. Comm. 15 (1968)

VI

De wijze waarop Purnendra Nath Sen en Sadhan Basu de werkzame doorsnede voor excitatie van benzeen met electronen van 5 tot 50 eV berekenen, is aan bedenkingen onderhevig.

Purnendra Nath Sen en Sadhan Basu, Internat. J. Quantum Chem. 1, 591 (1967)

VII

Het voor de reactie van 1,1-diphenylaetheen met tetranitromethaan gepostuleerde mechanisme is niet in overeenstemming met de tijdens de reactie gemeten absorptiespectra.

S. Penczek, J. Jagur-Grodzinski en M. Szwarc, J. Am. Chem. Soc. 90, 2174 (1968)

VIII

Voor een berekening van de energieverandering bij een draaiing van een van de CH_2-groepen van aetheen om de C-C band is een 'molecular orbital' methode weinig geschikt.

IX

De voordelen die hoogvacuum kan bieden voor het uitsluiten van zuurstof tijdens reacties in verdunde oplossingen, worden in de organische chemie nog te weinig benut.

X

Het feit dat alkanen in sterk zure media reactiviteit vertonen, betekent niet dat deze verbindingen geen paraffinen genoemd kunnen worden.

H.M. Buck, Chem. Weekblad 63, 392 (1967)
G.A. Olah en R.H. Schlosberg, J. Am. Chem. Soc. 90, 2726 (1968)

W.J. van der Hart　　　　Leiden, 2 juli 1968.

Op verzoek van de Faculteit der Wiskunde- en Natuurwetenschappen volgt hieronder een kort overzicht van mijn studie:

Na het behalen van het einddiploma HBS B aan het St. Franciscus College te Rotterdam ben ik van 1952 tot 1957 als analyst werkzaam geweest bij van den Bergh's en Jurgens' Fabrieken N. V. te Rotterdam. In deze periode werden examens afgelegd voor het analyst-diploma A en voor het diploma U. T. K.
In september 1957 begon ik met de studie aan de Rijksuniversiteit te Leiden.
Het candidaatsexamen in de natuur- en scheikunde met bijvak wiskunde (letter E) werd in juni 1959 afgelegd. De studie werd voortgezet onder leiding van de hoogleraren dr L. J. Oosterhoff, dr S. R. de Groot en dr C. Visser. Het doctoraal examen met hoofdvak theoretische organische scheikunde en bijvakken theoretische natuurkunde en wiskunde werd cum laude afgelegd in december 1961.

Van april tot december 1961 was ik als candidaat-assistent en van januari 1962 tot december 1964 als doctoraal-assistent verbonden aan de afdeling Theoretische Organische Chemie. In januari 1965 werd ik benoemd tot wetenschappelijk ambtenaar.

De in dit proefschrift beschreven metingen zouden niet mogelijk zijn geweest wanneer drs G. Horsman de bestaande e. s. r. apparatuur niet grondig verbeterd had. Voor de door hem en door drs A. H. Huizer verleende hulp bij de metingen en de met hen gevoerde discussies ben ik zeer erkentelijk.
Dr W. Th. A. M. van der Lugt en drs J. J. C. Mulder dank ik voor het gebruik van door hen opgestelde computer-programma's en voor de hulp bij de berekeningen.
Het personeel van het Organisch Chemisch Laboratorium ben ik erkentelijk voor de waardevolle medewerking. Speciaal wil ik hierbij vermelden de glasinstrumentmakerij onder leiding van de Heer C. J. van der Poel en de instrumentmakerij onder leiding van de Heer W. C. Bauer.
De tekeningen en de foto's van de e. s. r. spectra werden verzorgd door de Heer M. Pison.