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HYPERFINE INTERACTIONS

IN

ORGANIC FRAGMENTS

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PREFACE

This thesis, the first thesis in theoretical chemistry submitted for the degree of Master of Science at Victoria University of Wellington, has been designed to illustrate two alternative approaches to theoretical studies. The first five chapters illustrate the modern use of operator methods; the last two are concerned mainly with molecular orbital calculations for large organic molecules, using a giant high speed electronic computer.

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Chapter 1

INTRODUCTION

1.1 The Problem

The aim of this thesis is to consider two theoretical mechanisms which give rise to hyperfine effects in the electron spin resonance (ESR) and nuclear magnetic resonance (NMR) spectra of organic fragments. Hyperfine effects arise from the interaction of the nuclear magnetic moment with the electronic magnetic moment. The two mechanisms to be considered are spin polarisation and hyperconjugation. Spin polarisation is an exchange interaction between paired σ electrons and unpaired π electrons. Hyperconjugation is a delocalisation of π electrons from a conjugated region to a region usually considered as non-conjugated.

The relative importance of these two mechanisms in different organic systems is discussed, by comparing the value calculated for the hyperfine coupling constant of protons in aromatic fragments, on the basis of these two possible mechanisms, with the experimental values for these coupling constants from ESR and NMR studies of paramagnetic molecules.

1.2 Fundamental Theory of Hyperfine Interactions

NMR, ESR and Mössbauer spectroscopy reveal the presence of large internal magnetic fields in molecules, due to unpaired electrons. These magnetic fields lead to a coupling between the angular momenta of the electrons and that associated with the nucleus. This coupling is referred to as hyperfine interaction. Hyperfine interactions may be represented by the general n electron spin Hamiltonian [1],

which is derived from Dirac's fundamental equation for the electron. This Hamiltonian may be written [1] in the form

$$\mathcal{H} = g\beta g_N \beta_N \langle r^{-3} \rangle \sum_i \left\{ 1_i I + \frac{2}{(21_i - 1)(21_i + 3)} [1_i(1_i + 1)s_i - \frac{3}{2}(1_i s_i)s_i - \frac{3}{2}1_i(1_i s_i)] I \right\} \\ + \frac{8\pi}{3} g\beta g_N \beta_N \sum_i \delta(r_i - r_N) s_i I$$

where g is the gyromagnetic ratio for the electron
 g_N is the gyromagnetic ratio for the nucleus N
 β is the Bohr magneton
 β_N is the nuclear magneton
 $\delta(r_i - r_N)$ is the Dirac delta function of the distance
of the i 'th electron from nucleus N.

The first term arises from the direct dipolar forces between the magnetic moments of the electron and the nucleus. When the molecule is in dilute liquid solution, this dipolar interaction averages to zero, provided the g -tensor for the molecules is isotropic. In this case, only the second term need be considered, and the hyperfine Hamiltonian becomes simply

$$\mathcal{H} = \frac{8\pi}{3} g\beta g_N \beta_N \sum_i \delta(r_i - r_N) s_i I$$

which is usually written as

$$\mathcal{H} = a_N^h S \cdot I$$

where

$$a_N = \frac{8\pi}{3h} g\beta g_N \beta_N \sum_i \delta(r_i - r_N) \quad .$$

This term is referred to as the Fermi contact Hamiltonian. When the magnetic field strength is high, as in ESR and NMR measurements, the hyperfine splitting is small compared with

the splittings of the Zeeman levels, and the "strong-field" approximation is valid, giving

$$\mathcal{H} = \frac{8}{3} \pi g \beta g_N \beta_N \sum_i \delta(r_i - r_H) s_{iz} I_z.$$

Throughout this thesis it is assumed that only the Fermi contact term need be considered in discussing the observed hyperfine properties of organic radicals in solution. If the g-tensor is anisotropic, the dipolar term will not average to zero, giving rise to the pseudo-contact term [2].

If a fragment is represented by a wave function $|\Psi\rangle$, the hyperfine coupling constant a_H of a proton in the fragment is determined by the average value of the Fermi contact hyperfine Hamiltonian given above:

$$\langle \Psi | a_H h S_z I_z | \Psi \rangle = \langle \Psi | \frac{8}{3} \pi g \beta g_N \beta_N \sum_i \delta(r_i - r_H) s_{iz} I_z | \Psi \rangle$$

$$\text{ie } a_H h \langle S_z \rangle M_I = M_I \langle \Psi | \frac{8}{3} \pi g \beta g_N \beta_N \sum_i \delta(r_i - r_H) s_{iz} | \Psi \rangle$$

and so

$$a_H = \frac{1}{\langle S_z \rangle} \frac{8 \pi g \beta g_N \beta_N}{3 h} \langle \Psi | \sum_i \delta(r_i - r_H) s_{iz} | \Psi \rangle$$

where r_H is the coordinate of the particular proton studied.

All observable hyperfine properties are then determined by this hyperfine coupling constant. For example, in NMR studies, the change in the effective magnetic field, ΔH , at the nucleus due to the unpaired electrons in a paramagnetic molecule is [3]

$$\Delta H = \frac{a_N h}{g_N \beta_N} \langle S_z \rangle.$$

The hyperfine splitting in the ESR spectrum of an aromatic radical is determined by a_N .

The properties of the Dirac delta function [4] are such that $\langle \Psi | \sum \delta(r_i - r_H) s_{iz} | \Psi \rangle$ is non-zero only if there is a non-zero spin density at the coordinates of the proton. Thus if a given wave function has no unpaired electron density at the coordinates of the nucleus studied, the hyperfine coupling constant for that nucleus would be zero.

1.3 Systems to be Considered

The organic fragments considered are $C' - C_n H$, where C' is part of an aromatic system, $C_n H$ is non-aromatic, and C' has net (electron) spin density in its orbitals.

The highest energy occupied orbitals and the lowest energy unoccupied orbitals in aromatic molecules are of π type. Consequently the unpaired electron in an aromatic radical is expected to be in a π orbital. Until recently the occupied σ orbitals have been assumed to be of lower energy than the occupied π orbitals, and the unoccupied (antibonding) σ orbitals of higher energy than the unoccupied π orbitals. Recently one electron molecular orbital (MO) studies of aromatic compounds [5] have shown that some of the occupied σ orbitals are of about the same energy as the occupied π orbitals, but in all cases studied so far, the highest occupied orbital and the lowest unoccupied orbital, in the neutral molecule, have always been of π type. Thus it is assumed that in discussing hyperfine effects in fragments $C' - C_n H$ of aromatic radicals, the electron spin density is of π type.

If the terminal proton in the fragment $C' - C_n H$ is in the plane of the aromatic section, which is the nodal plane for the π orbitals, there should not be any net spin density at the proton, according to simple bonding theories.

Furthermore, for $n > 1$, and when the terminal proton is not in the nodal plane of the π orbitals, the exponential factor in the analytic expression for the π orbitals at C' causes only a vanishingly small spin density at that proton. Consequently in either case the proton hyperfine coupling constant a_H should be zero.

Experimentally this is not the case. The simplest cases, C'-H, are found experimentally to have hyperfine coupling constants of up to 20 Mc/s, and some C'-CH₂ protons have a_H values of up to 40 Mc/s. For a spin density at C' of about 0.1, the value of a_H expected at a C'-CH₂ proton due to just the value of the C' π wave function at the protons is about 1 Mc/s. Clearly simple bonding theories are not adequate for interpreting these results.

1.4 Spin Polarisation

This is a mechanism by which the spatial distribution of the spins of the electrons in the σ orbitals of the C'-C_nH fragment is altered without a net transfer of electrons into these orbitals. This rearrangement, which gives rise to spin density at the proton, arises from the exchange interactions between the unpaired π electron at C' and the paired electrons in the σ bonds.

Consider the simplest case, C'-H. There are two electrons in the C'-H σ bond, with spin states $|+\frac{1}{2}\rangle$ and $|-\frac{1}{2}\rangle$ respectively. Suppose that the unpaired π electron has spin state $|+\frac{1}{2}\rangle$. The exchange interaction of the $|+\frac{1}{2}\rangle$ state unpaired π electron with the $|+\frac{1}{2}\rangle$ σ bond electron is different from that with the $|-\frac{1}{2}\rangle$ σ bond electron. Consequently, there is a small difference in the spatial arrangement of the two

σ bond electrons, leading to a small predominance of one spin state over the other, at the coordinates of the proton.

A simple pictorial valence bond (VB) description can be given here as an illustration. There are two possible arrangements of the electrons in the three orbitals π, sp^2 and s :

[where $\uparrow$ stands for $m_s = +\frac{1}{2}$, $\downarrow$ for $m_s = -\frac{1}{2}$].

There is a tendency for the sp^2 electron to orient its spin parallel to that of the π electron, so that II is the slightly preferred configuration. This results in small net spin densities in the carbon sp^2 and hydrogen $1s$ orbitals, the latter giving rise to the hyperfine structure characteristic of π electron radicals.

Calculations are presented in chapters 2 to 5 for the cases $C'-H$, $C'-C-H$, $C'-C-C-H$ and $C'-C_nH$, respectively.

1.5 Hyperconjugation

This is the second mechanism used to account for the net spin densities at the $C'-C_nH$ protons. In this case the net spin density at the terminal protons in a non-linear fragment $C'-C_nH$ arises from the probability of finding the unpaired electron in the $1s$ orbital about the proton.

This delocalisation of the π electrons, referred to as hyperconjugation, arises from the symmetry of the terminal protons in fragments $C'-C_nH_2$. Instead of considering the $1s$ orbitals about the terminal protons separately, the

linear combinations

$$\psi = N(1s_u + 1s_l)$$

$$\phi = \bar{N}(1s_u - 1s_l)$$

are considered, where $1s_u$, $1s_l$ are the $1s$ atomic orbitals (AO's) associated with the hydrogen atoms located above and below the aromatic plane, respectively, and N , $\bar{N}$ are normalising constants. The orbital ϕ has π type symmetry with respect to the molecular plane of the aromatic system, and can therefore combine with the π MO's of this aromatic portion, to give a delocalisation of the aromatic π MO's out to the terminal protons.

This mechanism is discussed quantitatively by performing π MO calculations for the whole molecule, including the pseudo π AO's ϕ in the basis set. Calculations are presented in chapters 7 and 8 for molecules containing the fragments $C'-CH_2$ and $C'-C-CH_2$, respectively.

1.6 Literature Survey

Hyperfine structure in the ESR spectra of aromatic radicals was first encountered experimentally in 1953 [6]. As shown in section 1.3, this hyperfine structure was quite unexpected on the basis of the then accepted properties of aromatic radicals, assuming the unpaired electron was in a π type MO, which would have a nodal plane at the protons.

At first it was thought that a possible explanation was that bending vibrations of the $C'-H$ σ bonds out of the molecular plane might allow a non-zero Fermi interaction of the unpaired π electron with the protons, but experiments with deuterated compounds showed [7] that the splitting resulting from this mechanism would be orders of magnitude

less than the observed splittings.

In 1956 McConnell [8] gave an acceptable theoretical interpretation of the phenomenon, showing that σ - π exchange interaction (ie spin polarisation) could lead to a splitting of the observed order of magnitude. McConnell's treatment was based on a VB study of a C'-H fragment. In the same year, Weissman [9] gave an outline of an MO treatment for this same fragment. McConnell later [10] summarised and extended both of these treatments. None of these earlier papers applied their theoretical findings to the experimental results in any great detail.

A later and much more extensive treatment of a C'-H fragment was given by Colpa and Bolton [11] using second order perturbation theory rather than the simple first order perturbation theory used by McConnell and Weissman. There is, unfortunately, a mistake in sign in one of their equations. This is discussed in chapter 6. Carrington, in a review article [12] on ESR spectra, gave a summary of the experimental results and the theoretical attempts to explain them, up till 1962.

Recently, Colpa and de Boer [13] have given an MO treatment of spin polarisation in an aromatic C'-CH₂ fragment. Using an MO treatment rather than a VB treatment, they were able to separate the effects of spin polarisation and hyperconjugation in this fragment. McLachlan [13] had earlier given a VB treatment of the ethyl radical, but because of the correlation terms introduced into a VB treatment, it is not possible to determine separately the effects of spin polarisation and hyperconjugation from his treatment.

Colpa and de Boer [13] also gave a MO treatment of

hyperconjugation in $C'-CH_2$ fragments. There are several features in this treatment which are discussed in detail in chapter 7. In that chapter a much more extensive range of calculations for hyperconjugation in molecules containing $C'-CH_2$ fragments is presented.

No theoretical calculations by either a spin polarisation approach or a hyperconjugation approach have been performed for the cases $n \geq 2$. There has been a considerable amount of interest in the $C'-H$ case, but very little work has been done on the longer fragments.

Chapter 2

SPIN POLARISATION CALCULATIONS FOR
ORGANIC FRAGMENTS

2.1 Introduction

A model is set up to determine the spin density at the proton terminating a chain of carbon atoms, say $C'-C_nH$, where there is unpaired electron density confined to the initial carbon atom C' , considered to be part of an aromatic system. The terminal hydrogen atom is assumed to lie in the nodal plane of the π orbital at C' , or else to be sufficiently distant from C' that the amplitude of the wave function describing the unpaired π electron at C' is vanishingly small at the coordinates of the terminal proton. There is assumed to be no hyperconjugation in the fragment.

A spin polarisation treatment is used: the spatial distribution of the spins of the σ electrons of $C'-C_nH$ is altered as a result of $\sigma-\pi$ exchange interaction, but there is no net transfer of electrons, paired or unpaired, into these orbitals.

A wave function $|\Psi\rangle$ representing the ground state of the fragment is chosen by some suitable method. The proton hyperfine coupling constant a_H is then calculated as shown in section 1.2:

$$a_H = \frac{1}{\langle S_z \rangle} \frac{8\pi}{3h} g\beta g_N\beta_N \langle \Psi | \sum_i \delta(r_i - r_H) s_{iz} | \Psi \rangle.$$

The configuration interaction method is used to set up the wave function Ψ representing the ground state of the fragment: allowance for electronic interaction causes certain excited states Ψ_i to be mixed into the zero order representation of the ground state, Ψ_0 , to give

$$\Psi = (1 + \sum \lambda_i^2)^{-1/2} (\Psi_0 + \sum \lambda_i \Psi_i)$$

for which the proton coupling constant a_H is

$$a_H = \frac{8\pi}{3} g\beta g_N \beta_N Q(p)$$

where $Q(p)$ is the spin density at the coordinates p of the proton. It is shown in appendix II that $Q(p)$ is expressed, correct to second order, as

$$Q(p) = 2 \sum_i \left[-\frac{H_{0i}}{E_i} + \sum_{k \neq i} \frac{H_{0k} H_{ki}}{E_k E_i} \right] Q_{0i}(p) + \sum_i \frac{H_{0i}^2}{E_i^2} Q_{11}(p) \\ + 2 \sum_{i > j} \frac{H_{0j} H_{0i}}{E_j E_i} Q_{ij}(p)$$

where

$$Q_{ij}(p) = \frac{1}{\langle S_z \rangle} \langle \Psi_i | \sum_i \delta(r_i - r_H) s_{iz} | \Psi_j \rangle$$

$$H_{ij} = \langle \Psi_i | \sum_{i > j} e^2 / r_{ij} | \Psi_j \rangle$$

E_i = energy of state Ψ_i above state Ψ_0 .

Calculations are performed for the fragments C'-H, C'-C-H and C'-C-C-H in chapters 2, 3 and 4, and for the general case C'-C_{n-1}H in chapter 5. Both the valence bond (VB) and molecular orbital (MO) methods are used in turn to set up the wave function $|\Psi\rangle$ for the fragment C'-H; for the fragments C'-C-H, C'-C-C-H and C'-C_{n-1}H only the MO method is used, since it is simpler from a computational viewpoint for the longer fragments.

Once the calculations have been performed for the fragment C'-C_nH it is easy to extend the results to the fragment C'-C_nH₂, where the two terminal protons are no longer in the nodal plane of the π orbitals at C'.

The calculated values of the hyperfine coupling constants a_H for the protons in $C'-H$ and $C'-CH_2$ are then compared with the experimental values, obtainable from ESR measurements. Experimental values are also available, from NMR measurements, for the proton hyperfine coupling constants in systems

where the nitrogen atom may be considered as a pseudo aromatic carbon atom, in the sense that it appears to have a significant unpaired electron density.

AROMATIC $C'-H$ FRAGMENT

2.2 Introduction

It is assumed that the hydrogen atom lies in the plane of the aromatic ring. This plane is the nodal plane for the carbon π electrons, and therefore there is zero probability of finding the unpaired electron of the carbon π orbital at the hydrogen nucleus. Since the hydrogen atom is in the nodal plane of the aromatic carbon π orbitals, there is no delocalisation of the π electrons onto the hydrogen atom. However, $\sigma-\pi$ exchange interaction can lead to a significant spin density at the hydrogen nucleus, giving rise to a non-zero hyperfine coupling constant a_H .

VALENCE BOND TREATMENT OF AROMATIC C'-H FRAGMENT

2.3 The Model

The notation for the orbitals is:

π is the singly occupied carbon $2p_\pi$ AO

h is the carbon $sp^2\sigma$ hybrid pointing towards the hydrogen

s is the hydrogen $1s$ AO.

There are three electrons to be considered, each occupying one orbital. The zero order VB wave functions describing the fragment are constructed from both the space and spin parts of the separate AO wave functions. The space part of each wave function is given by

$$\phi(1,2,3) = \pi(1)h(2)s(3)$$

where the numbers refer to the electrons. There is just one unpaired electron in the fragment and therefore the spin parts of the wave functions must be constructed to be eigenfunctions of S^2 and S_z with eigenvalues $3/4$ and $1/2$ respectively, in atomic units. In appendix I these are determined using Wigner coefficients:

$$\phi_0 = 1/\sqrt{2}(\alpha\alpha\beta - \alpha\beta\alpha)$$

$$\phi_1 = 1/\sqrt{6}(\alpha\alpha\beta + \alpha\beta\alpha - 2\beta\alpha\alpha)$$

where the symbol $\alpha\alpha\beta$ is short for $\alpha(1)\alpha(2)\beta(3)$, and α, β stand for $m_s = +1/2, -1/2$ respectively.

The complete zero order VB wave functions for the fragment are

$$\Psi_0 = |\pi h s| \quad 1/\sqrt{2}(\alpha\alpha\beta - \alpha\beta\alpha)$$

$$\Psi_1 = |\pi h s| \quad 1/\sqrt{6}(\alpha\alpha\beta + \alpha\beta\alpha - 2\beta\alpha\alpha).$$

Here the notation $|\pi h s|$ stands for a 3×3 determinant, and includes the antisymmetrisation and renormalisation operations, as shown in appendix III.

Ψ_0 describes a bond between C and H, since the two electrons in the h and s orbitals have opposite spin; Ψ_1 describes a doublet state corresponding to antibonding between C and H. This antibonding means that Ψ_1 has a higher energy than Ψ_0 , and therefore Ψ_0 must provide the best zero order VB approximation for the ground state of the C'-H fragment.

The zero order representation for the ground state, Ψ_0 , cannot give rise to hyperfine splitting at H since it has no spin density in the σ type orbitals, h and s. However, when allowance is made for the electronic interaction term $\sum e^2/r_{ij}$ in the Hamiltonian, some of the excited state Ψ_1 is mixed into the zero order ground state Ψ_0 , to give a representation of the ground state

$$\Psi = \Psi_0 + \lambda \Psi_1$$

where the mixing coefficient λ is given by first order perturbation theory as $\lambda = -H_{01}/E_1$, where $H_{01} = \langle \Psi_1 | \frac{e^2}{r_{ij}} | \Psi_0 \rangle$ and E_1 is the energy of state Ψ_1 above state Ψ_0 . When there is only one excited state to be considered, as here, second order perturbation theory is equivalent to first order, as can be seen from the second order expression for the coefficients λ_i in appendix II. This representation Ψ_1 leads to hyperfine splitting, since Ψ_1 has net spin density in the orbitals h and s.

If allowance is made for the overlap between h and s in setting up the zero order VB wave functions, then

$$\begin{aligned}\Psi_0 &= [2(1+S^2)]^{-1/2} |\pi hs| \quad (\alpha\alpha\beta - \alpha\beta\alpha) \\ \Psi_1 &= [6(1-S^2)]^{-1/2} |\pi hs| \quad (\alpha\alpha\beta + \alpha\beta\alpha - 2\beta\alpha\alpha)\end{aligned}$$

where $S = \langle h | s \rangle$.

For the case where the spin density at C' in π is ρ , where ρ is less than one, the appropriate first order

representation of the ground state is

$$\Psi = \Psi_0 + \lambda e \Psi_1$$

where λ is as given above.

2.4 The Calculations

A representation has been found for the ground state wave function of the C'-H fragment, which leads to hyperfine splitting by the hydrogen atom. The hyperfine coupling constant a_H is evaluated from

$$a_H = \frac{8\pi}{3} \frac{g\beta g_N \beta_N Q(p)}{h}$$

where

$$Q(p) = \frac{1}{\langle \bar{S}_z \rangle} \langle \Psi | \sum_i \delta(r_i - r_H) s_{iz} | \Psi \rangle$$

and

$$\Psi = \Psi_0 + \lambda e \Psi_1$$

The wave functions making allowance for overlap are used to evaluate $Q(p)$. The operator $\sum_i \delta(r_i - r_H) s_{iz}$ is handled as shown in appendix II, to give

$$\begin{aligned} Q(p) &= 2 \left\{ -\lambda e [3(1-S^4)]^{-1/2} + \lambda^2 e^2 [3(1-S^2)]^{-1} \right\} |s(p)|^2 \\ &= -2 e \lambda [3(1-S^4)]^{-1/2} |s(p)|^2 \quad \text{since } \lambda e \ll 1 \end{aligned}$$

and assuming that $|h(p)|^2 \neq 0$, where $\phi(p)$ is the value of wave function ϕ at the coordinates p of the proton.

The mixing coefficient λ is now expressed in terms of exchange integrals, by evaluating $\lambda = -H_{01}/E_1$ using the VB representations for Ψ_0 and Ψ_1 . The method of reducing an expression such as H_{01} to a sum of exchange integrals is outlined in appendix III. This gives

$$H_{01} = \frac{-\sqrt{3}}{2\sqrt{1-S^4}} [J(\pi h) - J(\pi s)]$$

where $J(\pi h)$ is the exchange integral between π and h .

An estimate of the energy separation E_1 between states

Ψ_0 and Ψ_1 is also required. Both doublet states Ψ_0 and Ψ_1 have the same space part, and therefore the energy difference between them arises purely from the electrostatic repulsion term $\sum e^2/r_{ij}$. Thus E_1 may be determined by setting up the matrix for $H = \sum e^2/r_{ij}$ and determining the difference between the two eigenvalues of this matrix. The matrix elements are

$$H_{00} = -\frac{1}{2} (1+S^2)^{-1} [J(\pi_h) + J(\pi_s) - 2J(hs)]$$

$$H_{11} = \frac{1}{2} (1-S^2)^{-1} [J(\pi_h) + J(\pi_s) - 2J(hs)]$$

$$H_{10} = -\frac{1}{2}\sqrt{3}(1-S^4)^{-\frac{1}{2}} [J(\pi_h) - J(\pi_s)] .$$

The difference of the eigenvalues of this matrix is found to be

$$(1-S^4)^{-1} \left[(4-3S^4) [J(\pi_h) + J(\pi_s)]^2 - 12(1-S^4) J(\pi_h) J(\pi_s) - 4J(hs) [J(\pi_s) + J(\pi_h) - J(hs)] \right]^{\frac{1}{2}} .$$

Thus the proton coupling constant is

$$\begin{aligned} a_H &= \frac{8\pi}{3h} g\beta g_N \beta_N \frac{2 H_{10} \rho |s(p)|^2}{\sqrt{3} E_1 (1-S^4)^{\frac{1}{2}}} \\ &= -1423 \rho [J(\pi_h) - J(\pi_s)] \left\{ (4-3S^4) [J(\pi_h) + J(\pi_s)]^2 - 12(1-S^4) J(\pi_h) J(\pi_s) - 4J(hs) [J(\pi_s) + J(\pi_h) - J(hs)] \right\}^{-\frac{1}{2}} \\ &\quad \text{Mc/s} \end{aligned}$$

since $\frac{8\pi}{3h} g\beta g_N \beta_N |s(p)|^2$, the hyperfine coupling constant for a free hydrogen atom, is 1423 Mc/s.

If the overlap integral $S = \langle h|s \rangle$ is neglected throughout the calculations, the above formula may be simplified, to give

$$Q(p) = \frac{2 H_{10} \rho |s(p)|^2}{\sqrt{3} E_1}$$

where $H_{10} = -\frac{\sqrt{3}}{2} [J(\pi_h) - J(\pi_s)]$

$$E_1 = \sqrt{2} \left\{ [J(\pi_h) - J(\pi_s)]^2 + [J(\pi_h) - J(hs)]^2 + [J(hs) - J(\pi_s)]^2 \right\}^{1/2}$$

and so

$$a_H = \frac{-1423}{\sqrt{2}} [J(\pi_h) - J(\pi_s)] \left\{ [J(\pi_h) - J(\pi_s)]^2 + [J(\pi_h) - J(hs)]^2 + [J(hs) - J(\pi_s)]^2 \right\}^{-1/2} \text{ Mc/s.}$$

2.5 Numerical Evaluation

Values of the exchange integrals $J(\pi_h)$, $J(\pi_s)$, $J(hs)$ and of the overlap integral $\langle h|s \rangle$ are required. The overlap integral can be estimated using Slater wave functions for h and s , as shown in appendix V. For a C-H distance of 1.08 Å, the value of S , obtained from Mulliken's tables [35], is 0.720.

To obtain the values of the exchange integrals requires tedious computation and careful analysis of the rates of convergence of the processes, as well as simplifying approximations such as the use of Slater orbitals. Values of the required exchange integrals are available in the literature. Altmann, using Slater wave functions, gives [15] the values

$$J(\pi_h) = 1.81 \text{ e.v.}$$

$$J(\pi_s) = 0.745 \text{ e.v.}$$

Although Slater wave functions are not a faithful representation of self-consistent field (SCF) wave functions, they represent the outer parts of the SCF wave function, at the distances corresponding to normal bond distances, very well. Now for a two centre integral, such as $J(\pi_s)$, these outer parts are where the major contribution to the exchange integral is expected, so Altmann's value for $J(\pi_s)$ is probably reasonable. The integral $J(\pi_h)$, however, is an atomic integral, ie a one centre integral, and the value

given by Altmann is too large, because Slater wave functions do not represent the inner parts of the actual radial wave functions where there is a strong contribution to the atomic integral.

A more satisfactory method of estimating the atomic integral $J(\pi h)$ is by the method given by Condon and Shortley [16]. This leads to $J(\pi h) = (G_1 + 2F_2)/3 = 0.88 \text{ e.v.}$ [17], where G_1 and F_2 are the radial exchange and coulomb integrals respectively. Voge [18] obtained G_1 and F_2 empirically by adjusting these parameters to fit the electron energy levels of carbon. From Voge's data, McConnell [19] estimated that $J(\pi h) = 1.17 \text{ e.v.}$ Fraenkel [20] estimated that $J(\pi h) = 1.26 \text{ e.v.}$, but this is not a true theoretical value, since Fraenkel slightly adjusted some of his values to fit the experimental hyperfine data for C^{13} splittings in methyl radicals. However, Fraenkel also gives values for several of the other exchange integrals required in later chapters, so his values will be used for consistency. This may cause small systematic errors, but the main purpose of this numerical evaluation is to get an estimate of the order of magnitude of the expected proton hyperfine coupling constant. Fraenkel also gives values for $J(\pi s)$ and $J(hs)$, of 0.79 and -3.92 e.v. respectively.

All the data necessary to evaluate a_H is now available. To determine how sensitive the calculated values of a_H are to the choice of values for the exchange integrals, two sets of calculations are given, set I for Fraenkel's values, and set II for Altmann's $J(\pi s)$, McConnell's $J(\pi h)$, and Fraenkel's $J(hs)$.

Calculated values are given for a_H using these two sets of parameters, considering the case when overlap is neglected and the case when the overlap integral $S = \langle h | s \rangle$

is allowed for. Values are also given for the electrostatic integral H_{10} , the energy separation E_1 between the two doublet states, and the mixing coefficient λ .

Table 2.1 Calculated a_H Values for C'-H Fragment

	set I		set II	
	allowing for S	neglecting S	allowing for S	neglecting S
$H_{10}(\text{e.v.})$	-0.476	-0.407	-0.435	-0.372
$E_1(\text{e.v.})$	13.5	9.9	13.4	9.8
λ	.0353	.0412	.0326	.0376
$a_H(\text{Mc/s})$	-67.6ρ	-67.6ρ	-62.2ρ	-62.2ρ

Clearly neglect of the overlap integral S throughout the calculations makes no difference to the calculated value of a_H , although it does affect the values of the other quantities such as the energy separation E_1 . Neglect of S appears to overestimate the amount of mixing of the excited state Ψ_1 into Ψ_0 by about 15 %.

The value of a_H does not appear to be particularly sensitive to the choice of values for the exchange integrals. This VB treatment has indicated that the proton hyperfine coupling constant at the hydrogen atom adjacent to a carbon atom having spin density ρ in its π orbital should be about -65ρ Mc/s.

A comparison of this value with experiment is deferred until after a MO treatment of this fragment has been given in the next section.

MOLECULAR ORBITAL TREATMENT OF AROMATIC C'-H FRAGMENT

2.6 The Model

The notation used for the orbitals is:

π is the singly occupied carbon $2p_\pi$ AO [or one of the components of a π MO of the aromatic system]

b is the σ bonding MO of the C'-H bond

a is the σ antibonding MO of the C'-H bond.

There are three electrons to feed into the MO's; for the ground state one electron is placed in π , since the model requires one unpaired π -electron, two electrons in b, and none in a. The wave function representing this ground state is written as a Slater determinant

$$\Psi_0 = |\pi \ b \ b| \alpha\alpha\beta$$

where the notation is the same as that used in the VB section.

This Ψ_0 cannot lead to hyperfine splitting, since there is no spin density in the b orbital. However, this choice of ground state wave function has made no allowance for electronic interaction, given by a term $\sum e^2/r_{ij}$ in the Hamiltonian. When allowance is made for this term, some of the excited states Ψ_i are mixed into the zero order representation, Ψ_0 , of the ground state, to give a representation

$$\Psi = (1 + \sum \lambda_i^2)^{-1/2} (\Psi_0 + \sum \lambda_i \Psi_i)$$

for the ground state. The mixing coefficients λ_i are given by perturbation theory. This mixing of certain excited states into Ψ_0 gives a representation which leads to a non-zero proton hyperfine coupling constant.

Only those excited states that have the same value of M_s as Ψ_0 , namely $1/2$, can be mixed into Ψ_0 , since all other states have $H_{0i} = 0$, making the λ_i zero. It is assumed that there is only one unpaired electron in the fragment, and

therefore only those states with $S = \frac{1}{2}$ are considered. Excited states which do not lead to spin density at the terminal proton are not considered, since the wave function Ψ is used for calculating the proton hyperfine coupling constant, which depends only on the spin density $Q(p)$ at the proton. Therefore excited states corresponding to excitation in the π type orbitals need not be considered, since no π type orbital can give spin density at the coordinates of the proton, which is at a nodal plane for the π orbitals.

Consider an excited state with space function $|\pi b a|$. Spin product functions are required which are eigenfunctions of S^2 and S_z with eigenvalues $3/4$, $\frac{1}{2}$ respectively. As shown in appendix I, these may conveniently be determined using Wigner coefficients. There are two permitted doublet state configurations,

$$\Psi_1 = |\pi b a| 1/\sqrt{2} (\alpha\alpha\beta - \alpha\beta\alpha)$$

$$\Psi_2 = |\pi b a| 1/\sqrt{6} (2\beta\alpha\alpha - \alpha\alpha\beta - \alpha\beta\alpha) .$$

Now Ψ_1 has no net spin density in the σ orbitals, and therefore does not contribute to $Q(p)$. Therefore Ψ_1 need not be considered in Ψ , when Ψ is used to calculate $Q(p)$. Ψ_2 does contribute to $Q(p)$.

The doubly excited state $|\pi a a|$ need not be considered, since the only possible spin function is $\alpha\alpha\beta$, which has zero spin density in a .

The ground state of the C'-H fragment is thus represented by the wave function

$$\Psi = \Psi_0 + \lambda \Psi_2$$

when allowance is made for electronic interaction, and only those excited states contributing to the spin density $Q(p)$ have been considered. Since there is only one excited state being considered, the mixing coefficient λ is determined

from first order perturbation theory as $\lambda = -H_{02}/E_2$, in the notation of section 2.3.

In the more general case where the net spin density in π is ρ , where ρ is less than one, the appropriate ground state wave function for the C'-H fragment is

$$\Psi = \Psi_0 + \lambda \rho \Psi_2$$

where λ is as given above.

2.7 The Calculations

A representation has been found for the ground state of the C'-H fragment, which leads to a non-zero proton hyperfine coupling constant, since the mixing of the excited state Ψ_2 into Ψ_0 introduced net spin density into the orbitals.

The coupling constant a_H is evaluated from the relation

$$a_H = \frac{8\pi}{3h} g\beta g_N \beta_N Q(p)$$

where

$$Q(p) = \frac{1}{\langle S_z \rangle} \langle \Psi | \sum_i \delta(\mathbf{r}_i - \mathbf{r}_H) s_{iz} | \Psi \rangle .$$

A general expression for $Q(p)$ is given in appendix II. For this calculation only first order perturbation theory is used, as explained above, so the general expression for $Q(p)$ is reduced to

$$Q(p) = - 2 \frac{H_{02}}{E_2} Q_{02}(p) .$$

The matrix element $Q_{02}(p)$ is evaluated according to the general rules given in appendix II, to give

$$\begin{aligned} Q_{02}(p) &= 1/\sqrt{6} [\frac{1}{2} b(p)a(p) + \frac{1}{2} b(p)a(p)] / \frac{1}{2} \\ &= \frac{\sqrt{6}}{3} b(p)a(p) \end{aligned}$$

where $\phi(p)$ is the value of wave function ϕ at the coordinates

p of the proton. Thus the hyperfine coupling constant is

$$a_H = - \frac{4}{\sqrt{6}} \frac{H_{02}}{E_2} \frac{8\pi}{3} g\beta_N \beta_N b(p)a(p)\rho.$$

The electrostatic matrix element H_{02} is evaluated as shown in appendix III, to give

$$\begin{aligned} H_{02} &= 1/\sqrt{6} [-2(\pi b, a\pi) - (b\pi, a\pi) - (bb, ab) + (b\pi, a\pi) - (b\pi, \pi a) + (bb, ab)] \\ &= -\frac{1}{2}\sqrt{6}(b\pi, \pi a) \end{aligned}$$

where (ab, cd) denotes $\langle ab | \sum e^2/r_{ij} | cd \rangle$.

The energy difference E_2 cannot readily be evaluated, since Ψ_0 and Ψ_2 do not have the same space parts, as was the case in the VB treatment. Thus E_2 is left as a parameter, to be estimated from experimental data, or a more refined theoretical treatment of say the benzene molecule than is available at present.

The expression for a_H may be simplified by the linear combination of atomic orbitals (LCAO) approximation:

$$b = [2(1+S)]^{-1/2}(h+s) \quad a = [2(1-S)]^{-1/2}(h-s)$$

where h is an sp^2 hybrid at C' pointing to H, and s is the H 1s AO. S is the overlap integral $\langle h|s \rangle$. This gives

$$\begin{aligned} H_{02} &= - \frac{\sqrt{6}}{4\sqrt{1-S^2}} [J(\pi h) - J(\pi s)] \\ b(p)a(p) &= \frac{-|s(p)|^2}{2\sqrt{1-S^2}}, \text{ assuming } |h(p)|^2 \neq 0, \end{aligned}$$

and finally,

$$a_H = - \frac{[J(\pi h) - J(\pi s)]}{2 E_2 (1-S^2)} 1423 \rho \text{ Mc/s}$$

since $\frac{8\pi}{3h} g\beta_N \beta_N |s(p)|^2 = 1423 \text{ Mc/s}$.

If overlap is neglected, then $a_H = - \frac{[J(\pi h) - J(\pi s)]}{2 E_2} \rho 1423 \text{ Mc/s}$.

2.8 Numerical Evaluation

Unfortunately an experimental value is not available for the energy difference E_2 , which corresponds to a $\sigma \rightarrow \sigma^*$ transition for an aromatic compound, such as benzene. These transitions are apparently swamped by the much more intense $\pi \rightarrow \pi^*$ transitions. A value for E_2 could be obtained theoretically from a fully self-consistent field treatment of benzene, but such a study has not as yet been done. It is usually assumed [8,11] that E_2 is about 6-16 e.v., and is usually taken as 10 e.v. This value probably should be used in the formula making allowance for the overlap S . This overlap integral would certainly have to be considered in any detailed study of the σ electrons in benzene, since it is by no means small (0.720), and therefore it is reasonable to use the formula making allowance for overlap. This gives a_H about -67ρ Mc/s.

Thus a MO treatment of the C'-H fragment gives about the same predicted value of the proton hyperfine coupling constant, although until such time as an accurate value of E_2 is available, too much importance should not be attached to the exact calculated value of a_H from the MO treatment.

2.9 Comparison with Experiment

To compare the predicted coupling constants a_H with the experimental values, obtained from the hyperfine splitting in the ESR spectra of aromatic radicals, estimates are needed for the spin densities ρ at the aromatic carbon atoms adjacent to the hydrogen atoms. In both the VB and MO treatments of the fragment C'-H, no allowance was made for any of the carbon atoms other than C'; the required ρ should therefore be calculated from a valence theory making

no allowance for overlap of the carbon $2p_{\pi}$ AO's, in determining the wave functions for the molecule, or at least from an orthonormal representation of the wave function. Simple Hückel theory is based on precisely this assumption, and so should be suitable for estimating the spin densities ρ . For the benzene negative ion, both simple Hückel MO and VB theory predict $\rho = 1/6$, which gives a predicted a_H of about -10.8 Mc/s. The experimental value is -10.7 Mc/s [21]. Considering the simplicity of the model and the calculation details, the agreement between theory and experiment is even better than would be expected.

A further comparison with experiment is given in chapter 6, for a range of aromatic radicals.

2.10 Spin Polarisation in a N-H Fragment

The formula given for the proton coupling constant in C'-H is also valid for N-H, containing spin density in the π orbital of the N atom, provided the appropriate values are used for the exchange integrals. $J(\pi_s)$ and $J(h_s)$ may be obtained approximately (due to two interpolations for each integral) from Kotani's table of molecular integrals [22]. The integral $J(\pi_h)$ is evaluated from the relation $(G_1 + 2F_2)/3$ with the parameters G_1 and F_2 obtained from emission spectral data. Hinze and Jaffe [17], using a least squares procedure, give, for N, $F_2 = 2,084 \text{ cm}^{-1}$, $G_1 = 24,085 \text{ cm}^{-1}$. This gives $J(\pi_h) = 1.17 \text{ e.v.}$ From Kotani's tables, $J(\pi_s) = 0.61$ and $J(h_s) = -4.05 \text{ e.v.}$ Substitution of these values in the formula for a_H making no allowance for overlap, given in section 2.4, gives $a_H = -80\rho \text{ Mc/s}$, which is similar to the value for the C'-H fragment.

3.1 Introduction

In this chapter calculations are performed to determine the value of the proton hyperfine coupling constant a_H for the terminal proton of a fragment C'-C-H, containing π type spin density at C'. MO theory is used to obtain the wave function for the ground state of the fragment. Electronic interaction leads to a mixing of certain excited states into the zero order MO representation, Ψ_0 . Certain of these excited states which are mixed into Ψ_0 give rise to spin density at the terminal proton.

An expression is given in section 3.4 for a_H in terms of certain exchange integrals. Numerical evaluation shows

$$a_H = -4.4\rho \text{ Mc/s}$$

where ρ is the spin density at C'.

3.2 The Model

The notation for the orbitals is:

π is the singly occupied carbon C' $2p_\pi$ AO

$b_1(a_1)$ is the bonding (antibonding) MO of the C'-C bond

$b_2(a_2)$ is the bonding (antibonding) MO of the C-H bond.

The zero order MO representation of the ground state of the C'-C-H fragment is

$$\Psi_0 = |\pi b_1 b_1 b_2 b_2|^{\alpha\alpha\beta\alpha\beta}.$$

When allowance is made for the electronic interaction term $\sum e^2/r_{ij}$ in the Hamiltonian, certain excited states Ψ_i are mixed into Ψ_0 , to give a representation

$$\Psi = (1 + \sum \lambda_i^2)^{-1/2} (\Psi_0 + \sum \lambda_i \Psi_i)$$

for the ground state. The coefficients λ_i are given by second order perturbation theory as

$$\lambda_i = - \frac{H_{0i}}{E_i} + \sum_{k \neq i} \frac{H_{0k} H_{ki}}{E_k E_i}$$

where

$$H_{ij} = \langle \Psi_i | \sum e^2 / r_{ij} | \Psi_j \rangle$$

and E_i is the energy difference between Ψ_0 and Ψ_i .

Only those excited states with $M_s = \frac{1}{2}$ have $H_{0i} \neq 0$ and therefore have non-zero λ_i . In the π electron radicals to which these theoretical results are to be applied, there is only one unpaired electron, and therefore the excited state configurations to be mixed into Ψ_0 must have $S = \frac{1}{2}$. In calculating a_H , only those excited states which make non-zero contributions to $Q(p)$, the spin density at the proton, need be considered in mixing the Ψ_i into Ψ_0 . Therefore excitation in the π type orbitals is not considered, since this cannot lead to spin density at the proton.

Consider the excited state with space function $|\pi b_1 b_1 b_2 a_2|$. The spin function for this state must be $|\pi b_1 b_1 b_2 a_2|^{\alpha\beta..}$ to satisfy the Pauli principle. The spin functions of the remaining three non-equivalent electrons are determined by the $|S M_s\rangle = |\frac{1}{2} \frac{1}{2}\rangle$ spin eigenfunctions for three electrons, given in appendix I. This gives two spin states,

$$1/\sqrt{6}(2\beta\alpha\beta\alpha\alpha\alpha\alpha\alpha\beta\beta\alpha\alpha\alpha\beta\alpha\beta)$$

$$1/\sqrt{2}(\alpha\alpha\beta\beta\alpha\alpha\alpha\beta\alpha\beta) .$$

The second set of $|\frac{1}{2} \frac{1}{2}\rangle$ three electron spin eigenfunctions given in AI.4 has been used. This is quite arbitrary.

The second of the above spin eigenfunctions for the C'-C-H

fragment does not give net spin density in the σ orbitals, whereas the first one does. Therefore, the required excited state doublet configuration which can mix into Ψ_0 and lead to spin density at the proton is

$$\Psi_1 = |\pi b_1 b_1 b_2 a_2| 1/\sqrt{6} (2\beta\alpha\beta\alpha\alpha - \alpha\alpha\beta\beta\alpha - \alpha\alpha\beta\alpha\beta) .$$

Similarly for an excited state with space function $|\pi b_1 a_1 b_2 b_2|$ the required doublet state configuration is

$$\Psi_2 = |\pi b_1 a_1 b_2 b_2| 1/\sqrt{6} (2\beta\alpha\alpha\alpha\beta - \alpha\alpha\beta\alpha\beta - \alpha\beta\alpha\alpha\beta) .$$

The next excited state to be considered is the doubly excited one, with space function $|\pi b_1 a_1 b_2 a_2|$. There are no restrictions imposed on the spin functions in this case, except that the state must have $S = 1/2$, $M_s = 1/2$. The spin eigenfunctions for five non-equivalent electrons are given in appendix I. There are five eigenfunctions $|1/2 1/2\rangle$; the only ones contributing to a_H are those leading to spin density at the proton, and those having a non-zero matrix element of electrostatic interaction with Ψ_0 , since this determines the mixing of the excited states into the ground state.

Of the five eigenfunctions given in AI.6, only one, e, has $H_{0i} = 0$. Now any linear combination of these five spin eigenfunctions $|1/2 1/2\rangle$ is also a spin eigenfunction $|1/2 1/2\rangle$. In the next section it is shown by taking certain orthogonal linear combinations of the four eigenfunctions that do not have $H_{0i} = 0$, that only one of these combinations makes any contribution to $Q(p)$. The other three either have $Q_{ij}(p) = 0$, $H_{0i} = 0$, or $H_{il} = 0$. From the general form of $Q(p)$, given in appendix II, it is seen that such wave functions make no contribution to $Q(p)$. The required doublet state configuration is shown to be

$$\Psi_3 = |\pi b_1 a_1 b_2 a_2| 1/2\sqrt{3} (2\alpha\beta\beta\alpha\alpha - \alpha\beta\alpha\beta\alpha - \alpha\beta\alpha\alpha\beta - \alpha\alpha\beta\beta\alpha - \alpha\alpha\beta\alpha\beta + 2\alpha\alpha\alpha\beta\beta) .$$

There are no other doubly excited states, or even more highly excited states, which make any contribution to $Q(p)$. For all possible cases, either zero $Q_{ij}(p)$ or H_{ij} matrix elements mean that these states can make no contribution to $Q(p)$. This is because the $Q_{ij}(p)$ are the matrix elements of a one-electron operator, and so vanish if states i and j differ by more than one of their individual one electron quantum numbers. Several other $Q_{ij}(p)$ are virtually zero since they are functions only of $a_1(p)b_1(p)$, which are negligibly small. The H_{ij} matrix elements are from a two electron operator, and so vanish if states i and j differ by more than two of their individual one electron quantum numbers.

Thus the improved representation of the ground state, as regards hyperfine properties, is

$$\Psi = [1 + \sum \lambda_i^2]^{-1/2} [\Psi_0 + \lambda_1 \Psi_1 + \lambda_2 \Psi_2 + \lambda_3 \Psi_3].$$

The general expression for $Q(p)$, given in appendix II, is thus reduced to the simpler form

$$Q(p) = 2 \left[-\frac{H_{01}}{E_1} + \sum_{k \neq 1} \frac{H_{0k} H_{k1}}{E_k E_1} \right] Q_{01}(p) + \frac{H_{01}^2}{E_1^2} Q_{11}(p) + 2 \frac{H_{03} H_{02}}{E_3 E_2} Q_{23}(p)$$

since it is shown in the next section that $Q_{0i}(p) = 0$, $i \neq 1$ and $Q_{ii}(p) = 0$, $i \neq 1$.

The choice of the doubly excited state configurations, to simplify the formula for $Q(p)$, has not so far involved any approximations or assumptions. The procedure amounted merely to choosing convenient linear combinations of the initial set of spin eigenfunctions.

3.3 The Calculations

The wave function chosen above to represent the ground state of the C'-CH fragment is now used to calculate

the hyperfine coupling constant a_H . The wave functions involved are:

$$\begin{aligned}
 \Psi_0 &= |\pi b_1 b_1 b_2 b_2|^{\alpha\alpha\beta\alpha\beta} \\
 \Psi_1 &= |\pi b_1 b_1 b_2 a_2| \frac{1}{\sqrt{6}} (2\beta\alpha\beta\alpha\alpha - \alpha\alpha\beta\alpha\beta - \alpha\alpha\beta\beta\alpha) \\
 \Psi_2 &= |\pi b_1 a_1 b_2 b_2| \frac{1}{\sqrt{6}} (2\beta\alpha\alpha\alpha\beta - \alpha\alpha\beta\alpha\beta - \alpha\beta\alpha\alpha\beta) \\
 \Psi_3 &= |\pi b_1 a_1 b_2 a_2| \frac{1}{2\sqrt{3}} (2\alpha\beta\beta\alpha\alpha - \alpha\beta\alpha\beta\alpha - \alpha\beta\alpha\alpha\beta - \alpha\alpha\beta\beta\alpha - \alpha\alpha\beta\alpha\beta + 2\alpha\alpha\alpha\beta\beta) \\
 \Psi_{3a} &= |\pi b_1 a_1 b_2 a_2| \frac{1}{2\sqrt{3}} (2\alpha\alpha\alpha\beta\beta - 2\alpha\alpha\beta\alpha\beta - \alpha\beta\alpha\beta\alpha + \alpha\beta\beta\alpha\alpha - \beta\alpha\alpha\beta\alpha + \beta\alpha\beta\alpha\alpha) \\
 \Psi_{3b} &= |\pi b_1 a_1 b_2 a_2| \frac{1}{6} (2\alpha\alpha\beta\alpha\beta + 2\alpha\alpha\alpha\beta\beta - 4\alpha\alpha\beta\beta\alpha - 2\alpha\beta\alpha\alpha\beta - 2\beta\alpha\alpha\alpha\beta \\
 &\quad + \alpha\beta\alpha\beta\alpha + \alpha\beta\beta\alpha\alpha + \beta\alpha\alpha\beta\alpha + \beta\alpha\beta\alpha\alpha) \\
 \Psi_{3c} &= |\pi b_1 a_1 b_2 a_2| \frac{1}{2} (\alpha\beta\alpha\beta\alpha - \alpha\beta\beta\alpha\alpha - \beta\alpha\alpha\beta\alpha + \beta\alpha\beta\alpha\alpha) \\
 \Psi_{3d} &= |\pi b_1 a_1 b_2 a_2| \frac{1}{2\sqrt{3}} (2\alpha\beta\alpha\alpha\beta - 2\beta\alpha\alpha\alpha\beta - \alpha\beta\alpha\beta\alpha - \alpha\beta\beta\alpha\alpha + \beta\alpha\alpha\beta\alpha + \beta\alpha\beta\alpha\alpha) \\
 \Psi_{3e} &= |\pi b_1 a_1 b_2 a_2| \frac{1}{3\sqrt{2}} (3\beta\beta\alpha\alpha\alpha + \alpha\alpha\beta\beta\alpha + \alpha\alpha\beta\alpha\beta + \alpha\alpha\alpha\beta\beta - \alpha\beta\alpha\beta\alpha \\
 &\quad - \alpha\beta\alpha\alpha\beta - \alpha\beta\beta\alpha\alpha - \beta\alpha\alpha\alpha\beta - \beta\alpha\alpha\beta\alpha - \beta\alpha\beta\alpha\alpha).
 \end{aligned}$$

The required matrix elements are H_{01} , H_{02} , H_{03} , H_{21} , H_{31} , $Q_{01}(p)$, $Q_{11}(p)$ and $Q_{23}(p)$. Other matrix elements for Ψ_{3i} , $i = a, b, c, d, e$ are also required, to show that Ψ_3 is the only doubly excited state that need be considered.

Using the methods outlined in appendix III, the electrostatic matrix elements are evaluated to give

$$\begin{aligned}
 H_{01} &= -\frac{1}{2}\sqrt{6} (b_2 \pi, \pi a_2) \\
 H_{02} &= -\frac{1}{2}\sqrt{6} (b_1 \pi, \pi a_1) \\
 H_{03a} &= \frac{1}{2}\sqrt{3} [2(b_1 b_2, a_2 a_1) - (b_1 b_2, a_1 a_2)] \\
 H_{03b} &= \frac{3}{2} (b_1 b_2, a_1 a_2) \\
 H_{03c} &= \frac{1}{2} [(b_1 b_2, a_1 a_2) - 2(b_1 b_2, a_2 a_1)] \\
 H_{03d} &= -\frac{1}{2}\sqrt{3} (b_1 b_2, a_1 a_2) \\
 H_{03e} &= 0 \\
 H_{21} &= - (a_1 b_2, a_2 b_1) .
 \end{aligned}$$

The spin density matrix elements are evaluated by the methods given in appendix II, assuming that $b_1(p)a_1(p) = 0$. The non-zero matrix elements are

$$\begin{aligned} Q_{01}(p) &= \frac{1}{3}\sqrt{6} b_2(p)a_2(p) \\ Q_{11}(p) &= \frac{2}{3} [b_2^2(p) + a_2^2(p)] \\ Q_{23a}(p) &= -\frac{\sqrt{2}}{12} b_2(p)a_2(p) \\ Q_{23b}(p) &= -\frac{\sqrt{6}}{36} b_2(p)a_2(p) \\ Q_{23c}(p) &= \frac{\sqrt{6}}{4} b_2(p)a_2(p) \\ Q_{23d}(p) &= \frac{\sqrt{2}}{4} b_2(p)a_2(p) \\ Q_{23e}(p) &= \frac{2\sqrt{3}}{9} b_2(p)a_2(p) \end{aligned}$$

where $\psi(p)$ is the value of the wave function ψ at the coordinates p of the proton.

Linear combinations of the four doubly excited state configurations Ψ_{3a} to Ψ_{3d} are now chosen, to simplify the expression for $Q(p)$. Two linear combinations Ψ_{3f} and Ψ_{3g} of Ψ_{3a} to Ψ_{3d} can be chosen so that $H_{03f} = H_{03g} = 0$. The linear combination

$$\Psi_{3j} = N(c_a \Psi_{3a} + c_b \Psi_{3b} + c_c \Psi_{3c} + c_d \Psi_{3d})$$

has

$$\begin{aligned} H_{03j} &= N(c_a H_{03a} + c_b H_{03b} + c_c H_{03c} + c_d H_{03d}) \\ &= (b_1 b_2, a_2 a_1) [\sqrt{3}c_a - c_c] + \frac{1}{2}(b_1 b_2, a_1 a_2) \times \\ &\quad [3c_b + c_c - \sqrt{3}c_a - \sqrt{3}c_d] \end{aligned}$$

and this is zero if $c_c = \sqrt{3}c_a$ and $c_d = \sqrt{3}c_b$. Therefore, by taking

$$\Psi_{3f} = 1/2\sqrt{2}(\Psi_{3a} + \Psi_{3b} + \sqrt{3}\Psi_{3c} + \sqrt{3}\Psi_{3d})$$

and

$$\Psi_{3g} = 1/2\sqrt{2}(\Psi_{3a} - \Psi_{3b} + \sqrt{3}\Psi_{3c} - \sqrt{3}\Psi_{3d})$$

$H_{03f} = H_{03g} = 0$ and $Q_{03f}(p) = Q_{03g}(p) = 0$, since $Q_{03i}(p) = 0$ for $i = a, b, c, d$.

Another linear combination Ψ_{3h} can be chosen so that $Q_{23h}(p) = 0$, since

$$Q_{23j}(p) = N[c_a Q_{23a}(p) + c_b Q_{23b}(p) + c_c Q_{23c}(p) + c_d Q_{23d}(p)]$$

$$= \frac{N\sqrt{6}}{36} [-\sqrt{3}c_a - c_b + 9c_c + 3\sqrt{3}c_d] b_2(p) a_2(p)$$

which is zero if $c_a = \sqrt{3}$, $c_b = -3$, $c_c = -1$, $c_d = \sqrt{3}$.

Thus

$$\Psi_{3h} = 1/4(\sqrt{3}\Psi_{3a} - 3\Psi_{3b} - \Psi_{3c} + \sqrt{3}\Psi_{3d})$$

has $Q_{23h}(p) = 0$.

The fifth eigenfunction, say Ψ_3 , must be orthogonal to each of Ψ_{3f} , Ψ_{3g} , Ψ_{3h} , and therefore is completely determined once these other three have been chosen. These orthogonality conditions give

$$\Psi_3 = 1/4(3\Psi_{3a} + \sqrt{3}\Psi_{3b} - \sqrt{3}\Psi_{3c} - \Psi_{3d})$$

and from the above expression for $Q_{23j}(p)$ it follows that

$$Q_{23}(p) = -\frac{\sqrt{2}}{3} b_2(p) a_2(p).$$

The wave functions for Ψ_{3h} and Ψ_3 are now expanded in terms of the basis set of spin product functions, in order to evaluate the matrix elements $H_{3h,1}$ and H_{31} :

$$\Psi_{3h} = |\pi b_1 a_1 b_2 a_2| 1/2(\alpha\beta\alpha\alpha\beta + \alpha\alpha\beta\beta\alpha - \alpha\beta\alpha\beta\alpha - \alpha\alpha\beta\alpha\beta)$$

$$\Psi_3 = |\pi b_1 a_1 b_2 a_2| 1/2\sqrt{3}(2\alpha\beta\beta\alpha\alpha - \alpha\beta\alpha\beta\alpha - \alpha\beta\alpha\alpha\beta - \alpha\alpha\beta\beta\alpha - \alpha\alpha\beta\alpha\beta + 2\alpha\alpha\alpha\beta\beta).$$

The required matrix elements are

$$Q_{33}(p) = Q_{3h3h}(p) = 0$$

$$Q_{33h}(p) = 0$$

$$H_{3h,1} = 0$$

$$H_{31} = \frac{1}{2}\sqrt{2} (\pi a_1, b_1 \pi) .$$

Clearly the doubly excited state configuration Ψ_{3h} makes no contribution to $Q(p)$, and as stated in section 3.2, Ψ_3 is the only doubly excited state configuration which makes a contribution to $Q(p)$.

The general expression for $Q(p)$ thus becomes

$$Q(p) = 2 \left[\frac{H_{01}}{E_1} + \frac{H_{02}H_{21}}{E_2 E_1} + \frac{H_{03}H_{31}}{E_3 E_1} \right] Q_{01}(p) + \frac{H_{01}^2}{E_1^2} Q_{11}(p) \\ + 2 \frac{H_{02}H_{03}}{E_2 E_3} Q_{23}(p)$$

where the non-zero matrix elements are

$$H_{01} = -\frac{1}{2}\sqrt{6} (b_2 \pi, \pi a_2) \\ H_{02} = -\frac{1}{2}\sqrt{6} (b_1 \pi, \pi a_1) \\ H_{03} = \sqrt{3} (b_1 b_2, a_2 a_1) \\ H_{21} = - (a_1 b_2, a_2 b_1) \\ H_{31} = \frac{1}{2}\sqrt{2} (a_1 \pi, \pi b_1) \\ Q_{01}(p) = \frac{1}{3} \sqrt{6} b_2(p) a_2(p) \\ Q_{11}(p) = \frac{2}{3} [b_2^2(p) + a_2^2(p)] \\ Q_{23}(p) = -\frac{\sqrt{2}}{3} b_2(p) a_2(p) .$$

To simplify this expression and make a numerical evaluation of the matrix elements possible, the LCAO approximation is made for the MO's a_1, a_2, b_1, b_2 :

$$b_1 = 1/\sqrt{2}(h_1 + h_2) \quad a_1 = 1/\sqrt{2}(h_1 - h_2) \\ b_2 = 1/\sqrt{2}(h_3 + s) \quad a_2 = 1/\sqrt{2}(h_3 - s)$$

where h_1 is an sp^2 hybrid orbital at C' pointing to C
 h_2 " " " " " " C " " C'
 h_3 " " " " " " C " " H
 s is the H 1s AO.

Assuming that $|h_3(p)|^2 = 0$, this gives

$$\begin{aligned} Q_{01}(p) &= \sqrt{\frac{6}{6}} |s(p)|^2 \\ Q_{11}(p) &= \frac{2}{3} |s(p)|^2 \\ Q_{23}(p) &= \sqrt{\frac{2}{6}} |s(p)|^2, \end{aligned}$$

and for the electrostatic matrix elements,

$$\begin{aligned} (b_2\pi, \pi a_2) &= \frac{1}{2}[J(\pi h_3) - J(\pi s)] \\ (b_1\pi, \pi a_1) &= \frac{1}{2}[J(\pi h_1) - J(\pi h_2)] \\ (b_1b_2, a_2a_1) &= (a_1b_2, a_2b_1) \\ &= \frac{1}{4}[J(h_1h_3) - J(h_1s) + J(h_2s) - J(h_2h_3)]. \end{aligned}$$

It is further assumed that the energy of the doubly excited state Ψ_3 above the ground state Ψ_0 , E_3 , is given by the sum of the energies for the corresponding two single excitations, $E_3 = E_2 + E_1$.

The final expression for the spin density at the proton is then

$$Q(p) = [A + A^2 + B] |s(p)|^2$$

and for the proton hyperfine coupling constant,

$$a_H = 1423 [A + A^2 + B] \text{ Mc/s}$$

where $A = \frac{-1}{2E_1} [J(\pi h_3) - J(\pi s)]$

$$B = - \left[\frac{J(\pi h_1) - J(\pi h_2)}{2E_2} \right] \left[\frac{J(h_1h_3) - J(h_1s) + J(h_2s) - J(h_2h_3)}{2E_1} \right].$$

The first order term, A, describes the spin polarisation in

the bond between C and H caused by the net spin density in π . The second order term, B, may be interpreted in an interesting manner: the first bracket represents the spin polarisation of the bond between C' and C by the spin density in π , and the second bracket represents the spin polarisation of the bond between C and H resulting from the spin density already induced in the first bond. This is referred to as a consecutive polarisation mechanism.

3.4 Numerical Evaluation

In making a numerical evaluation of the various exchange integrals and hence a_H , all the h_i are taken as sp^2 hybrids. This is not realistic for h_2 and h_3 , but allows an immediate extension of the results to the case for $C'-CH_2$, which is of considerably more interest than $C'-C-H$, since experimental results are available for two radicals containing the fragment $C'-CH_2$.

Karplus and Fraenkel [20] give values for most of the required exchange integrals:

$$\left. \begin{array}{l} J(\pi h_1) = 1.26 \text{ e.v.} \\ J(\pi h_2) = 0.932 \text{ e.v.} \\ J(h_2 h_3) = 0.921 \text{ e.v.} \\ J(h_1 h_3) = 0.573 \text{ e.v.} \end{array} \right\} \text{ for } sp^2 \text{ hybrids } h_i$$

and Altmann [15] gives $J(\pi h_3) = 0.036 \text{ e.v.}$ Karplus and Fraenkel's value for $J(h_1 h_3)$ actually refers to a carbon-carbon internuclear distance of $1.40 \text{ \AA}$ rather than the $1.54 \text{ \AA}$ to be expected for an aliphatic chain. However, this value is used since the main purpose is to obtain an order of magnitude estimate of a_H , not a highly accurate value. The values of the other exchange integrals are assumed negligible (eg $J(\pi s) = 0$).

In the evaluation of a_H for a C'-H fragment, in section 2.8, an analogous expression to A was obtained, namely

$$\frac{-[J(\pi_h) - J(\pi_s)]}{2E_1}$$

except that the numerical values of the two exchange integrals was not the same. For the C'-H fragment, $[J(\pi_h) - J(\pi_s)] = 0.47$ e.v., using Fraenkel's values, which gave $a_H = -68$ Mc/s, whereas for this C'-C-H fragment, $[J(\pi_{h_3}) - J(\pi_s)] = 0.036$ e.v. Thus, assuming that E_1 is about the same as the E_2 in the C'-H fragment, $1423A = -68 \times 0.036/0.47 = -5.2$ Mc/s. This gives $A = .0035$ and clearly A^2 is negligible compared with A.

Similarly, $1423[J(\pi_{h_1}) - J(\pi_{h_2})]/2E_2 = 68 \times 0.33/0.47 = 47.7$ Mc/s. Assuming $E_1 \div 10$ e.v., then

$$1423B = -47.7 \times [0.573 - 0.912]/20 = +0.81 \text{ Mc/s.}$$

Thus $a_H = -5.2 + 0.8 \text{ Mc/s}$
 $= -4.4 \text{ Mc/s.}$

For the case where the spin density in π is ρ , where ρ is less than one, the proton hyperfine coupling constant becomes

$$a_H = -4.4\rho \text{ Mc/s.}$$

3.4 Extension to Aromatic C'-CH₂ Fragment

The conclusions for the C'-C-H fragment are also valid for a C'-CH₂ fragment, where the terminal hydrogens no longer lie in the plane of the aromatic system. The C'-CH₂ fragment is considered to have a bonding orbital B_i and an antibonding orbital A_i in each C-H bond [$i=1,2$]. Rather than use these MO's directly, symmetry adapted linear combinations are taken:

Considering only the π orbitals of the fragment, the ground state is $|\psi_2\psi_2\pi|\alpha\beta\alpha$, which does not have net spin density in the orbitals about the protons. However, configuration interaction with some excited π states would lead to net spin density. Consider the excited state $|\psi_2\psi_2\psi_4|\alpha\beta\alpha$ giving a first order approximation for the ground state

$$|\psi_2\psi_2\pi|\alpha\beta\alpha + \lambda |\psi_2\psi_2\psi_4|\alpha\beta\alpha = |\psi_2\psi_2(\pi + \lambda\psi_4)|\alpha\beta\alpha.$$

Clearly configuration interaction with excited π states is equivalent to mixing between π , ψ_2 and ψ_4 . However, usually this mixing is referred to as hyperconjugation, so that neglect of hyperconjugation means spin polarisation can occur only in the σ orbitals, and as shown above this leads to a proton hyperfine coupling constant of -4.4 Mc/s.

A comparison with experiment is deferred until section 6.3, where it is shown that the observed a_H values in two molecules containing $C'-CH_2$ fragments are considerably larger than those predicted by spin polarisation in the σ orbitals of the $C'-CH_2$ fragment. Thus there is no justification for ignoring this mixing of the π orbitals, and in fact when this mixing is allowed for, in a full hyperconjugation treatment, the calculated values are in much more satisfactory agreement with experiment. A hyperconjugation treatment of radicals containing $C'-CH_2$ fragments is given in chapter 7.

Chapter 4

SPIN POLARISATION IN AN AROMATIC

C'-C-C-H FRAGMENT

4.1 Introduction

A calculation is performed to determine the value of the proton hyperfine coupling constant a_H for a fragment C'-C-C-H, containing π type spin density at C'. MO theory gives a representation

$$\Psi = (1 + \sum \lambda_i^2)^{-1/2} (\Psi_0 + \sum \lambda_i \Psi_i)$$

of the ground state of the fragment, where the Ψ_i are excited states which must be considered to be mixed into the zero order representation of the ground state, Ψ_0 , when allowance is made for electronic interaction.

An expression for a_H in terms of certain exchange integrals is given in section 4.3. Numerical evaluation shows that

$$a_H = +0.15\rho \text{ Mc/s}$$

where ρ is the spin density at C'. However, there is some uncertainty in the magnitude, and possibly even the sign, of a_H , because values are not available for some of the required exchange integrals.

4.2 The Model

The notation for the orbitals is:

π is the singly occupied carbon C' $2p_\pi$ AO

$b_1(a_1)$ is the bonding (antibonding) MO of the C'-C bond

$b_2(a_2)$ " " " C-C "

$b_3(a_3)$ " " " C-H " .

The zero order representation of the ground state of the C'-C-C-H fragment is

$$\Psi_0 = |\pi b_1 b_1 b_2 b_2 b_3 b_3| \alpha\alpha\beta\alpha\beta\alpha\beta .$$

When allowance is made for the electronic interaction term $\sum e^2/r_{ij}$, certain excited states Ψ_i are mixed into Ψ_0 . Only those excited states which contribute to $Q(p)$ are considered; therefore only excited states corresponding to excitations in the σ orbitals are considered.

As explained in section 3.2, only states $|S M_S\rangle = |\frac{1}{2} \frac{1}{2}\rangle$ need be considered. There are twenty four different excited states which give rise to $|\frac{1}{2} \frac{1}{2}\rangle$ states, and many of these have more than one possible spin function. Thus there are a great number of possible excited state configurations to be considered. The space parts of these wave functions are

$$\begin{aligned}
 \Psi_1 &= |\pi b_1 b_1 b_2 b_2 b_3 a_3| & \Psi_{13} &= |\pi b_1 a_1 a_2 a_2 b_3 b_3| \\
 \Psi_2 &= |\pi b_1 b_1 b_2 a_2 b_3 b_3| & \Psi_{14} &= |\pi a_1 a_1 b_2 a_2 b_3 b_3| \\
 \Psi_3 &= |\pi b_1 a_1 b_2 b_2 b_3 b_3| & \Psi_{15} &= |\pi a_1 a_1 b_2 a_2 b_3 a_3| \\
 \Psi_4 &= |\pi b_1 b_1 b_2 a_2 b_3 a_3| & \Psi_{16} &= |\pi b_1 a_1 a_2 a_2 b_3 a_3| \\
 \Psi_5 &= |\pi b_1 a_1 b_2 b_2 b_3 a_3| & \Psi_{17} &= |\pi b_1 a_1 b_2 a_2 a_3 a_3| \\
 \Psi_6 &= |\pi b_1 a_1 b_2 a_2 b_3 b_3| & \Psi_{18} &= |\pi b_1 b_1 a_2 a_2 a_3 a_3| \\
 \Psi_7 &= |\pi b_1 b_1 b_2 b_2 a_3 a_3| & \Psi_{19} &= |\pi a_1 a_1 b_2 b_2 a_3 a_3| \\
 \Psi_8 &= |\pi b_1 b_1 a_2 a_2 b_3 b_3| & \Psi_{20} &= |\pi a_1 a_1 a_2 a_2 b_3 b_3| \\
 \Psi_9 &= |\pi a_1 a_1 b_2 b_2 b_3 b_3| & \Psi_{21} &= |\pi b_1 a_1 a_2 a_2 a_3 a_3| \\
 \Psi_{10} &= |\pi b_1 a_1 b_2 a_2 b_3 a_3| & \Psi_{22} &= |\pi a_1 a_1 b_2 a_2 a_3 a_3| \\
 \Psi_{11} &= |\pi b_1 a_1 b_2 b_2 a_3 a_3| & \Psi_{23} &= |\pi a_1 a_1 a_2 a_2 b_3 a_3| \\
 \Psi_{12} &= |\pi b_1 b_1 b_2 a_2 a_3 a_3| & \Psi_{24} &= |\pi a_1 a_1 a_2 a_2 a_3 a_3| .
 \end{aligned}$$

Fortunately most of these wave functions make no contribution to $Q(p)$, and hence need not be considered in the second order representation of the ground state of the fragment.

As in section 3.3 a large number of these wave functions have either $Q_{ij}(p)$ or H_{ij} equal to zero, and so make no contribution to $Q(p)$. The spin density matrix elements $Q_{ij}(p)$ are significantly different from zero only if they are functions of $b_3(p)$ or $a_3(p)$, since the values of the wave functions b_1, a_1, b_2, a_2 are virtually zero at the coordinates of the terminal proton.

All of the wave functions Ψ_{10} to Ψ_{24} differ from Ψ_0 by more than two of the individual sets of one electron quantum numbers, and therefore the matrix elements H_{0i} are zero for $i = 10, 11, \dots, 24$. Thus none of these wave functions need be considered in the second order representation of the ground state. The matrix element H_{61} is also zero.

The only non-zero $Q_{0i}(p)$ is for $i = 1$. The only other spin density matrix elements that need be considered are $Q_{ij}(p)$ for $i, j = 1, 2, \dots, 9$. Inspection of the space parts of the wave functions shows that the only ones which are not identically zero or else virtually zero are $Q_{11}(p)$, $Q_{24}(p)$ and $Q_{35}(p)$.

Thus the representation of the ground state of the C'-C-C-H fragment, for hyperfine studies, is

$$\Psi = [1 + \sum \lambda_i^2]^{-1/2} [\Psi_0 + \sum_{i=1}^5 \lambda_i \Psi_i]$$

where the mixing coefficients λ_i are given by second order perturbation theory. The appropriate spin parts of these five excited state wave functions must now be chosen.

All five of the wave functions have limitations on the spin functions imposed by the Pauli principle. Ψ_1 must have a spin function $^{\alpha\beta\alpha\beta}$, the spin functions for the remaining three positions being determined by the spin eigenfunctions for three non-equivalent electrons, as given in appendix I. There is no unique set of spin eigenfunctions $|\frac{1}{2} \frac{1}{2}\rangle$ for three non-equivalent electrons, but for

convenience set II is used. Thus there are two possible spin product functions for Ψ_1 :

$$\begin{aligned} & 1/\sqrt{2}(\alpha\alpha\beta\alpha\beta\alpha - \alpha\alpha\beta\alpha\beta\alpha) \\ & 1/\sqrt{6}(2\beta\alpha\beta\alpha\beta\alpha - \alpha\alpha\beta\alpha\beta\alpha - \alpha\alpha\beta\alpha\beta\alpha) . \end{aligned}$$

The first one gives $Q_{01}(p) = 0$, whereas the second gives a non-zero $Q_{01}(p)$. Thus the spin function for Ψ_1 is chosen as

$$\Psi_1 = |\pi b_1 b_1 b_2 b_2 b_3 a_3| 1/\sqrt{6}(2\beta\alpha\beta\alpha\beta\alpha - \alpha\alpha\beta\alpha\beta\alpha - \alpha\alpha\beta\alpha\beta\alpha) .$$

The spin functions for Ψ_2 and Ψ_3 are derived in exactly the same way, and are

$$\begin{aligned} \Psi_2 &= |\pi b_1 b_1 b_2 a_2 b_3 b_3| 1/\sqrt{6}(2\beta\alpha\beta\alpha\alpha\alpha\beta - \alpha\alpha\beta\alpha\beta\alpha\beta - \alpha\alpha\beta\alpha\alpha\alpha\beta) \\ \Psi_3 &= |\pi b_1 a_1 b_2 b_2 b_3 b_3| 1/\sqrt{6}(2\beta\alpha\alpha\alpha\beta\alpha\beta - \alpha\alpha\beta\alpha\beta\alpha\beta - \alpha\beta\alpha\alpha\beta\alpha\beta) . \end{aligned}$$

Ψ_4 must have a spin function $\alpha\beta\dots$, the remaining spin functions being determined from the $|\frac{1}{2} \frac{1}{2}\rangle$ spin eigenfunctions for five non-equivalent electrons, as given in appendix I. Linear combinations are chosen from these five eigenfunctions to give configurations having spin density at the proton, and which have H_{0i} and/or H_{1i} equal to zero for as many of the linear combinations as possible. This considerably simplifies the expression for $Q(p)$. This is the same type of problem that was encountered in the preceding chapter, and proceeding in the same way, the only spin eigenfunction which makes any contribution to $Q(p)$, when suitable linear combinations are chosen, is

$$\Psi_4 = |\pi b_1 b_1 b_2 a_2 b_3 a_3| 1/2\sqrt{3}(2\alpha\alpha\beta\beta\beta\alpha\alpha - \alpha\alpha\beta\beta\alpha\beta\alpha - \alpha\alpha\beta\beta\alpha\alpha\beta - \alpha\alpha\beta\alpha\beta\beta\alpha - \alpha\alpha\beta\alpha\beta\alpha\beta + 2\alpha\alpha\beta\alpha\alpha\beta\beta) .$$

The spin function for Ψ_5 must be of the form $\dots\alpha\beta\dots$ and as for Ψ_4 there are five spin eigenfunctions for Ψ_5 . Linear combinations of these are chosen so that only one of these makes any contribution to $Q(p)$. This is the wave function

$$\Psi_5 = |\pi b_1 a_1 b_2 b_2 b_3 a_3| 1/2\sqrt{3} (2\alpha\beta\beta\alpha\beta\alpha\alpha - \alpha\beta\alpha\alpha\beta\beta\alpha - \alpha\beta\alpha\alpha\beta\alpha\beta - \alpha\alpha\beta\alpha\beta\beta\alpha - \alpha\alpha\beta\alpha\beta\alpha\beta + 2\alpha\alpha\alpha\alpha\beta\beta\beta).$$

The last excited state wave function to be considered is Ψ_6 . Once again, there are five possible spin eigenfunctions for this. By taking the same kind of linear combinations as for Ψ_4 , it follows that there is only one linear combination which makes any contribution to $Q(p)$. However, in this case $Q_{26}(p) \sim b_1(p)a_1(p) \div 0$, as well as $H_{61} = 0$. Consequently, Ψ_6 makes no contribution to $Q(p)$.

Thus the only excited state configurations which need be considered in the second order representation of the ground state of the C'-C-C-H fragment are Ψ_1 , Ψ_2 , Ψ_3 , Ψ_4 and Ψ_5 where the spin functions for these are as given above. The general expression for the spin density $Q(p)$ at the proton, given in appendix II, is so reduced to

$$Q(p) = 2 \left[\frac{H_{01}}{E_1} + \frac{H_{02}H_{21}}{E_2 E_1} + \frac{H_{03}H_{31}}{E_3 E_1} + \frac{H_{04}H_{41}}{E_4 E_1} + \frac{H_{05}H_{51}}{E_5 E_1} \right] Q_{01}(p) + \frac{H_{01}^2}{E_1^2} Q_{11}(p) + 2 \frac{H_{02}H_{04}}{E_2 E_4} Q_{24}(p) + 2 \frac{H_{03}H_{05}}{E_3 E_5} Q_{35}(p).$$

4.3 The Calculations

The wave functions are

$$\begin{aligned} \Psi_0 &= |\pi b_1 b_1 b_2 b_2 b_3 b_3| \alpha\alpha\beta\alpha\beta\alpha\beta \\ \Psi_1 &= |\pi b_1 b_1 b_2 b_2 b_3 a_3| 1/\sqrt{6} (2\beta\alpha\beta\alpha\beta\alpha\alpha - \alpha\alpha\beta\alpha\beta\alpha\beta - \alpha\alpha\beta\alpha\beta\beta\alpha) \\ \Psi_2 &= |\pi b_1 b_1 b_2 a_2 b_3 b_3| 1/\sqrt{6} (2\beta\alpha\beta\alpha\alpha\alpha\beta - \alpha\alpha\beta\alpha\beta\alpha\beta - \alpha\alpha\beta\beta\alpha\alpha\beta) \\ \Psi_3 &= |\pi b_1 a_1 b_2 b_2 b_3 b_3| 1/\sqrt{6} (2\beta\alpha\alpha\alpha\beta\alpha\beta - \alpha\alpha\beta\alpha\beta\alpha\beta - \alpha\beta\alpha\alpha\beta\alpha\beta) \\ \Psi_4 &= |\pi b_1 b_1 b_2 a_2 b_3 a_3| 1/2\sqrt{3} (2\alpha\alpha\beta\beta\beta\alpha\alpha - \alpha\alpha\beta\beta\alpha\beta\alpha - \alpha\alpha\beta\beta\alpha\alpha\beta - \alpha\alpha\beta\alpha\beta\beta\alpha - \alpha\alpha\beta\alpha\beta\alpha\beta + 2\alpha\alpha\beta\alpha\alpha\beta\beta) \end{aligned}$$

$$\Psi_5 = |\pi b_1 a_1 b_2 b_3 a_3| 1/2 \sqrt{3} (2\alpha\beta\alpha\beta\alpha\alpha - \alpha\beta\alpha\beta\beta\alpha - \alpha\beta\alpha\alpha\beta\alpha - \alpha\alpha\beta\alpha\beta\beta\alpha - \alpha\alpha\beta\alpha\alpha\beta\alpha + 2\alpha\alpha\alpha\alpha\beta\beta\beta)$$

$$\Psi_{4i} = |\pi b_1 b_1 b_2 a_2 b_3 a_3| \phi_i$$

where

$$\phi_a = 1/2 \sqrt{3} (2\alpha\alpha\beta\alpha\alpha\beta\beta - 2\alpha\alpha\beta\alpha\beta\alpha\beta - \alpha\alpha\beta\beta\alpha\beta\alpha + \alpha\alpha\beta\beta\beta\alpha\alpha - \beta\alpha\beta\alpha\alpha\beta\alpha + \beta\alpha\beta\alpha\beta\alpha\alpha)$$

$$\phi_b = 1/6 (2\alpha\alpha\beta\alpha\beta\alpha\beta + 2\alpha\alpha\beta\alpha\alpha\beta\beta - 4\alpha\alpha\beta\alpha\beta\beta\alpha - 2\alpha\alpha\beta\beta\alpha\alpha\beta - 2\beta\alpha\beta\alpha\alpha\alpha\beta + \alpha\alpha\beta\beta\alpha\beta\alpha + \alpha\alpha\beta\beta\beta\alpha\alpha + \beta\alpha\beta\alpha\alpha\beta\alpha + \beta\alpha\beta\alpha\beta\alpha\alpha)$$

$$\phi_c = 1/2 (\alpha\alpha\beta\beta\alpha\beta\alpha - \alpha\alpha\beta\beta\beta\alpha\alpha - \beta\alpha\beta\alpha\alpha\beta\alpha + \beta\alpha\beta\alpha\beta\alpha\alpha)$$

$$\phi_d = 1/2 \sqrt{3} (2\alpha\alpha\beta\beta\alpha\alpha\beta - 2\beta\alpha\beta\alpha\alpha\alpha\beta - \alpha\alpha\beta\beta\alpha\beta\alpha - \alpha\alpha\beta\beta\beta\alpha\alpha + \beta\alpha\beta\alpha\alpha\beta\alpha + \beta\alpha\beta\alpha\beta\alpha\alpha)$$

$$\phi_e = 1/3 \sqrt{2} (3\beta\alpha\beta\beta\alpha\alpha\alpha + \alpha\alpha\beta\alpha\beta\beta\alpha + \alpha\alpha\beta\alpha\beta\alpha\beta + \alpha\alpha\beta\alpha\alpha\beta\beta - \alpha\alpha\beta\beta\alpha\alpha\beta - \alpha\alpha\beta\beta\alpha\beta\alpha - \alpha\alpha\beta\beta\beta\alpha\alpha - \beta\alpha\beta\alpha\alpha\alpha\beta - \beta\alpha\beta\alpha\alpha\beta\alpha - \beta\alpha\beta\alpha\beta\alpha\alpha)$$

The required matrix elements are H_{01} , H_{02} , H_{03} , H_{04} , H_{05} , H_{21} , H_{31} , H_{41} , H_{51} , $Q_{01}(p)$, $Q_{11}(p)$, $Q_{24}(p)$, $Q_{35}(p)$. Other matrix elements for Ψ_{4i} are also required, to show that Ψ_4 as given above is the only configuration with this space function which need be considered.

Using the methods given in appendices II and III, the required matrix elements are

$$H_{01} = -\frac{1}{2}\sqrt{6} (\pi b_3, a_3 \pi)$$

$$H_{02} = -\frac{1}{2}\sqrt{6} (\pi b_2, a_2 \pi)$$

$$H_{03} = -\frac{1}{2}\sqrt{6} (\pi b_1, a_1 \pi)$$

$$H_{04} = \sqrt{3} (b_2 b_3, a_3 a_2)$$

$$H_{05} = \sqrt{3} (b_1 b_3, a_3 a_1)$$

$$H_{21} = - (a_2 b_3, a_3 b_2)$$

$$H_{41} = \frac{1}{2}\sqrt{2} (\pi a_2, b_2 \pi)$$

$$H_{04a} = \frac{1}{2}\sqrt{3} [(b_2 b_3, a_3 a_2) - (b_2 b_3, a_2 a_3)]$$

$$Q_{01}(p) = \frac{\sqrt{6}}{3} b_3(p) a_3(p)$$

$$Q_{11}(p) = \frac{2}{3} [b_3^2(p) + a_3^2(p)]$$

$$Q_{24}(p) = -\frac{\sqrt{2}}{3} b_3(p) a_3(p)$$

$$Q_{35}(p) = -\frac{\sqrt{2}}{3} b_3(p) a_3(p)$$

$$H_{31} = - (a_1 b_3, a_3 b_1)$$

$$H_{51} = \frac{1}{2}\sqrt{2} (\pi a_1, b_1 \pi)$$

$$H_{04b} = \frac{3}{2} (b_2 b_3, a_2 a_3)$$

$$H_{04c} = \frac{1}{2} [(b_2 b_3, a_2 a_3) - (b_2 b_3, a_3 a_2) 2]$$

$$H_{04d} = -\frac{1}{2} \sqrt{3} (b_2 b_3, a_2 a_3)$$

$$H_{04e} = 0$$

$$Q_{24a}(p) = -\frac{\sqrt{2}}{12} b_3(p) a_3(p)$$

$$Q_{24b}(p) = -\frac{\sqrt{6}}{36} b_3(p) a_3(p)$$

$$Q_{24c}(p) = \frac{\sqrt{6}}{4} b_3(p) a_3(p)$$

$$Q_{24d}(p) = \frac{\sqrt{2}}{4} b_3(p) a_3(p)$$

$$Q_{24e}(p) = \frac{2\sqrt{2}}{9} b_3(p) a_3(p) \quad .$$

Proceeding as in the previous chapter, and choosing the linear combinations

$$\Psi_{4f} = 1/2 \sqrt{2} (\Psi_{4a} + \Psi_{4b} + \sqrt{3} \Psi_{4c} + \sqrt{3} \Psi_{4d})$$

$$\Psi_{4g} = 1/2 \sqrt{2} (\Psi_{4a} - \Psi_{4b} + \sqrt{3} \Psi_{4c} - \sqrt{3} \Psi_{4d})$$

$$\Psi_{4h} = 1/4 (\sqrt{3} \Psi_{4a} - 3 \Psi_{4b} - \Psi_{4c} + \sqrt{3} \Psi_{4d})$$

$$\Psi_4 = 1/2 \sqrt{3} (3 \Psi_{4a} + \sqrt{3} \Psi_{4b} - \sqrt{3} \Psi_{4c} - \Psi_{4d})$$

$$\Psi_{4e},$$

then $H_{04f} = H_{04g} = 0$, $Q_{24h}(p) = 0$, $H_{14h} = 0$, so that only Ψ_4 makes any contribution to $Q(p)$. The expression given here reduces to the expression given in section 4.3 for Ψ_4 , in terms of spin product functions, when Ψ_{4a} to Ψ_{4d} are expanded in terms of the basis set of spin product functions.

A similar analysis follows for states Ψ_5 and Ψ_6 , to give the spin functions listed at the beginning of this section, for Ψ_5 . As shown in section 4.2, the wave function Ψ_6 makes no contribution to $Q(p)$.

To proceed further, the LCAO approximation is made for b_i , a_i :

$$\begin{aligned} b_1 &= 1/\sqrt{2}(h_1+h_2) & a_1 &= 1/\sqrt{2}(h_1-h_2) \\ b_2 &= 1/\sqrt{2}(h_3+h_4) & a_2 &= 1/\sqrt{2}(h_3-h_4) \\ b_3 &= 1/\sqrt{2}(h_5+s) & a_3 &= 1/\sqrt{2}(h_5-s) \end{aligned}$$

where h_1 is a hybrid at C' pointing to the next carbon, etc, and s is the H 1s AO. This gives

$$\begin{aligned} H_{01} &= -\frac{1}{4}\sqrt{6}[J(\pi h_5)-J(\pi s)] & Q_{01}(p) &= -\frac{\sqrt{6}}{6} |s(p)|^2 \\ H_{02} &= -\frac{1}{4}\sqrt{6}[J(\pi h_3)-J(\pi h_4)] & Q_{11}(p) &= \frac{2}{3} |s(p)|^2 \\ H_{03} &= -\frac{1}{4}\sqrt{6}[J(\pi h_1)-J(\pi h_2)] & Q_{24}(p) &= \frac{\sqrt{2}}{6} |s(p)|^2 \\ & & Q_{35}(p) &= \frac{\sqrt{2}}{6} |s(p)|^2 \end{aligned}$$

$$\begin{aligned} H_{04} &= \frac{\sqrt{3}}{4} [J(h_3 h_5)-J(h_4 h_5)+J(h_4 s)-J(h_3 s)] \\ H_{05} &= \frac{\sqrt{3}}{4} [J(h_1 h_5)-J(h_2 h_5)+J(h_2 s)-J(h_1 s)] \\ H_{21} &= -\frac{1}{4}[J(h_3 h_5)-J(h_4 h_5)+J(h_4 s)-J(h_3 s)] \\ H_{31} &= -\frac{1}{4}[J(h_1 h_5)-J(h_2 h_5)+J(h_2 s)-J(h_1 s)] \\ H_{41} &= \frac{1}{4}\sqrt{2}[J(\pi h_3)-J(\pi h_4)] \\ H_{51} &= \frac{1}{4}\sqrt{2}[J(\pi h_1)-J(\pi h_2)] . \end{aligned}$$

Substitution of these values in the above formula for $Q(p)$ gives, when the assumption that $E_4 = E_1 + E_2$, $E_5 = E_1 + E_3$ is applicable,

$$Q(p) = [A + A^2 + B + C] |s(p)|^2$$

and $a_H = 1423[A + A^2 + B + C] \text{ Mc/s}$

where $A = - \frac{[J(\pi h_5)-J(\pi s)]}{2E_1}$

$$B = \left[\frac{J(\pi h_3)-J(\pi h_4)}{2E_2} \right] \left[\frac{\{J(h_3 s)-J(h_3 h_5)\} - \{J(h_4 s)-J(h_4 h_5)\}}{2E_1} \right]$$

$$C = \left[\frac{J(\pi h_1) - J(\pi h_2)}{2E_3} \right] \left[\frac{\{J(h_1 s) - J(h_1 h_5)\} - \{J(h_2 s) - J(h_2 h_5)\}}{2E_1} \right]$$

Factor A represents the spin polarisation induced in the C-H bond by the unpaired electron in π . Factor B is the product of two terms: the first represents the spin density induced in the bond between C and C by the unpaired electron in π , and the second represents the spin density induced in the bond between C and H by the spin density already induced in the bond between C and C. Similarly factor C makes allowance for the consecutive polarisation from π to bond C'-C and in turn to bond C-H. This consecutive polarisation mechanism is further discussed in the next chapter, for the general case C'-C_{n-1}H.

4.4 Numerical Evaluation

Literature values are available for some of the required exchange integrals:

$$\left. \begin{array}{l} J(\pi h_1) = 1.26 \text{ e.v.} \\ J(\pi h_2) = 0.932 \text{ e.v.} \\ J(h_3 h_5) = 0.573 \text{ e.v.} \\ J(h_4 h_5) = 0.921 \text{ e.v.} \end{array} \right\} \begin{array}{l} \text{from Karplus and} \\ \text{Fraenkel [20]} \end{array}$$

$$J(\pi h_3) = 0.036 \text{ e.v.} \quad \text{from Altmann [15].}$$

The other exchange integrals are very small and for most purposes can be assumed zero. However, even though small, they cannot be neglected in this problem, since owing to the multiplying factor of 1423 Mc/s they make a significant contribution to a_H . In section 6.5 it is shown that temperature dependence of NMR spectra enable the determination of a_H values in paramagnetic molecules as small as 10^{-4} Mc/s.

To make a reasonable estimate of a_H , at least some of

the remaining integrals are required, and in particular probably $J(h_2h_5)$ and $J(h_4s)$. The evaluation of these requires the services of a fast electronic computer. Unfortunately such a computer was not available in New Zealand in time for this thesis work. Consequently, only a very approximate estimation of a_H can be made, using the above values. From this it appears that

$$a_H = +0.15 \text{ Mc/s}$$

and therefore, for the case where the spin density at C' is ρ ,

$$a_H = +0.15\rho \text{ Mc/s.}$$

Note that the sign of a_H is opposite to that for the C'-H and C'-C-H fragments. However, until reliable values are available for the other exchange integrals, even this sign is slightly uncertain.

A further complication is that even if all the required exchange integrals were available, there would be considerable doubt about the validity of the values for such large internuclear distances. All the exchange integrals used here, and those usually reported in the literature are evaluated using single term Slater wave functions of the form $N_r r^{n-1} e^{-\mu r} Y_l^m(\theta, \phi)$ [see appendix V for discussion on Slater wave functions]. Single term Slater wave functions provide a reasonable representation of AO's in the region between two adjacent atoms at normal bonding distances, but it has recently been shown [23], by using self-consistent field (SCF) wave functions for carbon, that Slater orbitals considerably underestimate the values of overlap and exchange integrals for much larger distances, of greater than 2 Å. For a carbon-carbon distance of 4 Å a single Slater wave function underestimates the exchange integral between two $2p_\sigma$ orbitals by a factor of six, compared

with the value obtained from the SCF wave functions. This also occurs when allowance is made for the fact that the effective "atomic" orbitals needed in molecules are rather less extended in space than the SCF AO's, due to shifts in electron density needed for binding.

Proceeding as in section 3.4, the results for the C'-C-C-H fragment can be extended to apply to a C'-C-CH₂ fragment, when hyperconjugation is neglected, to give about the same value of a_H , namely +0.15 Mc/s.

No experimental a_H values are available for radicals containing a C'-C-C-H or C'-C-CH₂ fragment. The negative ion of perinaphthene should be suitable for an ESR study, if this ion can be prepared. The corresponding ion of acenaphthene has been prepared [13] and its ESR spectrum measured.

perinaphthene

acenaphthene

In chapter 8 a MO hyperconjugation study of perinaphthene is presented. This shows that the effects of hyperconjugation at the C'-C-CH₂ protons are much greater than those from spin polarisation arising from spin density at C'.

Chapter 5

SPIN POLARISATION IN AN AROMATIC

C'-C_{n-1}H FRAGMENT

5.1 Introduction

An expression is derived for the proton hyperfine coupling constant a_H of the terminal proton in a fragment C_nH , containing π type spin density at the first carbon. It is assumed that there is no hyperconjugation in the fragment. MO theory gives a representation

$$\Psi = (1 + \sum \lambda_i^2)^{-1/2} (\Psi_0 + \sum \lambda_i \Psi_i)$$

for the ground state of the fragment. The Ψ_i represent excited states which are mixed into the zero order MO representation of the ground state, Ψ_0 , when allowance is made for electronic interaction.

The proton coupling constant a_H is expressed in terms of certain exchange integrals. The general expression given in section 5.3 reduces to the cases given in the previous chapters for specific values of n . An interpretation of the mathematical form of this general expression for a_H leads to the concept of spin polarisation transmission throughout a fragment $C'-C_{n-1}H$ by a consecutive polarisation mechanism.

5.2 The Model

π is the singly occupied $2p_\pi$ AO at C'_1
 $b_i(a_i)$ is the bonding (antibonding) MO of the σ bond between atoms i and $i+1$. The zero order MO representation of the ground state of the fragment is

$$\Psi_0 = |\pi b_1 b_1 b_2 b_2 \dots b_n b_n| \alpha \alpha \beta \alpha \beta \dots \alpha \beta$$

which has $Q(p) = 0$ and so cannot lead to spin density at the proton. When allowance is made for the electronic interaction term $\sum e^2/r_{ij}$, certain excited states Ψ_i are mixed into the zero order representation, Ψ_0 . As explained in sections 3.2 and 4.2, the only excited states which need be considered are those contributing to $Q(p)$; the appropriate excited states were seen in section 4.2 to correspond to just one or two excitations in the σ orbitals. Furthermore, those doubly excited states where both of the excitations are in the same orbital, or those where one of the excitations is not in the b_n orbital, need not be considered, since in both cases either the $Q_{ij}(p)$ or the H_{ij} are zero. This was seen in section 4.2 for the specific case $n = 3$. The only excited state wave functions that can contribute to $Q(p)$ are

$$\begin{aligned}\Psi_1 &= |\pi b_1 b_1 b_2 b_2 \dots b_n a_n| \\ \Psi_2 &= |\pi b_1 b_1 b_2 b_2 \dots b_{n-1} a_{n-1} b_n b_n| \\ &\cdot \\ &\cdot \\ &\cdot \\ \Psi_n &= |\pi b_1 a_1 b_2 b_2 \dots b_n b_n| \\ \Psi_{n+1} &= |\pi b_1 b_1 b_2 b_2 \dots b_{n-1} a_{n-1} b_n a_n| \\ &\cdot \\ &\cdot \\ &\cdot \\ \Psi_{2n-1} &= |\pi b_1 a_1 b_2 b_2 \dots b_n a_n| \cdot\end{aligned}$$

The spin parts of these wave functions, which must have $|S M_s\rangle = |\frac{1}{2} \frac{1}{2}\rangle$, are determined in the same manner as in section 4.2. Wave functions corresponding to a single excitation have orbitals which are doubly occupied, and

so must have $\alpha\beta$ for their spin functions; the three remaining singly occupied orbitals have their spin functions determined by the spin eigenfunctions for three non-equivalent electrons, as $1/\sqrt{6}(2\beta\alpha\alpha-\alpha\alpha\beta-\alpha\beta\alpha)$. The other spin eigenfunction $1/\sqrt{2}(\alpha\alpha\beta-\alpha\beta\alpha)$ leads to wave functions for which $Q_{01}(p) = 0$, and is consequently neglected. Similarly, for the wave functions corresponding to double excitations, orbitals which are doubly occupied must have spin functions $\alpha\beta$, and the spin functions for the remaining five singly occupied orbitals are determined by the spin eigenfunctions for five non-equivalent electrons. Proceeding as in sections 3.3 and 4.3, it is possible to choose linear combinations of the five original spin eigenfunctions for five non-equivalent electrons so that only one of them makes any contribution to $Q(p)$:

$$1/2\sqrt{3}(2\alpha\beta\beta\alpha\alpha-\alpha\beta\alpha\beta\alpha-\alpha\beta\alpha\alpha\beta-\alpha\alpha\beta\beta\alpha-\alpha\alpha\beta\alpha\beta+2\alpha\alpha\alpha\beta\beta) .$$

From an inspection of the space parts of the above wave functions it is readily found which $Q_{ij}(p)$ are non-zero, since the $Q_{ij}(p)$ are the matrix elements of a one electron operator. Thus the general expression for $Q(p)$, given in appendix II, is reduced to

$$Q(p) = 2 \left[\frac{H_{01}}{E_1} + \sum_{i=2}^{2n-1} \frac{H_{0i}H_{i1}}{E_i E_1} \right] Q_{01}(p) + \frac{H_{01}^2}{E_1^2} Q_{11}(p) \\ + 2 \sum_{i=2}^n \frac{H_{0i}H_{0,n+i-1}}{E_i E_{n+i-1}} Q_{i,n+i-1}(p) .$$

5.3 The Calculations

The matrix elements are evaluated as explained in appendices II and III, to give

$$Q_{01}(p) = \sqrt{\frac{6}{3}} b_n(p) a_n(p)$$

$$Q_{01}(p) = \frac{\sqrt{6}}{3} b_n(p) a_n(p)$$

$$Q_{11}(p) = \frac{2}{3} [b_n^2(p) + a_n^2(p)]$$

$$Q_{i,i+n-1}(p) = -\frac{\sqrt{2}}{3} b_n(p) a_n(p)$$

$$H_{0i} = -\frac{1}{2}\sqrt{6} (\pi b_{n-i+1}, a_{n-i+1} \pi) \quad i = 1, 2, \dots, n$$

$$H_{0,n+j} = \sqrt{3} (b_{n-j} b_n, a_n a_{n-j}) \quad j = 1, 2, \dots, n-1$$

$$H_{i1} = - (a_{n-i+1} b_n, a_n b_{n-i+1}) \quad i = 1, 2, \dots, n$$

$$H_{n+j,1} = \frac{1}{2}\sqrt{2} (\pi a_{n-j}, b_{n-j} \pi) \quad j = 1, 2, \dots, n-1.$$

$$\text{Thus} \quad \left. \begin{aligned} H_{0j} &= -\sqrt{3} H_{n+j-1,1} \\ H_{0,n+j} &= -\sqrt{3} H_{j+1,1} \end{aligned} \right\} \quad \begin{aligned} j &= 1, 2, \dots, n \\ j &= 1, 2, \dots, n-1 \end{aligned} \quad (A)$$

and so the expression for $Q(p)$ becomes

$$\begin{aligned} \frac{Q(p)}{b_n(p) a_n(p)} &= -\frac{2}{3} \sqrt{6} \frac{H_{01}}{E_1} + \frac{b_n^2(p) + a_n^2(p)}{b_n(p) a_n(p)} \frac{2}{3} \frac{H_{01}^2}{E_1^2} \\ &+ \frac{2}{3} \sqrt{6} \sum_{j=2}^n \left[\frac{H_{0j} H_{j1}}{E_j E_1} + \frac{H_{0,n+j-1} H_{n+j-1,1}}{E_{n+j-1} E_1} - \frac{1}{\sqrt{3}} \frac{H_{0j} H_{0,n+j-1}}{E_j E_{n+j-1}} \right] \end{aligned}$$

and then using the relations (A) above,

$$\begin{aligned} \frac{Q(p)}{b_n(p) a_n(p)} &= -\frac{2}{3} \sqrt{6} \frac{H_{01}}{E_1} + \frac{b_n^2(p) + a_n^2(p)}{b_n(p) a_n(p)} \frac{2}{3} \frac{H_{01}^2}{E_1^2} \\ &+ \frac{2}{3} \sqrt{6} \sum_{j=2}^n H_{0j} H_{j1} \left[\frac{1}{E_j E_1} + \frac{1}{E_{n+j-1} E_1} + \frac{1}{E_j E_{n+j-1}} \right]. \end{aligned}$$

So far this result is exact to second order; no approximations or assumptions have been made other than that the only excitations of significance are in the π orbitals,

and that the system has the terminal proton in the nodal plane of the π orbital at C_1' , so that hyperconjugation cannot contribute to the spin density at the proton.

To further reduce this expression, several assumptions and approximations are made:

1) a reasonable assumption is that the energies of the doubly excited states, E_{n+i} , are given by the sum of the energies of the two singly excited states corresponding to the same excitations: $E_{n+i} = E_1 + E_{i+1}$, $i = 1, 2, \dots, n-1$.

This reduces the above expression to

$$\frac{Q(p)}{b_n(p)a_n(p)} = -\frac{2\sqrt{6}}{3} \frac{H_{01}}{E_1} + \frac{b_n^2(p)+a_n^2(p)}{b_n(p)a_n(p)} \frac{2}{3} \frac{H_{01}^2}{E_1^2} + \frac{\sqrt{6}}{3} \sum_{j=2}^n \frac{H_{0j}H_{j1}}{E_j E_1}.$$

2) The MO's a_i , b_i are now approximated by LCAO:

$$b_i = 1/\sqrt{2}(h_{2i-1}+h_{2i}) \quad a_i = 1/\sqrt{2}(h_{2i-1}-h_{2i})$$

where h_{2i} is a hybrid orbital on atom $i+1$, pointing to atom i .

This gives

$$b_n(p)a_n(p) = -\frac{1}{2}|s(p)|^2 \quad \text{where } s = h_{2n}$$

$$(\pi b_k, a_k \pi) = \frac{1}{2} [J(\pi h_{2k-1}) - J(\pi h_{2k})]$$

$$(b_i b_j, a_j a_i) = (a_i b_j, a_j b_i)$$

$$= \frac{1}{4} [\{ J(h_{2i-1} h_{2j-1}) - J(h_{2i-1} h_{2j}) \} + \{ J(h_{2i} h_{2j}) - J(h_{2i} h_{2j-1}) \}]$$

and the expression for $Q(p)$ becomes

$$Q(p) = [A + A^2 + \sum_{j=2}^n C_j] |s(p)|^2$$

$$\text{and so} \quad a_H = 1423 [A + A^2 + \sum_{j=2}^n C_j] \quad \text{Mc/s}$$

$$\text{where} \quad A = \frac{-1}{2E_1} [J(\pi h_{2n-1}) - J(\pi h_{2n})]$$

$$C_j = \frac{-1}{2 E_j 2 E_1} [J(\pi h_{2(n-j)+1}) - J(\pi h_{2(n-j)+2})] \times$$

$$\left[\{J(h_{2(n-j)+2} h_{2n}) - J(h_{2(n-j)+2} h_{2n-1})\} - \{J(h_{2(n-j)+1} h_{2n}) - J(h_{2(n-j)+1} h_{2n-1})\} \right] .$$

This general expression for a_H reduces to the expressions given in chapters 2, 3 and 4 for the specific values 1, 2 and 3 of n .

5.4 Limitations

The approximations and assumptions involved in the derivation of the above expression for a_H are:-

- (1) The Fermi contact Hamiltonian $\mathcal{H} = \frac{8\pi}{3} g\beta g_N \beta_N \sum_i \delta(r_i - r_H) s_i I$ is the one appropriate for discussing hyperfine effects in aromatic radicals, and the perturbation derivation of this Hamiltonian is accurate enough for these studies.
- (2) Hyperconjugation does not contribute to the spin density $Q(p)$ at the proton.
- (3) Excitation in the π orbitals need not be considered.
- (4) The mixing coefficients λ_i are small, so that perturbation theory may be used.
- (5) The energies of the doubly excited states are given by $E_{n+i} = E_1 + E_{i+1}$, $i = 1, 2, \dots, n-1$.
- (6) $b_{n-i}(p)a_{n-i}(p)$, $i = 1, 2, \dots, n-1$ are negligible compared with $b_n(p)a_n(p)$.
- (7) The LCAO-MO approximation for a_i , b_i is a reasonable one.
- (8) Overlap integrals may be neglected.

The first two are statements of the model. (4) and (6) are mathematical approximations, and as such can be easily checked for their validity; in chapter 2, the mixing

coefficients were calculated to be of the order 0.04, for the specific case $n = 1$. (5) is physically reasonable, and corresponds to the one electron approximation in constructing MO energy level diagrams. In a more accurate treatment, slight differences between E_{n+i} and $E_1 + E_{i+1}$ due to different exchange interactions, would have to be allowed for. (8) has been shown to be valid for the specific case $n = 1$. Thus (3) and (7) are the main approximations. (7) seems to be reasonable for σ type bonds, in that these are usually highly localised, and so should be adequately represented as above.

5.5 Interpretation of the Results of the Calculations

(i) The numerical variation of a_H with n

For $n \gg 3$, all of the factors A , A^2 , C_j become very small. However, A becomes $\ll C_j$ as n increases, and probably for $n \gg 3$, A (and therefore A^2) can be neglected, so that after this the C_j are the main features determining both the magnitude and sign of a_H . For $n = 3$ it appeared from the calculations in chapter 4 that a_H could well change sign: for $n = 1$ and 2, a_H is negative, but for $n \gg 3$ a_H appears to be positive. This will, however, have to be checked by computing the required exchange integrals.

(ii) Interpretation of the formula in terms of "consecutive polarisation"

This arises from an interpretation of the mathematical form of the coefficients C_j , which are products of the two factors. The first factor represents the spin density induced in the bond between atoms $n-j+1$, $n-j+2$ by the unpaired electron in the orbital π . The second factor

then represents the spin density induced in the bond between atoms C_n and H by the spin density already induced in the bond between atoms $n-j+1$, $n-j+2$.

This is called a consecutive polarisation. This is a two step consecutive polarisation, corresponding to steps such as

with one such step for each possible σ bond. Note from the expression for $Q(p)$ or a_H that there is no consecutive polarisation of more than second order, corresponding to say

To obtain this type with m steps, it would have been necessary to use m 'th order perturbation theory in calculating $Q(p)$.

Although this idea of consecutive polarisation has emerged from the particular mathematical form of the results, it seems physically reasonable. However, this is a consequence of the choice of MO formalism and the use of perturbation theory. If other methods were used to obtain approximations of the eigenfunctions of the Fermi contact Hamiltonian, then a different form would be expected for a_H .

Chapter 6

COMPARISON WITH EXPERIMENT

6.1 Introduction

The four preceding chapters have given theoretical expressions for the proton hyperfine coupling constants for spin polarisation in $C'-C_nH$ systems, where C' is an aromatic carbon atom having spin density in its π orbital. These hyperfine coupling constants are expressed as

$$a_H = Q\rho$$

where

$$\begin{aligned} \rho &= \text{spin density in the } \pi \text{ orbital at } C' \\ Q &= -65 \text{ Mc/s for } n = 0 \\ &= -4.4 \text{ Mc/s for } n = 1 \\ &= +1.5 \text{ Mc/s for } n = 2. \end{aligned}$$

Experimental values are available for the cases $n = 0, 1$ from ESR spectra. Hyperfine coupling constants determined experimentally from ESR spectra are usually expressed in gauss, since the measurements are made by fixing the frequency and scanning the magnetic field, to detect the resonance signal. The conversion factor from Mc/s to gauss is found from the relation $g\beta H = h\nu$ to be 1 gauss = 2.8029 Mc/s. Thus the above constants Q have the values -23, -1.6, +0.05 gauss, for $n = 0, 1, 2$ respectively. Magnetic field units (gauss) are used in the remainder of this thesis, when predicting a_H values to be compared with values obtained from ESR spectra.

Experimental values are available for the proton hyperfine coupling constants in $N-C_nH$ fragments, obtained from the temperature dependence of the NMR spectra of dithiocarbamate complexes containing these fragments.

The experimental a_H values for these protons are expressed in Mc/s, although they could be given in gauss. In this case the relation $g_N \beta_N H = h\nu$ gives the conversion factor 1 gauss (proton) = 2.128×10^{-3} Mc/s, whereas 1 gauss (electron) = 2.803 Mc/s. To avoid confusion between the two types of gauss units, all results relating to NMR studies are given in Mc/s.

6.2 C'-H Proton Hyperfine Coupling Constants

In chapter 2 the relation $a_H = -23\rho$ gauss was predicted. It is reasonable to assume that Q is approximately the same for all C-H bonds in a given aromatic molecule, and to a first approximation for all C-H bonds in any aromatic molecule. The hyperfine splitting in the ESR spectra of aromatic radicals can therefore be used to determine the relative unpaired electron densities at each of the ring carbon atoms. If the unpaired electron densities at the ring carbon atoms in aromatic radicals can be calculated from a suitable bonding theory, the theoretical prediction $a_H = Q\rho$, where Q is a constant, can be checked. This is the approach used here.

To a first approximation the aromatic spin densities ρ can be obtained from simple Hückel calculations. In deriving $a_H = Q\rho$, no allowance was made for any exchange interactions of the paired σ electrons in the C'-H bond with unpaired π electrons at carbon atoms other than C'. Therefore the spin densities ρ are calculated on the assumption of no overlap of the carbon $2p_\pi$ AO's, or at least from a set of orthonormal vectors. The former corresponds to the standard form of Hückel theory. A discussion of various other forms of Hückel theory is

given in chapter 7, section 7.2 Hückel calculations are usually performed on the assumption that all carbon-carbon bonds are of equal length. However, in the polynuclear aromatics it has been shown [24] by x-ray analysis that there are considerable variations in the bond lengths, from 1.35 Å to 1.46 Å within a given molecule. The spin densities ρ are therefore given as determined from two Hückel approaches,

$\rho(1)$: assuming all C-C bond lengths are equal

$\rho(2)$: making allowance for the observed variations in bond length by taking

$$\beta_{ij} = \text{constant} \times S_{ij}$$

where S_{ij} is the overlap between adjacent $2p_{\pi}$ AO's, as calculated with Slater AO's, using the observed x-ray internuclear distances, and β_{ij} is the resonance integral between AO's i and j .

Calculations were performed for naphthalene, anthracene, tetracene, perylene, phenanthrene, pyracene and acenaphthene. The experimental results are given by Colpa and de Boer [13] and Colpa and Bolton [11]. In the calculations for pyracene and acenaphthene, hyperconjugation was allowed for, as shown in chapter 7. The spin density at carbon atom i is simply c_i^2 , where c_i is the coefficient of the $2p_{\pi}$ AO at atom i in the MO containing the unpaired electron, and the MO coefficients are normalised so that $\sum c_i^2 = 1$. For a molecule with $2n$ aromatic carbon atoms, the MO containing the unpaired electron is ψ_{2n} for the positive ion and ψ_{2n+1} for the negative ion, where the MO's are numbered so that the most stable MO is ψ_1 .

Table 6.1 Calculated Spin Densities ρ and Experimental
Coupling Constants a_H for C'-H

molecule	ion	position	experimental a_H (gauss)	$\rho(1)$	$\rho(2)$
Naphthalene	negative	α	4.95	.1810	.1772
		β	1.87	.0691	.0728
Anthracene	negative	α	5.41	.1934	.1876
		β	2.76	.0967	.0949
		γ	1.53	.0483	.0512
	positive	α	6.65	.1934	.1876
		β	3.12	.0967	.0949
		γ	1.40	.0483	.0512
Tetracene	negative	α	4.25	.1473	.1442
		β	1.55	.0563	.0530
		γ	1.15	.0336	.0370
	positive	α	5.17	.1473	.1442
		β	1.72	.0563	.0530
		γ	1.06	.0336	.0370
Perylene	negative	α	3.53	.1078	.0965
		β	3.08	.0833	.0778
		γ	0.46	.0130	.0163
	positive	α	4.10	.1078	.0965
		β	3.10	.0833	.0778
		γ	0.46	.0130	.0163

Table 6.1 (continued)

Phenanthrene	negative	α	4.43	.1723	.1501
		β	3.71	.1157	.1137
		γ	0.43	.0018	.0020
		δ	2.88	.0991	.1071
		ϕ	0.63	.0541	.0579
Pyracene	negative	α	1.58	.0640	.0705
	positive	α	2.00	.0667	.0716
Acenaphthene	negative	α	4.17	.1651	.1706
		β	2.42	.0790	.0709
		γ	1.04	.0518	.0737

Figures 6.1 and 6.2 give a_H (experimental) as a function of $\rho(1)$ and $\rho(2)$ respectively. According to the theoretical predictions, a plot of a_H versus ρ should be linear, with a slope of about -23 gauss, and should pass through the origin. Figures 6.1 and 6.2 confirm this. Both methods of calculating ρ give graphs passing very close to the origin. A least square analysis gives a slope of -29.4 gauss for a_H versus $\rho(1)$ and -30.4 gauss for a_H versus $\rho(2)$. The standard deviations are 0.50 and 0.57 gauss respectively. The two methods of calculating the spin densities give very similar results. The slopes are slightly greater than expected, -23 gauss. This could arise in several ways:

(a) limitations in the method of calculating the spin

FIGURE 6.1

FIGURE 6.2

densities ρ , such as the neglect of overlap, and use of the same Slater exponent [see appendix V, section AV.1] for determining the MO's for both positive and negative ion;

- (b) neglect of exchange interactions of the C'-H σ electrons with other aromatic carbon $2p_{\pi}$ electrons;
- (c) the numerical values used for the exchange integrals $J(\pi_h)$ and $J(\pi_s)$, which were calculated with Slater AO's.

However, the general features of the graphs are as predicted, namely a linear relation between a_H and ρ , passing through the origin.

There are several features to be noted from these graphs. If it is assumed that the π electrons in pyracene and acenaphthene are restricted to the naphthalene nucleus, the ρ values to be used are those for naphthalene. If the experimental a_H values are plotted against these ρ values, the points lie further off the line of best fit than when they are plotted against the values of ρ making allowance for hyperconjugation. Hyperconjugation in these molecules is discussed in detail in chapter 7.

Both graphs show a general tendency for the positive ions to have larger Q values than the negative ions. Simple Hückel theory predicts that the ring carbon spin densities are the same for the positive and negative ions of the same molecule. When allowance is made for overlap of the carbon $2p_{\pi}$ AO's, or for non-adjacent β interactions, this symmetry is destroyed. In chapter 7, five forms of Hückel theory are used to determine the π MO's for pyracene and acenaphthene. These were also applied to naphthalene and anthracene. The assumptions of the methods, numbered

(1) to (5), are given in section 7.2. The prefix XR indicates that the x-ray bond lengths have been used. Since all the π AO's in these two molecules have the same coulomb integrals, methods (4) and (5) give identical MO's. Method (2) also gives the same spin densities as method (4), for these particular molecules. As shown in section 7.7, methods (2) and (3) are equivalent for determining spin densities. The spin densities are shown in table 6.2

Table 6.2 Spin Densities for Naphthalene and Anthracene,
Calculated with Different Forms of Hückel Theory

radical	position	method (1)	(4) =(2)=(5)	XR(1)	XR(4) =XR(2)=XR(5)
naphthalene	α	.1810	.1787	.1772	.1746
-ve ion	β	.0691	.0713	.0728	.0755
naphthalene	α	.1810	.1779	.1772	.1742
+ve ion	β	.0691	.0721	.0728	.0756
anthracene	α	.1934	.1961	.1876	.1878
-ve ion	β	.0967	.1043	.0949	.1063
	γ	.0483	.0549	.0512	.0597
anthracene	α	.1934	.1668	.1876	.1513
+ve ion	β	.0967	.0910	.0949	.0909
	γ	.0483	.0520	.0512	.0544

The numbering of the positions is as in table 6.1

All methods other than (1) and XR(1) predict greater spin densities for the negative ions than the positive ions, at the α position in naphthalene, and the α , β

positions for anthracene, and smaller values at the β position in naphthalene and the γ position in anthracene. This order is the reverse of the experimental order for the a_H values for anthracene.

This difference in the a_H values of corresponding positive and negative ions was the subject of a theoretical analysis by Colpa and Bolton [11], who derived an equation which appeared to account for the observed difference in terms of charge densities at the ring atoms, as well as spin densities. However, it was shown later [25] that there is an error of sign in their derivation. Discussion is still continuing on this subject [25] but as yet no satisfactory solution has been found. In the discussions so far the validity or significance of the simple Hückel spin densities has been neglected. Hückel theory neglects any electronic interaction, and this could lead to significant changes in the eigenfunctions, and so the spin densities.

6.3 C'-CH₂ Proton Hyperfine Coupling Constants

In chapter 3 the relation $a_H = -1.6\rho$ gauss was predicted, considering spin polarisation in the σ orbitals of a fragment C'-C-H. Experimental values are available for the pyracene positive and negative ions, and the acenaphthene negative ion.

pyracene

acenaphthene

Assuming that the π electrons are restricted to the aromatic region (the naphthalene nucleus), the spin density at C' to be used in $a_H = -1.6\rho$ gauss, should, to a first approximation, be that appropriate for the corresponding ion of naphthalene, namely 0.1810 for both the positive and negative ion, according to simple Huckel theory. Therefore the hyperfine coupling constant at the C'-CH₂ protons should be about $-1.6 \times .1810 = -0.29$ gauss, if only spin polarisation in the σ orbitals leads to spin density at the CH₂ protons, and this value should be observed for both the positive and negative ions of pyracene and acenaphthene. Since the C'-CH₂ protons are not in the nodal plane of the π orbital at C', there is a small contribution to the spin density at these protons from the value of the C' 2p π wave function at the coordinates of the protons. Assuming that the C' 2p π wave function can be adequately represented by a Slater A0 at a distance of about 2.15 Å, this leads to a contribution of about +4.0 ρ gauss, where ρ is the spin density at C'. Thus the net contribution to a_H is about +2.4 ρ gauss, which for $\rho = .1810$ gives a proton hyperfine coupling constant of about +0.43 gauss for either the positive or negative ion, for both pyracene and acenaphthene.

Experimentally it is found [13] that the C'-CH₂ a_H values for these radicals are much larger than 0.43 gauss, and are not the same for positive and negative ions:

pyracene negative ion	$a_H = 6.58$ gauss
pyracene positive ion	$a_H = 12.80$ gauss
acenaphthene negative ion	$a_H = 7.53$ gauss.

The assumption that the spin density at the C'-CH₂ protons arises only from spin polarisation in the σ bonds

or from the amplitude of the $C' 2p_{\pi}$ wave function at the coordinates of the protons is inadequate for explaining the experimental results.

The reason for this apparent discrepancy between theory and experiment is that the unpaired electron in the π orbital of the aromatic region is not confined to the aromatic region. There is a considerable degree of delocalisation of the π electrons of the aromatic region out to the orbitals of the CH_2 protons. Such delocalisation is usually referred to as hyperconjugation. This means that the formula for a_H in a $C'-CH_2$ fragment is not appropriate for discussing the observed $CH_2 a_H$ values in the ions of pyracene and acenaphthene, because hyperconjugation leads to net spin density about the CH_2 protons. Hyperconjugation in these radicals is considered in detail in chapter 7.

In these ions the net spin density ρ at C' , as determined from a hyperconjugation treatment of the whole molecule, still makes a contribution of -1.6ρ gauss to the a_H for the CH_2 protons, but this value, about -0.2 gauss, is almost negligible compared with the a_H arising from the direct probability of finding the unpaired π electron in the $1s$ orbitals about the CH_2 protons. Similarly there is a contribution of about $-28\rho'$ gauss to the $CH_2 a_H$ from the spin density ρ' at the carbon atom of the CH_2 group, this spin density arising from hyperconjugation. This is also a small contribution compared with the a_H arising from the unpaired π electron density at the CH_2 protons, being about -0.4 gauss for the positive ions and only -0.03 gauss for the negative ions.

The problem is thus to find a molecule containing the

fragment $C'-CH_2$ or $C'-C-H$, where hyperconjugation cannot lead to net spin density at the terminal protons.

6.4 $C'-C-CH_2$ Proton Hyperfine Coupling Constants

At present no experimental evidence is available for comparison with the values predicted from a spin polarisation mechanism in the σ bonds. Once again it is likely that hyperconjugation would be much more important than spin polarisation in any radical containing this fragment. A MO hyperconjugation treatment for a molecule containing this fragment, perinaphthane, is given in chapter 8. The ions of this molecule should be capable of ESR examination.

6.5 Proton Hyperfine Coupling Constants in $N-C_nH_{2n+1}$ Fragments

Experimental results are available for the proton hyperfine coupling constants in fragments $N-C_nH_{2n+1}-$, occurring in dithiocarbamate complexes. These a_H values have been determined from the temperature dependence of their NMR spectra, by Dr R.M. Golding [26], who has recently shown [3] that the a_H factors for protons in a paramagnetic molecule can be determined from the relation

$$\Delta H = a_H h \langle S_z \rangle / g_N \beta_N$$

where ΔH is the change in the effective magnetic field at the nucleus due to the unpaired electrons in the molecule. The advantage of this method is that it is possible to determine very small values of a_H , down to about 10^{-4} Mc/s, whereas using ESR measurements it is difficult to determine a_H values of less than 10^{-1} Mc/s. However, to perform NMR

measurements a reasonably stable species is required, and the concentrations needed with the present experimental methods are considerably greater than those required for ESR measurements, which can handle very low concentrations of unstable species.

This method has been applied by Dr Golding to dithiocarbamate complexes of the type

where R is an aliphatic chain. The NMR measurements permit the calculation of the proton a_{H} values for the iron atom not only in its ground electronic state for these complexes, $^2\text{T}_2$, but also in the first excited state, $^6\text{A}_1$. In the $^2\text{T}_2$ state there could be complications arising from the neglect of the pseudo-contact term in the hyperfine Hamiltonian [see section 1.2] but for the $^6\text{A}_1$ state there should not be any contribution from the pseudo-contact term, and the Fermi contact term should be solely responsible for the observed proton hyperfine coupling constants.

The experimental a_{H} values, given in table 6.3, indicate that there is a significant amount of spin density at the aliphatic and aromatic protons, arising from the unpaired electrons of the iron atom. This would also lead to spin density at the nitrogen atom, in its π orbitals. If this spin density at the nitrogen atom gives rise, through a spin polarisation mechanism in the σ orbitals, to the spin density implied at the protons by the observed a_{H} values, then the results $a_{\text{H}} = Q\rho$ derived for spin polarisation in $\text{C}'-\text{C}_{\text{n}}\text{H}$ fragments should also be valid for $\text{N}-\text{C}_{\text{n}}\text{H}$, apart from slight numerical changes for certain of the

exchange integrals. It was shown in section 2.10 that Q for N-H is about the same as for C'-H; it is assumed that Q for N-C_nH is about the same as for C'-C_nH.

The experimental results, kindly supplied by Dr R.M. Golding [26], are given in table 6.3, for the 6A_1 state of the iron atom.

Table 6.3 Proton Hyperfine Coupling Constants for the
 6A_1 States of Dithiocarbamate Complexes

Table 6.3 (continued)

molecule	a_H in Mc/s					
	$CH_2(1)$	$CH_2(2)$	CH_3	aromatic (para)	aromatic	aromatic
a	-	-	.668	-.0804	.0083	.0195
b	.455	-	.0542	-.0815	.0093	.0031
c	.435	.0930	.0389	-.0787	.0012	.0186
d	-	-	.838	-	-	-
e	.495	-	.0386	-	-	-
f	.469	.0648	.0313	-	-	-
g	.303	.0048	-	-	-	-
h	.261	.012	-	-	-	-

All of the fragments $N-C_nH$ imply a negative spin density at the nitrogen atom, arising from spin polarisation. If the formula for a_H for $C'-C-H$ is used as a rough guide for the implied values of the spin density at the nitrogen atom, it is seen that the $N-CH_2-$ fragments imply large negative spin densities at the nitrogen atom of about 0.1. Since there are three such nitrogen atoms in each complex, this corresponds to a large probability of the unpaired electrons from the iron atom having been delocalised, or at least having some effect, on the nitrogen atoms.

Furthermore, if the observed proton hyperfine coupling constants were the result of spin density at the nitrogen atom giving rise to spin density at the protons, by spin polarisation in the σ bonds of $N-C_nH$, the values of a_H in the sequence $N-CH_2-$, $N-C-CH_2-$, $N-C-C-CH_3$ would be expected to decrease in magnitude more rapidly than they are observed to, and a change in sign of a_H would be expected. It therefore

appears that spin polarisation in the σ orbitals is not the main mechanism contributing to the observed a_H values.

6.6 Conclusion

Comparison of experimental and theoretical results for proton hyperfine coupling constants in $C'-CH_2$ and $N-C_nH$ fragments have indicated that in these cases delocalisation of electrons from the region where the unpaired electrons are usually considered to be restricted to, may be much more important than spin polarisation, in accounting for the observed proton hyperfine coupling constants. For $C'-H$ fragments, where there is no possibility of delocalisation, spin polarisation in the σ bonds appears to account satisfactorily for the observed proton hyperfine coupling constants.

In the remainder of this thesis, detailed MO studies are made of delocalisation (hyperconjugation) in molecules containing $C'-CH_2$ and $C'-C-CH_2$ fragments. The methods developed are, in principle, applicable to any molecules.

Chapter 7

HYPERCONJUGATION IN AN AROMATIC

C'-CH₂ FRAGMENT

7.1 Introduction

Hyperconjugation, the other possible mechanism leading to spin density at the protons, is now considered, since the spin polarisation mechanism does not appear to be able to account quantitatively for the observed proton hyperfine coupling constants for C'-CH₂ groups.

MO calculations making allowance for hyperconjugation are presented in this chapter, for two molecules containing C'-CH₂ fragments, pyracene and acenaphthene. Five methods of calculating the MO's for these molecules are considered. A range of calculated values for the C'-CH₂ proton hyperfine coupling constants result, depending on the method used to determine the π MO's, and the assumptions made in calculating the a_H values from the MO wave functions. However, all methods lead to larger values for a_H than the spin polarisation mechanism discussed in chapter 3 and section 6.3, and all methods account for the observed facts that a_H is larger for the positive ion of pyracene than the negative ion, and that for the negative ions, acenaphthene has a slightly greater value of a_H than pyracene.

Calculations are presented to show the sensitivity of the results to certain parameters involved in the calculation of the MO's; in particular, the choice of values of some of the coulomb integrals, and the use of assumed bond lengths and angles. The calculated C'-CH₂ a_H values are found to be sensitive to the choice of coulomb integrals, but are little affected by the changes in bond lengths and angles required when the values for pyracene obtained from an

x-ray study are used.

From a MO viewpoint, hyperconjugation means an extension of the π electron system from conjugated regions, such as an aromatic system, to regions usually considered to be non-conjugated, such as a saturated aliphatic portion of a molecule. This delocalisation is basically a consequence of the symmetry properties of the molecule.

In an aromatic $C'-CH_2$ fragment such as occurs in pyracene, carbon atom C is bonded to another carbon atom as well as C' , and to the two hydrogens H_u and H_l , located above and below the aromatic plane respectively. These four bonds are usually considered to be of σ type.

Instead of considering the hydrogen 1s AO's separately, in forming bonds, the normalised linear combinations

$$\sigma_H = [2(1+S)]^{-1/2}(1s_u + 1s_l)$$

$$\pi_{H_i} = [2(1-S)]^{-1/2}(1s_u - 1s_l),$$

$$\text{where } S = \langle 1s_u | 1s_l \rangle$$

can be taken. These have σ and π symmetry respectively, with respect to the molecular plane. Therefore, π_{H_i} combines with the other π orbitals in the molecule, namely those of the aromatic region, to extend the conjugation of these aromatic π orbitals to the CH_2 groups. Symmetry considerations show that π_{H_i} cannot combine with the σ orbitals of the molecule, and σ_H cannot combine with the π orbitals. If the molecule contains an unpaired electron, which is in a π orbital for an aromatic molecule, this leads to spin density at the CH_2 groups.

The CH_2 group is therefore treated as having a π -type pseudo AO π_{H_i} . Consequently, the AO's for the carbon atom of the CH_2 group are taken as three hybrids of σ symmetry, pointing to σ_H and to two other carbon atoms respectively,

and one pure $2p_{\pi}$ AO.

Symmetry considerations have lead to the assignment of two π type AO's to each CH_2 group, the carbon $2p_{\pi}$ and π_{H} . The amount of π electron density at these atoms in the CH_2 groups is then determined by a MO calculation for the π electrons. Therefore these π AO's associated with the CH_2 groups are now included in the basis set of π AO's used in setting up the π MO's for the entire molecule, by the method of linear combination of atomic orbitals (LCAO). MO calculations for molecules as large as pyracene are most readily performed with some form of Hückel theory.

An alternative approach, discussed in section 7.8, is to determine the MO's for the entire molecule by including in the basis set of AO's all the high energy electrons, namely $2s$, $2p_x$, $2p_y$, $2p_z$ for carbon and $1s$ for hydrogen. This method does not involve any assumptions of a division into σ and π type electrons, or of the consideration of just the π orbitals. No arbitrary assumptions about the type of σ hybrid AO's at each atom are made, and with this method, the validity of assuming that the unpaired electron in the positive or negative ion is in a π type MO, can be checked. The main disadvantage of this method is that it requires considerably more computation than the π electron calculations, since the basis set contains almost four times as many AO's.

7.2 Hückel Theories

All Hückel theories are based on a one electron MO approach. The eigenfunctions for a single electron, in the field of all the nuclei, are determined by LCAO-MO. These are the one-electron MO's. The total number of electrons considered is then fed into these MO's, in accordance with

the aufbau principle, placing up to two electrons in each non-degenerate orbital. Since the Hamiltonian used in calculating these MO's is a one-electron Hamiltonian, this method neglects any electronic interaction, such as coulombic repulsion or exchange interaction.

All forms of Hückel theory are based on an expansion of the one-electron MO's in terms of a LCAO. The variation principle is applied, as shown in appendix IV, to minimise the energy of each one-electron eigenfunction, yielding the secular equation in matrix form,

$$HC = SCE$$

$$C^{\dagger}SC = 1$$

where H is the Hückel matrix,
 S is the overlap matrix,
 C is the MO matrix, whose column vectors give the coefficients of the AO's in the LCAO-MO's,
 E is the eigenvalue matrix, giving the energies of the MO's.

The matrix elements of S and H are given by

$$S_{ij} = \langle \phi_i | \phi_j \rangle$$

$$H_{ij} = \langle \phi_i | \mathcal{H} | \phi_j \rangle$$

where the $|\phi_i\rangle$ are the basis AO's and $\mathcal{H}$ is the effective one-electron Hamiltonian. Usually the exact form of the Hamiltonian is not specified. The diagonal elements of the Hückel matrix, denoted by α_i , are referred to as coulomb integrals; the off-diagonal elements, written as β_{ij} , are referred to as resonance or exchange integrals.

When dealing with molecules where there is only one type of π AO and only one value for the bond lengths, the values of the β_{ij} need not be further specified, when only nearest neighbour β interaction is considered. However, in

the molecules studied here, there are two different types of π AO's, carbon $2p_{\pi}$ and hydrogen π_H , and three different bond lengths. Therefore a variation of the resonance integrals β with atom type and bond length must be assumed. All forms of Hückel theory considered in this thesis assume a linear relation between β_{ij} and S_{ij} , often with a simple constant of proportionality. The overlaps S_{ij} are conveniently evaluated using Slater wave functions, as shown in appendix V.

Until recently, all Hückel calculations had been performed for just the π electrons, and it was implicitly assumed that the π electrons accounted for the chemical properties of conjugated compounds. Recently Hückel theory has been extended [5] to include all the high energy electrons. In this form it is applicable to many inorganic compounds as well as organic ones.

Five forms of Hückel theory are considered in this chapter. Since the observed proton hyperfine coupling constants depend on the spin density at the protons, such measurements provide a sensitive test for methods of constructing approximate eigenfunctions for molecules. The experimental results are therefore used to compare these five forms of Hückel theory. The first four methods consider only the π electrons.

Method (1): Simple Hückel Theory

By neglecting all the off-diagonal overlap matrix elements, i.e. by setting $S_{ij} = \delta_{ij}$, the secular equation $HC = SCE$ is simplified to $HC = CE$. This requires merely the evaluation of the eigenfunctions C_i and eigenvalues E_i of the Hückel matrix H .

This is the standard form of Hückel theory, and is often the only form considered. Only those resonance integrals

between AO's on adjacent atoms are considered. When there is more than one AO type, or more than one value for the bond lengths, the resonance integrals are evaluated by assuming a relation

$$\beta_{ij} = \text{constant} \times S_{ij}$$

and the S_{ij} are evaluated with Slater wave functions.

At first sight this approach appears to be self-contradictory, in that at one stage the S_{ij} are assumed zero for i not equal j , whereas at another stage they are calculated to be non-zero and used as such to determine the β_{ij} . This is, however, the standard form of Hückel theory, and has proved useful for predicting "resonance" energies and providing simple qualitative understandings of certain properties of conjugated molecules. However, its main advantage is its mathematical simplicity, and this is no doubt the reason that it was almost the only form of Hückel theory used for many years. It is important to note that there is no theoretical justification for setting $S_{ij} = \delta_{ij}$.

This method gives a highly symmetrical solution. The energy levels are equally spaced above and below the zero of energy, for molecules with only one type of AO, and the coefficients of given AO's in corresponding bonding and antibonding MO's are numerically equal.

Method (2)

All the overlap integrals are once again set equal to δ_{ij} , but allowance is made for all β_{ij} interactions, in assuming

$$\beta_{ij} = \text{constant} \times S_{ij}.$$

This makes little change to the binding energy of a given molecule, compared with method (1), but destroys the symmetry of the solutions: the energy levels are no longer equally

spaced above and below the zero of energy, and the coefficients of given AO's in corresponding bonding and antibonding MO's are no longer numerically equal.

Method (3): Löwdin's method making allowance for overlap

This method, due to Löwdin [27] makes full and exact allowance for overlap, in solving the secular equation, whereas methods (1) and (2) make no allowance for overlap. The basis set $\{\phi_i\}$ is no longer an orthogonal set. As shown in appendix IV, the eigenvalue problem $HC = SCE$ can be transformed to a tractable form

$$\begin{aligned} H'C' &= C'E \\ \text{where } H' &= S^{-1/2} H S^{-1/2} \\ C &= S^{-1/2} C'. \end{aligned}$$

The major problem with this method is the computation of the matrix $S^{-1/2}$, but this is readily accomplished with an electronic computer

In method (3), only those overlap matrix elements between AO's on adjacent atoms (i.e., bonded atoms, in the usual chemical sense) are considered. The β_{ij} integrals are evaluated as in method (1), although the method of solving the secular equation, making full allowance for overlap, is quite general.

Method (4)

This is the same as method (3), except that all overlap matrix elements are considered. The β_{ij} integrals are evaluated as in method (2). As discussed in appendix IV, the real matrix $S^{-1/2}$ exists if and only if S is positive definite. Now although the complete matrix S is positive definite, the matrix S with certain, even small, matrix elements neglected may not be positive definite, and in

such a case no real solution of the secular equation exists.

Methods (3) and (4) are of comparatively recent origin compared with method (1).

Method (5): Extended Hückel Theory

This method, developed recently for organic molecules by Hoffmann [5], considers all the high energy electrons. It is not restricted to conjugated organic molecules, but can be applied to any molecule, organic or inorganic. For organic compounds, the carbon $2s$, $2p_x$, $2p_y$, $2p_z$, and hydrogen $1s$ AO's are considered. Full allowance is made for overlap, using Löwdin's method [see appendix IV], and considering all overlap matrix elements. The overlap integrals may be evaluated using Slater wave functions, or self-consistent field (SCF) overlaps may be used. Hoffmann has developed the method so that just the x , y and z coordinates of each atom, together with four parameters, are fed into a computer, which computes the overlap integrals and then the MO's. A similar program is given in appendix VII of this thesis.

The coulomb integrals α_i are estimated from emission spectral data, being taken as the negative of the valence state ionisation energies (VSIE). The resonance integrals β_{ij} are evaluated from the assumed relation

$$\beta_{ij} = k \frac{1}{2}(\alpha_i + \alpha_j) S_{ij}$$

where k , a constant, is taken as 1.75 by Hoffmann.

This method gives an eigenvalue problem of order $4n+m$ for a molecule $C_n H_m$, whereas the π electron methods (1) to (4) give matrices of order $n+\frac{1}{2}m$, or less. Even for comparatively small molecules, such as benzene, this method leads to a considerable amount of computation, and since the solution of the secular equation requires two eigenvalue

extractions, is not suitable without a high speed electronic computer.

The method used here for evaluating the resonance integrals is more realistic than that used in methods (1) to (4), when there are AO's with different coulomb integrals. It makes allowance for the degree of bonding depending on the electronegativities of the two AO's overlapping to form the bond, as well as on the degree of overlap. Another method that has been suggested for evaluating the resonance integrals [28] is

$$\beta_{ij} = -k [\alpha_i \cdot \alpha_j]^{1/2} S_{ij}$$

where k , a positive constant, is usually taken as 2.0.

7.3 Hyperconjugation in Pyracene and Acenaphthene

All five of the above forms of Hückel theory are applied to these two molecules. Full computational details are given for pyracene, and just a summary of results for acenaphthene. The same methods were also applied to naphthalene. This provides a convenient basis for discussing the extent of hyperconjugation in pyracene and acenaphthene. The model used for the electron calculations is given first, and then the model for method (5). The π electron energy levels and MO's for all five methods are then discussed.

7.4 The Model for π Electron Calculations

For the molecules pyracene and acenaphthene, the σ and π type AO's and MO's belong to different irreducible representations of the point group appropriate for the molecule concerned. Consequently there is no overlap between any σ and π type orbitals, and the π electrons can be considered separately. This is not true, however, for the molecule

perinaphthene, discussed in the next chapter.

Each CH_2 group provides two π AO's for the basis set of the Hückel π electron calculations. This gives 18π AO's, and hence 18π MO's, for pyracene, and 14 for acenaphthene. In the negative ion of pyracene, 19 electrons are fed into these MO's, with two electrons in each of the bonding MO's and one electron in the lowest energy antibonding MO. In the positive ion of pyracene, 17 electrons are fed in, and in this case the highest energy bonding MO is singly occupied. In each case there is one π MO containing a single unpaired electron. This electron is responsible for the hyperfine properties of these radicals.

Group theory can be used to reduce the order of the matrices involved in methods (1) to (4), from one 18×18 matrix for pyracene, to two 4×4 and two 5×5 matrices. Instead of using the basis set $\{|\phi_i\rangle\}$ of AO's, a set of symmetry adapted linear combinations of the $|\phi_i\rangle$ are chosen, say $\{|\psi_i\rangle\}$, such that each $|\psi_i\rangle$ transforms as an irreducible representation of the symmetry group of the molecule, which is D_{2h} for pyracene and C_{2v} for acenaphthene. A theorem in group theory states that there are no matrix elements, of a scalar operator such as the Hamiltonian, between $|\psi_i\rangle$ belonging to different irreducible representations. Therefore the 18×18 matrix has blocked out diagonal form, and in the extraction of eigenvalues only the submatrix for each irreducible representation need be considered. The numbering of the AO's, and the symmetry adapted orbitals are given below.

Pyracene: numbering of π AO's, and symmetry orbitals

The AO's 1, 4, 16 and 18 are the pseudo AO's π_H associated with the CH_2 groups, and defined in section 7.1.

$$B_{2g} : \begin{aligned} & \frac{1}{2}(\phi_1 + \phi_4 - \phi_{16} - \phi_{18}) \\ & \frac{1}{2}(\phi_2 + \phi_3 - \phi_{15} - \phi_{17}) \\ & \frac{1}{2}(\phi_5 + \phi_7 - \phi_{12} - \phi_{10}) \\ & \frac{1}{2}(\phi_{14} + \phi_8 - \phi_{13} - \phi_9) \\ & \frac{1}{2}(\phi_6 - \phi_{11}) \end{aligned}$$

$$B_{1u} : \begin{aligned} & \frac{1}{2}(\phi_1 + \phi_4 + \phi_{16} + \phi_{18}) \\ & \frac{1}{2}(\phi_2 + \phi_3 + \phi_{15} + \phi_{17}) \\ & \frac{1}{2}(\phi_5 + \phi_7 + \phi_{12} + \phi_{10}) \\ & \frac{1}{2}(\phi_{14} + \phi_8 + \phi_{13} + \phi_9) \\ & \frac{1}{2}(\phi_6 + \phi_{11}) \end{aligned}$$

$$B_{3g} : \begin{aligned} & \frac{1}{2}(\phi_1 - \phi_4 + \phi_{16} - \phi_{18}) \\ & \frac{1}{2}(\phi_2 - \phi_3 + \phi_{15} - \phi_{17}) \\ & \frac{1}{2}(\phi_5 - \phi_7 + \phi_{12} - \phi_{10}) \\ & \frac{1}{2}(\phi_{14} - \phi_8 + \phi_{13} - \phi_9) \end{aligned}$$

$$A_u : \begin{aligned} & \frac{1}{2}(\phi_1 - \phi_4 - \phi_{16} + \phi_{18}) \\ & \frac{1}{2}(\phi_2 - \phi_3 - \phi_{15} + \phi_{17}) \\ & \frac{1}{2}(\phi_5 - \phi_7 - \phi_{12} + \phi_{10}) \\ & \frac{1}{2}(\phi_{14} - \phi_8 - \phi_{13} + \phi_9) \end{aligned}$$

Acenaphthene

A_2 states are antisymmetric with respect to reflection in the plane containing the z axis and perpendicular to the aromatic plane, whereas B_1 states are symmetric with respect to this reflection.

7.5 Calculation of Resonance Integrals

All the π electron methods use the relation

$$\beta_{ij} = \text{constant} \times S_{ij}.$$

For convenience in computation, all energies are measured in units of β_0 , the resonance integral between two carbon 2p AO's on adjacent atoms a distance 1.39 Å apart. The overlap S_{ij} for two such AO's is given in appendix V as nearly 1/4; therefore the above constant is taken for simplicity as 4, so that

$$\beta_{ij} = 4 S_{ij}$$

where all resonance integrals are measured in units of β_0 .

The overlap integrals are calculated as shown in appendix V, with Slater AO's, using an exponent of 1.625 for carbon, and 1.0 for hydrogen, as given by Slater's rules [29]. X-ray evidence [30] shows that all the carbon atoms in pyracene are planar, so that only the hydrogens of the CH_2 groups lie out of the molecular plane. The bond lengths for aromatic carbon-carbon, aliphatic carbon-carbon, and carbon-hydrogen, are taken as 1.39, 1.54 and 1.08 Å respectively. The angle H_uCH_1 within a CH_2 group is taken as $109^\circ 28'$, the tetrahedral angle. The internuclear distances and angles calculated from the x-ray data are used in a later study in section 7.16. As is clearly seen from table AV.4 in appendix V, the overlap S_{12} is dependent on the C-H distance and the angle H_uCH_1 . The larger overlap integrals are given below, although for methods (2) and (4), all overlap matrix elements were considered.

$S_{12} = .6399$	$S_{23} = .1919$	$S_{56} = .2484$
$S_{13} = .1137$	$S_{24} = .0436$	$S_{57} = .0352$
$S_{14} = .1164$	$S_{25} = .0311$	$S_{58} = .0020$
$S_{16} = .0235$	$S_{26} = .0013$	$S_{5,12} = .0157$

$$\begin{array}{lll} S_{17} = .0175 & S_{2,14} = .0179 & S_{1,14} = .0216 \\ & S_{18} = .0014 & \end{array}$$

7.6 Coulomb Integrals

The choice of coulomb integrals for the calculations is the mathematical way of allowing for the inductive effect. All the aromatic carbon $2p_{\pi}$ AO's are assumed initially to have the same value of the coulomb integral, say α_o . The α values for the aliphatic carbon $2p$ AO's and the pseudo AO's π_H are expressed as

$$\begin{array}{ll} \alpha_1 = \alpha_o + \delta_1 \beta_o & (\text{i.e. for } \pi_H) \\ \alpha_2 = \alpha_o + \delta_2 \beta_o & (\text{i.e. for the adjacent carbon } 2p_{\pi}). \end{array}$$

The values of δ_1 , δ_2 used initially are those chosen by Coulson and Crawford [31] for a study of hyperconjugation in toluene,

$$\begin{array}{l} \delta_1 = -0.5 \\ \delta_2 = -0.1. \end{array}$$

Since the methyl group in toluene is usually considered to be electron donating with respect to the aromatic ring, and since β_o is negative, a positive value of δ_1 might have been expected. However, as shown in section 7.11, these δ values do in fact lead to the CH_2 groups in pyracene and acenaphthene being electron donating to the aromatic rings, and, furthermore, it is shown in section 7.15 that the more negative the value of δ_1 is, the greater is the amount of π electron density donated from the CH_2 groups to the aromatic ring. The values of δ chosen by Coulson and Crawford were chosen to fit the experimental dipole moment data for toluene.

The valence state ionisation energies for carbon $2p$ and hydrogen $1s$ AO's, of -11.4 and -13.6 e.v. respectively,

according to Hoffmann [5], also appear to suggest that δ_1 should be positive. However, as shown in section 7.8, the coulomb integral for π_H , according to method (5), should be

$$\alpha_H(1-1.75 S)/(1-S)$$

where $S = \langle 1s_u | 1s_1 \rangle$ and α_H is the coulomb integral for a hydrogen $1s$ AO. With the assumed bond lengths and angles, this gives $\alpha_1 = -9.4980$ e.v., which corresponds to a negative value for δ_1 , of about -0.67 .

The dependence of the calculated α_H values, and the charge densities and binding energy, on δ_1 and δ_2 , is further discussed in section 7.15.

For convenience in computation, all energies for methods (1) to (4) are measured from α_O in units of β_O , which is inherently negative.

7.7 Calculation of the Proton Hyperfine Coupling Constants

(i) C'-CH₂ Protons

The proton hyperfine coupling constants (PHFCC) are determined from the MO containing the unpaired electron in the radical. If this MO is expressed as

$$\Psi = \sum_i c_i \phi_i$$

where the ϕ_i are the basis AO's, the spin density $Q(p)$ at one of the CH₂ protons, say the upper one of the pseudo AO ϕ_1 , is

$$Q(p) = [\Psi(p)]^2$$

$$\text{where } \Psi(p) = \sum_i c_i \phi_i(p)$$

and $\phi_i(p)$ is the value of the AO ϕ_i at the coordinates p of the proton. The $\phi_i(p)$ are evaluated with Slater wave functions, giving, ⁱ for the assumed bond lengths and angles,

$$\begin{aligned}\phi_1(p) &= .3914 & \phi_2(p) &= .2880 \\ \phi_3(p) &= .0494 & \phi_4(p) &= .0216 \\ \phi_5(p) &= .0494 & \phi_7(p) &= .0093 \\ \phi_{14}(p) &= .0112 .\end{aligned}$$

The proton HFCC a_H is then

$$a_H = \frac{8\pi g \beta_N \beta_N}{3h} Q(p) = 1594 [\Psi(p)]^2 \text{ gauss (electron).}$$

If contributions to $\Psi(p)$, and therefore a_H , are considered from only the π_H AO about the proton and the $2p\pi$ AO on the adjacent carbon atom, then

$$\Psi(p) = .3914c_1 + .2880c_2.$$

This was the method used by Colpa and de Boer [13] in a study of pyracene.

The above values of the $\phi_i(p)$ show that $\phi_1(p)$ and $\phi_2(p)$ are considerably larger than any of the others, which for most purposes may be assumed zero. However, the contribution of these small $\phi_i(p)$ to $\Psi(p)$, and hence a_H , is determined by $c_i\phi_i(p)$, not just $\phi_i(p)$, and for the singly occupied MO's of pyracene and acenaphthene, these c_i values are larger in magnitude than, and opposite in sign to, c_1 or c_2 . Consequently the contribution of these small $\phi_i(p)$ to a_H is not negligible; numerical evaluation in section 7.14 shows that neglect of these small $\phi_i(p)$ leads to a_H values which are about twice as large as otherwise, when allowance is made for all the $\phi_i(p)$. The HFCCs calculated by making allowance for all the $\phi_i(p)$ are labelled a_H in section 7.14; those calculated by considering just ϕ_1 and ϕ_2 are referred to as a_H' . A further set of values could be given, by correcting the a_H values for spin polarisation in the σ bonds of $C'-CH_2$, as explained in section 6.3. However, this leads to

only small changes from a_H : it decreases the values by about 0.3 gauss for negative ion, and 0.6 gauss for positive ions.

Since the contribution of $\phi_i(p)$ for $i \neq 1,2$ is not negligible, it is important to consider the significance of the values calculated with Slater AO's. These are generally considered to provide a reasonable representation of AO's for distances corresponding to normal bond lengths. However, the distances involved for these small $\phi_i(p)$ are considerably greater than normal bond lengths. The best test available at present is to compare these Slater AO's for carbon 2p states with SCF AO's. Such AO's have recently been determined for both the spectroscopic states of the 2p electrons in atomic carbon, and in simple molecules such as C_2 . Several MO studies of aromatic molecules have been made recently using LC-SCF-AO, in an attempt to get a better representation of the "tail" of the molecular wave functions than that provided by MO's constructed from simple Slater AO's. An analysis of these results [23] shows that at about 3.5 Å the overlap between two carbon 2p_σ AO's calculated with a Slater AO has only one third the value calculated with the SCF-AO's, whereas the exchange integral between two carbon 2p_σ electrons at the same distance, calculated with a Slater AO, is only one eighth of the value calculated with the SCF-AO's. This shows that Slater AO's underestimate the value of AO's at large distances, and more than justifies the inclusion of the terms arising from the small values of $\phi_i(p)$ in the calculation of a_H . Slater AO's may even underestimate the contribution of these small $\phi_i(p)$ to a_H , but since they have been used to determine all the overlap integrals in this chapter, they are used, for consistency, in the evaluation of a_H .

(ii) Aromatic Protons

The π MO containing the unpaired electron is also used to calculate the aromatic proton HFCC's. A comparison of the calculated spin densities and experimental proton HFCC's for the negative ion of naphthalene gives $a_H = -28\rho$ gauss, for all five methods, where ρ is the spin density at the adjacent carbon atom. Experimental data is not available for the positive ion of naphthalene; it is assumed that the above relation is also applicable for the positive ions of pyracene and acenaphthene. As observed in section 6.2, positive aromatic ions usually have somewhat larger a_H values than the corresponding negative ions. However, this makes only small differences to the calculated a_H values, and is not considered in this chapter, since all five methods predict a larger value of the aromatic a_H for the positive ion of pyracene than the negative ion, without additional assumptions.

As discussed in section 6.2, the carbon spin densities ρ are calculated from an orthonormal set of MO's, i.e. MO's which are orthogonal and normalised so that $\sum \bar{c}_i^2 = 1$. For methods (1) and (2), these are Ψ_H , the eigenvectors of the matrix H , which are also the MO's. For methods (3), (4) and (5) they are $\Psi_{H'}$, the eigenvectors of the matrix H' , since the MO's $\Psi = S^{-1/2} \Psi_H$ are not orthogonal. The spin density at atom i is $\bar{c}_i^2$, where $\bar{c}_i$ is the coefficient of the $2p\pi$ AO at atom i , in the orthonormal vector corresponding to the singly occupied level. An alternative method is to perform a Mulliken population analysis [40] for the MO's $S^{-1/2} \Psi_H$ of methods (3), (4) or (5), and use the net atomic population, as defined by Mulliken. This alternative is not considered here.

These orthonormal vectors are also used to calculate the charge distributions for the neutral molecules. The

total electronic charge associated with atom i is

$$2 \sum_{k=1}^{n/2} \bar{c}_{ik}^2$$

where the summation is over all the occupied levels, i.e. the bonding MO's, in the neutral molecule. The charge distribution for the negative and positive ions could be calculated similarly, but is not given for the π electron calculations.

7.8 The Model for the Extended Hückel Calculations

All carbon $2s$, $2p_x$, $2p_y$, $2p_z$ and all hydrogen $1s$ AO's in the molecule are considered. The overlap integrals are evaluated with Slater AO's, using an exponent of 1.625 for carbon and 1.0 for hydrogen, the values given by Slater's rules [29]. There have been suggestions [5,39] that a smaller value for carbon and a larger value for hydrogen might be more appropriate for molecules. Theoretical evidence for this, and a systematic means of allowing for it in the calculations, is discussed in section 7.19. The bond lengths and bond angles used are those given in section 7.5. In section 7.17, the x-ray bond lengths and angles for pyracene are used.

The coulomb integrals, taken as the negative of the atomic VSIE's, are evaluated from emission spectral data [32]. The values used by Hoffmann [5] are:

$$\begin{aligned} &-21.4 \text{ e.v. for C } 2s \\ &-11.4 \text{ e.v. for C } 2p \\ &-13.6 \text{ e.v. for H } 1s. \end{aligned}$$

However, the method of evaluating the VSIE's from the spectral data is somewhat arbitrary, and alternative values suggested by Gray [41] are -19.5 for C $2s$ and -10.8 for C $2p$. For the constant k , in $\beta_{ij} = k \frac{1}{2}(\alpha_i + \alpha_j) S_{ij}$, Hoffmann's value of

1.75 is taken. Hoffmann has shown [5] that the charge distributions for methane are independent of k , for k greater than 1.5, although the binding energy depends approximately on k , for k greater than 1. The effects of varying the coulomb integrals, and the constant k , on the calculated properties of pyracene and acenaphthene, are discussed in sections 7.15 and 7.16. The alternative method of setting up the off-diagonal Huckel matrix elements,

$$\beta_{ij} = -k [\alpha_i \alpha_j]^{1/2} S_{ij}$$

is also considered in section 7.16.

The overlap integrals are computed from the master formulae given in appendix V. All overlap matrix elements are considered, to ensure that the matrix $S^{-1/2}$ exists in real form, so that the energy levels are real. The computer program given in appendix VII was used to compute the overlap matrix from supplied cartesian coordinates of the atoms. It was found by bitter experience that overlap matrices for molecules as large as pyracene, were rarely positive definite, when set up by hand, due to the inaccuracies of expressing the data to only three significant figures, and the necessity of neglecting overlap integrals smaller than 0.02, to make it possible to set up the matrix by hand in a finite time.

Method of solving the secular equation

There are three possible ways of proceeding with an MO calculation for a given molecule, with method (5). The first way, which is the one requiring the greatest amount of computation time, takes directly the matrix of order $4n+m$, for a molecule $C_n H_m$, and solves the secular equation $HC = SCE$ using Löwdin's method. This is satisfactory for small molecules, of say less than six carbon atoms, but for

larger ones, the time of computation becomes excessively large. Furthermore, the computer available, an Elliott 503, cannot readily handle matrices of order greater than 50, for the ALGOL version of the Hückel calculation, given in appendix VI, or of order 75 for a machine code version.

To reduce the order of the largest matrices to be considered, some factorisation of the secular equation must be achieved. The greatest factorisation possible is to use group theory, to find the sets of symmetry adapted linear combinations of the basis AO's which transform as irreducible representations of the point group of the molecule. For pyracene, this reduces the problem from considering one 68x68 matrix to two 13x13, two 12x12, two 5x5 and two 4x4 matrices; for acenaphthene, the 58x58 matrix is reduced to one 23x23, one 21x21, one 8x8 and one 6x6 matrix. This results in a considerable reduction in the magnitude of the calculations, since the time for solving a given secular equation $HC = SCE$ of order n , depends approximately on the fourth power of the order n . For molecules with lower symmetry, the group theoretical factorisation of the secular equation is not as favourable; for example, for perinaphthane, a molecule with C_{2v} symmetry to be discussed in the next chapter, the initial 64x64 matrix can be factored only to one 36x36 and one 28x28 matrix.

An alternative factorisation is possible, provided that the σ and π type electrons belong to different irreducible representations of the point group of the molecule. For example, in pyracene, the σ type AO's belong to the irreducible representations B_{1g} , B_{2u} , B_{3u} and A_g , whereas the π type AO's belong to the representations B_{2g} , B_{1u} , B_{3g} and A_u . Thus, for pyracene, the 18 π type AO's, namely the 14 carbon $2p_{\pi}$ AO's and the 4 pseudo AO's π_H , defined in section 7.1,

may be considered separately. Similarly, for acenaphthene the 14 π type AO's can be considered separately. However, for molecules such as perinaphthene, discussed in the next chapter, both σ and π type AO's belong to the same irreducible representations, and a factorisation into σ and π type orbitals is not possible.

Calculation of overlap and Hückel matrix elements

The formula given earlier for method (5),

$$\beta_{ij} = k \frac{1}{2}(\alpha_i + \alpha_j) S_{ij}$$

must be modified, when the secular equation is factorised, either using group theory, or into σ and π type orbitals.

(i) Using group theory

Only those matrix elements within a given irreducible representation set are non-zero. The symmetry adapted linear combinations for a particular irreducible representation are written

$$\begin{aligned} |\psi_1\rangle &= N_1 \sum_{r=1}^n c_{1r} |\phi_r\rangle \\ |\psi_2\rangle &= N_2 \sum_{r=2}^n c_{2r} |\phi_r\rangle \\ &\vdots \\ |\psi_n\rangle &= N_n \sum_{r=1}^n c_{nr} |\phi_r\rangle \end{aligned}$$

where the $|\phi_r\rangle$ are the basis AO's, and the c_{ir} are integral constants. N_i is a normalising factor,

$$N_i = \left[\sum_{r=1}^n c_{ir}^2 \right]^{-1/2},$$

and n is the number of linear combinations for that irreducible representation. For a given $|\psi_i\rangle$, most of the c_{ir} are zero, and the maximum number of non-zero c_{ir} for any molecule studied in this thesis is eight. All of the AO's

$|\phi_r\rangle$ in a given $|\psi_i\rangle$ are of the same type, i.e. the same AO type and the same chemical species, and therefore they have the same coulomb integral and the same effective nuclear charge.

The group overlap matrix element between $|\psi_i\rangle$ and $|\psi_j\rangle$, usually denoted by G_{ij} , is

$$\begin{aligned} G_{ij} &= \langle \psi_i | \psi_j \rangle = N_i N_j \sum_{r=1}^n \sum_{s=1}^n c_{ir} c_{js} \langle \phi_r | \phi_s \rangle \\ &= N_i N_j \sum_{r=1}^n \sum_{s=1}^n c_{ir} c_{js} S_{rs} \end{aligned}$$

for c_{ir} , c_{js} real. The corresponding matrix element of the reduced Hückel matrix, H_{ij} , is

$$H_{ij} = \langle \psi_i | \mathcal{H} | \psi_j \rangle = N_i N_j \sum_{r=1}^n \sum_{s=1}^n c_{ir} c_{js} \langle \phi_r | \mathcal{H} | \phi_s \rangle .$$

The diagonal elements H_{ii} and the off-diagonal elements H_{ij} , $i \neq j$, must now be considered separately. The diagonal element is

$$H_{ii} = N_i^2 \sum_{r=1}^n \sum_{s=1}^n c_{ir} c_{is} \langle \phi_r | \mathcal{H} | \phi_s \rangle .$$

Now

$$\langle \phi_r | \mathcal{H} | \phi_r \rangle = \alpha_r$$

$$\langle \phi_r | \mathcal{H} | \phi_s \rangle = k \alpha_r S_{rs}$$

since all of the α_r for a given $|\psi_i\rangle$ are equal. Thus,

$$H_{ii} = \alpha_i [1 + k(G_{ii} - 1)]$$

where α_i is the coulomb integral of any one of the basis AO's with non-zero c_{ir} in the linear combination $|\psi_i\rangle$.

The off-diagonal elements of the reduced Hückel matrix are

$$H_{ij} = \langle \psi_i | \mathcal{H} | \psi_j \rangle = N_i N_j \sum_{r=1}^n \sum_{s=1}^n c_{ir} c_{js} k^{1/2} (\alpha_r + \alpha_s) S_{rs}$$

since for $i \neq j$, $\alpha_r \neq \alpha_s$, by symmetry.

Thus,

$$H_{ij} = \langle \phi_i | \mathcal{H} | \phi_j \rangle = k \frac{1}{2} (\alpha_i + \alpha_j) G_{ij} \quad \text{for } i \neq j$$

where α_j is the coulomb integral of any of the basis AO's with non-zero c_{js} in the linear combination $|\phi_j\rangle$.

Clearly the off-diagonal elements in the reduced Hückel matrix are constructed according to a formula similar to that for the non-reduced case. Note carefully, however, that it is the original coulomb integrals α_i that are used in constructing the off-diagonal elements in the reduced matrix, together with the appropriate reduced matrix group overlap integral G_{ij} , and not the corresponding diagonal elements in the reduced matrix.

The formula $H_{ii} = \alpha_i [1 + k(G_{ii}-1)]$ is also applicable for the alternative way of setting up the resonance integrals,

$$H_{rs} = -k [\alpha_r \alpha_s]^{\frac{1}{2}} S_{rs}$$

for which case the off-diagonal elements in the reduced Hückel matrix are

$$H_{ij} = -k [\alpha_i \alpha_j]^{\frac{1}{2}} G_{ij}.$$

The computer program for Hückel calculations using Löwdin's method, given in appendix VI, makes allowance for this use of group theory. For the non-reduced cases, $S_{ii} = 1$ and so $\alpha_i [1 + k(S_{ii}-1)] = \alpha_i$. Thus, the above formula for the diagonal elements of the reduced Hückel matrix is also valid for the non-reduced case, and the same computer program may be used for both cases.

Note carefully that the normalising factors N_i for the symmetry adapted linear combinations $|\phi_i\rangle$ do not make allowance for overlap between the AO's within that $|\phi_i\rangle$. This method seems preferable to the normalisation method used by Gray [41], making allowance for these internal

overlaps, since it leads to concise expressions for the elements H_{ii} and H_{ij} of the reduced Hückel matrix, in terms of the corresponding elements of the group overlap matrix G , instead of the rather more clumsy formulae of Gray.

(ii) Division into σ and π type electrons

Here the normalised π type pseudo AO's

$$\pi_H = [2(1-S)]^{-1/2}(1s_u - 1s_l)$$

are included in the basis set of π AO's. Since this is a pseudo AO, and not merely a symmetry adapted linear combination, the internal overlap factor $S = \langle 1s_u | 1s_l \rangle$ must be included in the normalisation, to ensure that $\langle \pi_H | \pi_H \rangle = 1$.

If α_H , α_{π_H} are the coulomb integrals for a hydrogen $1s$ AO, and π_H respectively, the diagonal element in the Hückel matrix, for π_H is

$$\begin{aligned} \alpha_{\pi_H} &= \langle \pi_H | \mathcal{H} | \pi_H \rangle = \frac{1}{2(1-S)} \langle 1s_u - 1s_l | \mathcal{H} | 1s_u - 1s_l \rangle \\ &= \alpha_H (1 - kS)/(1-S) . \end{aligned}$$

With $\alpha_H = -13.6$ e.v. and $k = 1.75$, this gives $\alpha_{\pi_H} = -9.4980$ e.v.

The off-diagonal element of the Hückel matrix, of π_H with a carbon $2p_{\pi}$ AO ϕ_i is

$$\begin{aligned} \langle \pi_H | \mathcal{H} | \phi_i \rangle &= [2(1-S)]^{-1/2} [\langle \phi_i | \mathcal{H} | 1s_u \rangle - \langle \phi_i | \mathcal{H} | 1s_l \rangle] \\ &= [2/(1-S)]^{1/2} \langle \phi_i | \mathcal{H} | 1s_u \rangle \\ &= k^{1/2} (\alpha_i + \alpha_H) \langle \phi_i | \pi_H \rangle . \end{aligned}$$

Once again, the off-diagonal elements are constructed from the coulomb integral for the hydrogen $1s$ AO, not that for the pseudo AO π_H . Consequently, a slight modification of the computer program in appendix VI is needed for this case.

To permit a direct comparison of method (5) with methods (1) to (4), the method using the factorisation into σ and π type states is used initially. In section 7.19, factorisation using group theory is considered, in a more sophisticated version of method (5). For sections 7.9 through to 7.18, method (5) refers to these π electron calculations, and the numbering of the basis AO's is the same as for the π electron calculations, in section 7.4.

7.9 Energy Levels and π MO Coefficients

The energy levels and π MO coefficients calculated from each of methods (1) to (5) are given in appendix VIII, for pyracene. Calculations were also performed for acenaphthene and naphthalene. The results from methods (3) and (4) for acenaphthene are also given, and for (3), the orthogonal vector coefficients, i.e. the matrix C' , are given, as well as the MO coefficients, to enable a comparison with the MO coefficients $S^{-1/2} C'$.

The coefficients of AO's not listed for pyracene can be obtained from those given by noting the symmetry of the level and consulting the appropriate symmetry adapted orbitals given in section 7.4.

All energies for methods (1) to (4) are measured in units of β_0 , from a zero at α_0 . For method (5), energies are measured in e.v., from a zero for the electron completely removed from the molecule.

7.10 Evaluation of the Results for the π Electrons

Five methods of calculating the π MO's have been considered. These are now compared, as regards charge distribution, energy levels, and calculated proton hyper-

fine coupling constants for the $C'-CH_2$ and aromatic protons. The calculation of these proton HFCC's permits a sensitive test of the five methods, and provides a novel way of checking bonding theories, being concerned directly with the wave functions rather than the energy levels.

7.11 Charge Distributions

Certain levels, namely $1b_{2g}$, $5b_{1u}$, $5b_{2g}$, $4b_{3g}$, $4a_u$ for pyracene and $6a_2$ for acenaphthene, are almost entirely restricted to the non-aromatic region, whereas other levels, namely $3b_{1u}$, $3b_{2g}$ for pyracene and $4b_1$, $5b_1$ for acenaphthene, are almost entirely restricted to the aromatic region. The MO's of interest for hyperfine studies of the positive and negative ions are $2a_u$, $3b_{3g}$ for pyracene, for the positive and negative ions respectively, and $3a_2$, $4a_2$ for acenaphthene. All five methods indicate a significant amount of electron density at the CH_2 groups, for the singly occupied orbitals.

The electron densities for all the occupied levels are conveniently compared by calculating the charge distributions for the neutral molecules, as explained in section 7.7. Table 7.1 gives the atomic charge densities for pyracene and acenaphthene. The numbering of the AO's is as in section 7.4.

Table 7.1 Atomic Charge Densities in Neutral Molecules

method	<u>PYRACENE</u>					$CH_2(\pi)$
	atom: 1	2	5	6	8	
1	.916	1.072	1.001	1.006	1.008	1.988
2	.908	1.041	.982	.997	1.071	1.949
3	.938	1.050	1.001	1.006	1.008	1.988
4	.932	1.017	.983	.997	1.069	1.949
5	.888	1.062	.976	.999	1.075	1.950

ACENAPHTHENE

	1	2	5	6	8	9	10	11	CH ₂
1	.916	1.072	.994	1.007	1.009	.999	1.007	.999	1.988
2	.903	1.038	.934	.999	1.079	1.001	1.065	.961	1.941
3	.937	1.050	.995	1.007	1.009	.999	1.007	.999	1.987
4	.927	1.015	.937	.998	1.077	1.001	1.063	.961	1.942
5	.884	1.059	.926	1.001	1.083	1.000	1.069	.961	1.943

Atom 1 refers to the pseudo AO π_H , and the CH₂ charge density is the sum of the values for atoms 1 and 2, giving a measure of the total π electron density associated with each CH₂ group.

The two methods which consider only nearest neighbour interactions, namely (1) and (3), give very similar charge distributions, being identical for the aromatic atoms, and for the CH₂ group density; similarly, the three methods (2), (4) and (5), which allow for all β_{ij} interactions, give very similar charge distributions, particularly for the aromatic atoms and the CH₂ group density. There are, however, significant differences between these two sets of methods; the methods making allowance for all β_{ij} interactions predict larger variations either side of the mean value.

The column headed CH₂ in table 7.1 shows that all methods indicate that the CH₂ groups donate π electrons to the aromatic system, as is expected in classical organic chemistry. The methods making allowance for all β_{ij} interactions imply the greatest donation of π electron density from the CH₂ groups to the aromatic rings.

7.12 Energy Levels and Binding Energies

Figures 7.1 and 7.2 show the predicted energy levels for pyracene, from the five methods. Methods (1) and (2)

Figure 7.1

ENERGY LEVELS: PYRACENE

Figure 7.2

ENERGY LEVELS FROM METHOD 5

give energy levels which are approximately symmetrically spaced above and below the zero of energy, at α_0 . Method (1) gives a completely symmetrical energy level diagram for naphthalene, with pairs of bonding and antibonding MO's equidistant above and below the zero at α_0 , and nearly symmetrical ones for pyracene and acenaphthene.

Methods (3), (4) and (5) indicate that the antibonding levels are spread over a considerably greater range of energies than the bonding levels: the centre of gravity of the energy levels lies in the antibonding states. This is a general feature of any MO method making allowance for overlap.

Table 7.2 gives the calculated binding energies for the π electrons, in the neutral molecules.

Table 7.2 Binding Energies for π Electrons

method	units	pyracene	acenaphthene	naphthalene
1	β_0	34.994	24.298	13.601
2	β_0	34.596	24.007	13.385
3	β_0	23.424	16.622	9.820
4	β_0	21.798	15.570	9.302
5	e.v.	37.085	28.532	19.884

The methods making allowance for overlap appear to predict smaller binding energies than methods neglecting overlap. However, none of methods (1) to (4) give a numerical value for β_0 , which is treated as an adjustable parameter to be obtained by comparison with experiment; there is no reason to expect β_0 to have the same numerical value for each method.

The uv spectra for pyracene, acenaphthene and naphthalene have been recorded by Danenberg [42]. The

p-band can easily be shown, using group theory, to correspond to the transition from the highest energy bonding level to the lowest energy antibonding level, i.e. to the transition $|2a_u\rangle \rightarrow |3b_{3g}\rangle$ for pyracene, or to $|3a_2\rangle \rightarrow |4a_2\rangle$ for acenaphthene. It is found experimentally [42] that the p-bands occur in the order pyracene, acenaphthene, and naphthalene, for increasing energy. The ratio of the energy of this transition for naphthalene to acenaphthene, and for naphthalene to pyracene, is 1.05: 1.07 experimentally. The values predicted from the five methods are, in order, 1.04: 1.08, 1.11: 1.22, 1.04: 1.07, 1.04: 1.08, 1.03: 1.06. All of the methods, except method (2), account satisfactorily for the observed ratio.

7.13 Comparison of Naphthalene with Pyracene and Acenaphthene

Insight into the significance of hyperconjugation in pyracene and acenaphthene can be gained by observing that ten of the π MO's in each of pyracene and acenaphthene correspond to the ten π MO's of naphthalene. A comparison of the AO coefficients in the MO's, symmetry types, and energies enables an identification of the "naphthalene MO's" in pyracene and acenaphthene. These corresponding MO's are shown in figure 7.3, as calculated from method (4), although similar results apply to any of the methods. The energies are measured, for each molecule, from a natural zero at $\sum \alpha_i/n$, where n is the number of π electrons. Non-corresponding levels are marked.

The two π MO's for each of pyracene and acenaphthene which were noted in section 7.11 to be restricted to the aromatic region, correspond to those two π MO's of naphthalene which have only small amounts of electron density at

Figure 7.3

CORRESPONDING MO'S: METHOD 4

----- non-corresponding MO's

atoms 5 and 7. The π MO's which contain the unpaired electron in the positive or negative ions of pyracene and acenaphthene correspond to the $1a_u$ and $2b_{3g}$ levels of naphthalene, respectively.

Figure 7.3 shows that the antibonding levels of pyracene and acenaphthene which are not extensions of naphthalene π MO's have considerably higher energy than the antibonding levels corresponding to naphthalene π MO's. However, the bonding MO's which are not extensions of naphthalene π MO's are not the most stable bonding MO's of pyracene or acenaphthene.

7.14 Predicted Proton Hyperfine Coupling Constants

The proton HFCC's a_H for the $C'-CH_2$ and aromatic protons of pyracene and acenaphthene are calculated as explained in section 7.7. The notation a_H , a'_H for the $C'-CH_2$ protons is as defined in that section.

The HFCC's for the aromatic and $C'-CH_2$ protons provide different tests of the MO containing the unpaired electron. For the aromatic protons, a_H depends on the spin density in an orbital, the $2p_\pi$ AO of the adjacent carbon atom, and does not require a knowledge of the analytic form of that AO other than that needed to calculate the overlap integrals in determining the MO's. However, for the $C'-CH_2$ protons, the HFCC depends on the value of the entire singly occupied MO at a particular point, namely the nucleus of one of the CH_2 protons. As well as requiring a knowledge of the AO coefficients in the singly occupied MO, this necessitates an accurate knowledge of the amplitudes of the AO's at this particular point. This is a much more exacting test of the wave function than that required for the calculation of the aromatic a_H values.

Tables 7.3 and 7.4 give the calculated proton HFCC's for the pyracene and acenaphthene ions. The experimental values are from Colpa and de Boer [13]; experimental data is not available for the acenaphthene positive ion.

Table 7.3 Calculated Aromatic Proton Hyperfine Coupling
Constants for Pyracene and Acenaphthene
(in gauss)

PYRACENE

method	positive ion	negative ion
1	1.87	1.83
2	2.11	1.56
3	1.84	1.82
4	2.07	1.57
5	2.18	1.55
experiment [13]	2.00	1.58

ACENAPHTHENE

position:	negative ion			positive ion		
	8	9	10	8	9	10
method						
1	1.90	1.86	4.92	2.20	1.61	4.89
2	1.15	2.42	4.56	3.22	.99	4.82
3	1.90	1.84	4.90	2.21	1.58	4.85
4	1.18	2.39	4.56	3.19	.98	4.76
5	1.10	2.46	4.56	3.28	1.03	4.93
experiment	1.04	2.42	4.17	-	-	-

Table 7.4 Calculated C'-CH₂ Proton Hyperfine Coupling
Constants for Pyracene and Acenaphthene
(in gauss)

PYRACENE

method	negative ion		positive ion	
	a _H	a' _H	a _H	a' _H
1	1.17	3.47	3.79	9.48
2	2.88	6.97	10.76	20.50
3	1.28	3.86	3.58	8.74
4	3.46	8.52	10.58	20.17
5	2.97	7.91	7.90	16.43

ACENAPHTHENE

1	1.20	3.56	4.17	10.29
2	3.39	8.11	17.11	25.91
3	1.32	3.97	3.97	9.54
4	3.98	9.71	13.89	25.03
5	3.47	9.00	9.74	19.18

Experimental values [13]:

pyracene negative ion 6.58 gauss
pyracene positive ion 12.80 "
acenaphthene negative ion 7.53 " .

The predicted values of the HFCC's for the aromatic protons in the pyracene and acenaphthene ions are in satisfactory agreement with experiment. All five methods account for the fact that the positive ion of pyracene has a larger value than the negative ion, although methods (1) and (3) underestimate the difference, whereas methods (2), (4) and (5) overestimate it. Methods (2), (4) and (5) all

indicate about the same values for the acenaphthene negative ion, and all account for the observed order of $a_{10} > a_9 > a_8$. The two methods (1) and (3) which consider only nearest neighbour β_{ij} interaction incorrectly predict that a_8 is slightly greater than a_9 , for the acenaphthene negative ion. For both pyracene and acenaphthene, it is seen that the two methods neglecting non-adjacent β_{ij} interactions predict very nearly the same values, as do the three methods (2), (4) and (5) which consider all β_{ij} interactions. Method (5) gives the best fit to the data for the acenaphthene negative ion, and method (4) the best fit for the pyracene ions.

Table 7.4 indicates a considerable range in the values calculated for the HFCC's of the C'-CH₂ protons in any given ion. For the negative ion of pyracene, the calculated values range from 1.17 to 8.52 gauss, depending on the method used to calculate the π MO's and the assumptions made regarding the $\phi_i(p)$, in calculating the HFCC's.

None of the a_H or a'_H values calculated by any one method of determining the π MO's accounts precisely for the experimental values for both the positive and negative ions of pyracene, and the negative ion of acenaphthene. The a'_H values from method (5) give the best fit, although in all three cases the calculated values are about 25 % too high. The a_{Hi} values calculated above appear to involve the most reasonable assumptions, and therefore method (4) provides the best interpretation of the experimental C'-CH₂ proton HFCC's for the three cases. However, the values for the negative ions are only about half the experimental values, and that for the positive ion of pyracene is only 83 % of the experimental value. For the a'_H values, method (2) gives the best fit for the negative ions, but for the

positive ion of pyracene, methods (2) and (4) significantly overestimate the value, and methods (1) and (5) give the best fit, being about 28 % too low and too high, respectively.

However, all methods of calculating the π MO's and both methods of evaluating the proton HFCC's for the C'-CH₂ protons from these MO's correctly predict that the HFCC for the acenaphthene negative ion is slightly greater than for the pyracene negative ion. Table 7.5 gives the ratio of the calculated values for the acenaphthene and pyracene negative ions.

Table 7.5 Ratio of C'-CH₂ Proton HFCC's for the Negative Ions of Acenaphthene and Pyracene

method	a_H	a'_H
1	1.02	1.03
2	1.18	1.16
3	1.03	1.03
4	1.15	1.14
5	1.17	1.14

The ratio of the experimental values of 1.14.

Methods (2), (4) and (5) all account satisfactorily for the observed ratio. The two methods which neglect non-adjacent β_{ij} interactions underestimate the value.

All of the methods also predict that the coupling constant for the positive ion of pyracene is significantly larger than for the negative ion, as is found experimentally, but the ratio is too large in all cases. The a'_H values from method (5) give a ratio of 2.07, which is the closest to the experimental ratio, 1.75, but the absolute a'_H values from method (5) are about 25 % too high.

Once again, as for the charge densities and the aromatic proton HFCC's, it is seen that the calculated C'-CH₂ proton HFCC's obtained from the two methods which consider only nearest neighbour β interaction are about the same, as are the values obtained from the three methods which allow for all β interactions.

In all cases, a_H is only about half the value of a'_H , which shows clearly that the contribution to the HFCC's of $\phi_i(p)$, for $i \neq 1,2$ is not negligible. However, as explained in section 7.7, Slater AO's may not provide a satisfactory means of evaluating these small $\phi_i(p)$. In section 7.7, it was suggested that Slater AO's may underestimate the contribution of these small $\phi_i(p)$. However, table 7.4 shows that in all three cases, the experimental value lies between the calculated a_H and a'_H values, suggesting that Slater AO's overestimate the contribution of these small $\phi_i(p)$. For example, if Slater AO's overestimate the contribution of these small $\phi_i(p)$ by a factor of two times, the values for the pyracene negative, pyracene positive, and acenaphthene negative ions, calculated from method (5), would be 5.44, 12.16 and 6.26 gauss, respectively, giving a much improved fit to the experimental data.

A surprising feature to be noted from table 7.4 is the large difference in calculated C'-CH₂ proton HFCC's obtained from methods (1) and (2), or from methods (3) and (4), the difference between the two methods being allowance for all β_{ij} interactions in the second one, in each case. The values from the methods considering all β_{ij} interactions are more than double those from methods considering just nearest neighbour interactions. Table 7.2 shows that the corresponding change in the binding energies is only a few percent.

Colpa and de Boer, in a study using a method similar to (4), report [13] calculated values of the proton HFCC's as follows:

	a_1	a_8	a_9	a_{10}
pyracene negative ion	7.72	1.86		
pyracene positive ion	13.50	1.92		
acenaphthene negative ion	8.29	2.01	1.89	4.77
acenaphthene positive ion	16.34	2.70	1.41	5.42

In calculating the a_1 values these authors considered only $\phi_1(p)$ and $\phi_2(p)$, so their a_1 values correspond to the a_H' values in table 7.4.

These authors appear to have an error in their calculations, arising from an incorrect value of the overlap S_{12} , taken from work by Muller [33]. Muller gives $S_{12} = 0.491$ or 0.512 for angle H_uCH_1 and $R_{C-H} = 105^\circ$, $1.09 \text{ \AA}$ and 120° , $1.14 \text{ \AA}$. From appendix V, the correct values for these parameters are 0.623 and 0.632 respectively. The value of S_{12} for $109^\circ 28'$ and $1.08 \text{ \AA}$ is 0.6399 , according to table AV.4 in appendix V; Coulson and Crawford [31] give the value 0.64 . It appears that Muller could have neglected the internal overlap $S = \langle 1s_u | 1s_1 \rangle$ in calculating S_{12} , since allowance for this increases the value of S_{12} .

Colpa's calculations were repeated here, using their parameter values ($S_{12} = 0.5$). The values obtained, in their notation, are:

	a_1	a_8	a_9	a_{10}
pyracene negative ion	5.73	1.76		
pyracene positive ion	17.77	1.70		
acenaphthene negative ion	5.98	1.91	1.78	4.82
acenaphthene positive ion	21.86	2.34	1.28	4.54

Colpa and de Boer calculated the aromatic proton HFCC's in a different way from that used here: they used a formula developed by Colpa and Bolton [11] in a discussion of the different a_H values for positive and negative ions of the same aromatic molecule. As mentioned in section 6.2, there is an error in sign in this formula. The a_1 values obtained above using Colpa's parameters are not the same as those given by Colpa. However, Colpa did not report the parameter values assumed for the angle H_uCH_1 and the distance C-H within a CH_2 group, and this could account for the differences. The calculated aromatic proton HFCC's for the acenaphthene negative ion, either as reported by Colpa and de Boer, or as calculated here with their parameters, are not in the same order as the experimental values. Furthermore, the calculations with Colpa's parameters predict that the positive ion of pyracene has a larger aromatic proton HFCC than the negative ion, which is contrary to the experimental results. Colpa and de Boer thought that this was possibly due to an inductive effect, but apparently it was due to an error in the value for the overlap S_{12} . Consideration of the inductive effect in section 7.15 shows that varying the coulomb parameters δ_1 and δ_2 , from δ_1 at -0.5 to -0.9 or to +0.3 does not affect the order $a_8 < a_9 < a_{10}$.

Before discussing further the calculated proton HFCC's, several assumptions involved in the calculation of the π MO's are considered. These are the values chosen for the coulomb integrals, and for the constant k , and the use of the assumed bond lengths and angles.

7.15 Variation of the Coulomb Integrals

The choice of coulomb parameters for π_H and the adjacent carbon $2p_\pi$, in section 7.6, was somewhat arbitrary.

Calculations were therefore performed in which the parameters δ_1 and δ_2 , defined in section 7.6, were varied over a wide range: for $\delta_1 = -0.9$ to $+0.5$, with δ_2 at -0.1 , and for $\delta_2 = -0.2$ to $+0.2$, with δ_1 at -0.5 . Method (4) was used, although similar results are found for method (2), and the effects on the C'-CH₂ and aromatic proton HFCC's, as well as on the binding energy and charge densities, calculated. Table 7.6 and figures 7.4, 7.5 give the calculated C'-CH₂ proton HFCC's, table 7.7 the aromatic proton HFCC's, and table 7.8 the binding energy and charge densities.

Table 7.6 Calculated C'-CH₂ Proton HFCC's for Pyracene
Positive and Negative Ions, as δ_1, δ_2 Vary

δ_1	δ_2	positive ion		negative ion	
		a_H	a'_H	a_H	a'_H
-0.9	-0.1	12.77	23.42	4.04	9.62
-0.7	-0.1	11.68	21.78	3.75	9.07
-0.5	-0.1	10.58	20.17	3.46	8.52
-0.3	-0.1	9.47	18.45	3.17	7.96
-0.1	-0.1	8.38	16.81	2.89	7.40
.1	-0.1	7.32	15.15	2.61	6.86
.3	-0.1	6.32	13.55	2.34	6.31
.5	-0.1	5.37	12.00	2.07	5.77
-0.5	-0.2	11.28	21.12	3.59	8.73
-0.5	-0.1	10.58	20.17	3.46	8.52
-0.5	0	9.90	19.22	3.33	8.31
-0.5	.1	9.22	18.25	3.20	8.10
-0.5	.2	8.58	17.31	3.08	7.89
-0.9	-0.2	13.67	24.63	4.21	9.92

Table 7.7 Calculated Aromatic Proton HFCC's for Pyracene

Positive and Negative Ions, as δ_1, δ_2 Vary

a_H (gauss)							
δ_1	δ_2	positive ion	negative ion	δ_1	δ_2	positive ion	negative ion
-.9	-.1	2.03	1.52	-.5	-.2	2.05	1.56
-.7	-.1	2.05	1.54	-.5	-.1	2.07	1.57
-.5	-.1	2.07	1.57	-.5	0	2.09	1.57
-.3	-.1	2.08	1.59	-.5	.1	2.10	1.58
-.1	-.1	2.10	1.62	-.5	.2	2.12	1.59
.1	-.1	2.11	1.64				
.3	-.1	2.11	1.66	-.9	-.2	2.01	1.51
.5	-.1	2.12	1.69				

Table 7.8 Calculated π Electron Binding Energy, and

Atomic Charge Densities for Pyracene, as

δ_1, δ_2 Vary							
δ_1	δ_2	binding energy	atomic charge densities at atom				
			1	2	5	8	CH_2
-.9	-.1	22.560	.8771	1.0620	.9855	1.0761	1.9391
-.5	-.1	21.798	.9322	1.0168	.9835	1.0692	1.9490
-.1	-.1	21.151	.9930	.9658	.9821	1.0622	1.9588
+.3	-.1	20.639	1.0596	.9086	.9813	1.0552	1.9682
+.5	-.1	20.438	1.0950	.8776	.9812	1.0516	1.9726
-.5	-.2	21.936	.9452	1.0024	.9842	1.0699	1.9476
-.5	-.0	21.668	.9189	1.0316	.9827	1.0686	1.9505
-.5	+.2	21.433	.8912	1.0621	.9813	1.0673	1.9533
-.9	-.2	22.672	.8895	1.0475	.9865	1.0770	1.9370

Figure 7.4

a_H VALUES FOR PYRACENE POSITIVE &
NEGATIVE IONS AS THE COULOMB
PARAMETERS VARY

Figure 7.5

a'_H VALUES FOR PYRACENE POSITIVE &
NEGATIVE IONS AS THE COULOMB
PARAMETERS VARY

Table 7.6 and figures 7.4, 7.5 indicate large variations in the C'-CH₂ proton HFCC's as δ_1 or δ_2 are varied; the HFCC's are seen to have about the same dependence on δ_2 as on δ_1 . However, table 7.7 indicates considerably less change for the aromatic proton HFCC's as δ_1 or δ_2 vary. There is relatively little change in the binding energy, shown in table 7.8, although the binding energy favours the more negative values of both δ_1 and δ_2 . The atomic charge densities for the AO's 1 and 2 do change significantly, although the charge densities at the aromatic atoms are only slightly affected. Note, however, that the total electron density associated with the CH₂ groups does not vary to a great extent.

Figure 7.4 shows that for the calculated a_H values, coulomb parameters of about -0.9 for δ_1 and -0.2 for δ_2 give the best fit to the experimental data. However, when considering the calculated a'_H values, coulomb parameters of about +0.3 for δ_1 and -0.1 for δ_2 provide the best fit to the experimental data, and give a better than that from the a_H values with their optimum choice of δ values. Now tables 7.7 and 7.8 show that both the calculated aromatic proton HFCC's and the binding energy favour the choice of -0.9 for δ_1 and -0.2 for δ_2 . Calculations were also performed for acenaphthene with these sets of parameters, giving the results shown in table 7.9.

Table 7.9 Acenaphthene Negative Ion Coupling Constants

δ_1	δ_2	C'-CH ₂ protons		aromatic protons		
		a_H	a'_H	a_8	a_9	a_{10}
- .9	- .1	4.76	11.19	1.08	2.44	4.50
+ .3	- .1	2.58	6.94	1.37	2.28	4.68
experiment		7.53		1.04	2.42	4.17

The variation of δ_1 has a comparatively small effect on the aromatic proton HFCC's, but definitely favours the choice of -0.9 for δ_1 . Once again, the a'_H value for the C'-CH₂ protons, with $\delta_1 = +0.3$ is in better agreement with experiment than the a_H value with $\delta_1 = -0.9$.

Calculations were also performed with method (5), in which the coulomb parameters for the AO's 1 and 2 were varied over a wide range. For AO 1, this corresponds to changing the coulomb integral for the hydrogen 1s AO; the resulting value for the coulomb integral for AO 1 is given by the formula in section 7.8. The binding energy, and proton HFCC's, for pyracene are given in table 7.10.

Table 7.10 Effect of Variation of Coulomb Integrals in method (5), for Pyracene π Electrons

α_H	α_2	binding energy	aromatic a_H		C'-CH ₂ protons			
			+ve	-ve	+ve ion		-ve ion	
					a_H	a'_H	a_H	a'_H
-13.0	-11.4	37.158	2.14	1.53	9.49	18.84	3.36	8.63
-13.6	-11.4	37.085	2.18	1.55	7.90	16.43	2.97	7.91
-14.0	-11.4	37.074	2.20	1.56	7.00	15.03	2.73	7.47
-14.6	-11.4	37.110	2.23	1.58	5.83	13.18	2.42	6.90
-14.8	-11.4	37.135	2.23	1.58	5.49	12.63	2.32	6.71
-13.6	-11.1	36.672	2.15	1.54	8.90	17.95	3.14	8.21
-13.6	-11.7	37.522	2.21	1.55	7.05	15.14	2.81	7.62

Calculations were also performed for the π electrons of acenaphthene, with method (5), for this same range of coulomb integrals, since the three aromatic proton HFCC's for the negative ion of acenaphthene provide a convenient check for the calculations with a given set of parameters. The results are given in table 7.11.

Table 7.11 Effect of Variation of Coulomb Integrals in
Method (5), for Acenaphthene π Electrons

α_H	α_2	binding energy	negative ion aromatic protons			C'-CH ₂ protons: a_H'	
			a_8	a_9	a_{10}	+ve ion	-ve ion
-13.0	-11.4	28.573	1.07	2.48	4.52	22.87	9.93
-13.6	-11.4	28.532	1.10	2.46	4.56	19.18	9.00
-14.0	-11.4	28.524	1.12	2.46	4.58	17.14	8.47
-14.6	-11.4	28.539	1.14	2.44	4.60	15.27	7.73
-14.8	-11.4	28.551	1.15	2.44	4.60	13.91	7.51
-13.6	-11.1	28.327	1.09	2.47	4.54	21.52	9.41
-13.6	-11.7	28.749	1.11	2.46	4.57	17.25	8.64

The first interesting feature to be noted from tables 7.10 and 7.11 is that the binding energy for both pyracene and acenaphthene passes through a minimum at about -13.9 e.v. for α_H . No analagous turning point was found earlier for method (4), when the coulomb parameters were varied.

The aromatic proton HFCC's and the C'-CH₂ a_H' values appear to favour the less negative values of α_H and α_2 , but the binding energies and C'-CH₂ proton HFCC's a_H favour the more negative values, in particular, $\alpha_H = -14.8$ e.v. With $\alpha_H = -14.8$ e.v., the calculated a_H values for the C'-CH₂ protons in pyracene positive ion, pyracene negative ion, and acenaphthene negative ion, are 12.63, 6.71 and 7.51, to be compared with the experimental values of 12.80, 6.58 and 7.53. The agreement between these calculated a_H' values with this set of parameters, and the experimental values, is excellent, and is better than the set of values obtained under optimum conditions with method (4).

Variation of the coulomb parameters for methods (4) and

(5) has shown that a considerably improved fit of the a'_H values to the experimental $C'-CH_2$ protons HFCC's can be obtained, by appropriate choice of coulomb parameters. The agreement between the calculated $C'-CH_2$ a'_H values and the experimental HFCC's can also be improved in the same manner, although even with optimum choice of coulomb parameters, this does not give as satisfactory a fit as the a'_H values.

According to method (4), the binding energy, the aromatic proton HFCC's and the $C'-CH_2$ a'_H values do not all favour the same set of parameters, but for method (5), both the binding energy and the $C'-CH_2$ a'_H values favour the choice of $\alpha_H = -14.8$ e.v. The values so calculated are in excellent agreement with the experimental HFCC's.

In section 7.19, an attempt is made to justify a particular choice of coulomb parameters.

7.16 Variation of the Constant k, for Method (5)

The constant k, in $\beta_{ij} = k \frac{1}{2}(\alpha_i + \alpha_j) S_{ij}$ was taken as 1.65, 1.75, and 1.85, and the effect on the proton HFCC's calculated, as well as on the atomic charge densities. The option $\beta_{ij} = -k [\alpha_i \alpha_j]^{\frac{1}{2}} S_{ij}$ was also considered, with k taken as 1.75, 1.80, 2.0. The notation $k = -1.75$, etc, is used to denote this second option. The π electron energy levels for $k = 1.75, 1.65, 1.85, -1.80$ are given in figure 7.2. The binding energy is found to depend approximately linearly on k. The calculated proton HFCC's, and atomic charge densities, are given in table 7.12.

Table 7.12 Effect of Variation of the Constant k,
in Method (5), for Pyracene π Electrons

k		1.65	1.75	1.85	-1.75	-2.00
atomic charge densities at atom:	1	.907	.888	.874	.887	.856
	2	1.046	1.062	1.073	1.062	1.087
	5	.975	.976	.977	.976	.978
	6	.999	.999	1.000	.999	1.004
	8	1.073	1.075	1.076	1.075	1.078
aromatic	+ve	2.19	2.18	2.17	2.18	2.15
proton HFCC's	-ve	1.56	1.55	1.54	1.55	1.52
C'-CH ₂ protons	a' _H	15.28	16.43	17.37	16.69	18.73
positive ion	a _H	7.16	7.90	8.51	8.07	9.40
C'-CH ₂ protons	a' _H	7.53	7.91	8.20	7.98	8.63
negative ion	a _H	2.77	2.97	3.12	3.01	3.14

Table 7.12 shows that the aromatic atom charge densities are virtually independent of k, and are independent of the option used to construct the resonance integrals. The charge densities at the π AO's in the CH₂ groups depend to some extent on the value of k, although the total CH₂ group π electron density is virtually independent of k.

The aromatic proton HFCC's are virtually independent of k, although the C'-CH₂ proton HFCC's are dependent on k to a small degree. The two methods

$$\beta_{ij} = 1.75 \frac{1}{2}(\alpha_i + \alpha_j) S_{ij}$$

and

$$\beta_{ij} = -1.75 [\alpha_i \cdot \alpha_j]^{\frac{1}{2}} S_{ij}$$

are seen to give almost identical results.

7.17 Use of X-ray Bond Lengths and Angles

An x-ray study of pyracene [30] gives the following bond lengths and angles for the carbon framework:

There are some significant variations from the bond lengths assumed in section 7.5, particularly bonds 2,3 8,9 and 6,11. Calculations were performed with these x-ray values for the carbon framework, and the values assumed in section 7.5 for the carbon hydrogen distances and angles. A prefix XR indicates that this x-ray data has been employed. The energy levels and

π MO coefficients for method XR(5) are given in appendix VIII. The energy levels for method XR(4) are given in figure 7.1. Table 7.13 gives the binding energies, and proton HFCC's calculated from methods XR(2), XR(4) and XR(5).

Table 7.13 Use of X-ray Parameters for Pyracene

method:		XR(2)	XR(4)	XR(5)
binding energy		34.601	21.933	37.419
aromatic proton	+ve	2.28	2.24	2.36
HFCC's a_H	-ve	1.69	1.69	1.67
C'-CH ₂ protons	a_H^+	20.00	19.39	15.52
positive ion	a_H	10.48	11.11	8.24
C'-CH ₂ protons	a_H^+	6.10	7.58	7.02
negative ion	a_H	2.42	3.61	3.14

The above values in table 7.13 should be compared with those given in tables 7.1, 7.3 and 7.4. This shows that the use of the x-ray parameters for the carbon framework makes little difference to the π electron binding energy, the π MO coefficients, the individual one-electron energy levels, or the C'-CH₂ proton HFCC's, although it does cause small changes in the aromatic protons HFCC's.

However, in all three cases, the binding energy is increased by using the x-ray data, and for methods XR(4) and XR(5), there is a slight improvement in the fit of both the C'-CH₂ a'_H and a_H values to the experimental data, in that the a'_H values are slightly decreased, and the a_H values slightly increased.

The use of the assumed bond lengths and angles in the earlier calculations therefore appears reasonable.

7.18 Variation of the Parameters for the CH₂ Groups

The remaining variables to be considered for the π electron calculations are the carbon-hydrogen distance, and the angle H_uCH_1 , in the CH₂ groups. Calculations were performed, using method (5), for a C-H distance of 1.08 Å, and for the angle H_uCH_1 taking the values 105°, 109°28' and 120°, and with the angle H_uCH_1 at 109°28', with the C-H distance as 1.08, 1.10, 1.13 Å.

The x-ray parameters were used for the carbon framework, and the values chosen in section 7.8 for the coulomb integrals. Method (5) was used, since this is the only one of the five methods which offers a systematic means of allowing for the effect of the variation of angle H_uCH_1 , and distance C-H, on the coulomb integrals for the AO's π_H . Table 7.14 gives the calculated binding energies, and HFCC's.

Table 7.14 Variation of CH₂ Group Parameters for Pyracene

Angle H _u CH _l	105°	109°28'	120°	109°28'	
distance C-H (Å)	1.08	1.08	1.08	1.10	1.13
binding energy	36.484	37.419	39.402	37.497	37.585
aromatic proton +ve	2.34	2.36	2.40	2.36	2.35
HFCC's a _H -ve	1.67	1.67	1.68	1.54	1.68
C'-CH ₂ protons a' _H	15.97	15.52	15.10	15.34	15.06
positive ion a _H	8.83	8.24	7.20	8.14	7.99
C'-CH ₂ protons a' _H	7.05	7.02	7.19	6.94	6.83
negative ion a _H	3.31	3.14	2.82	3.12	3.10

The values in table 7.14 should be compared with those in tables 7.1, 7.3, 7.4 and 7.13. The values of both the aromatic and C'-CH₂ proton HFCC's are remarkably independent of the angle H_uCH_l or the C-H distance. The calculated π electron binding energy appears to favour configurations with the CH₂ protons further apart than their separation at the usual carbon-hydrogen distance of 1.08 Å and at the tetrahedral angle.

7.19 Self-Consistent Field Approach

In this section, a form of self-consistent field MO (SCF-MO) theory, applicable to organic molecules such as pyracene, is developed. This is basically a refinement of the extended Hückel method, discussed in section 7.8. In the SCF modification of this method, a systematic way is found for allowing for the variation of the coulomb and Slater parameters with the atomic charge density, for each

atom in the molecule.

A cyclic procedure is used: the standard extended Hückel method (5) is used to determine the amount of electron density associated with each of the s and p type AO's in the basis set, for the neutral molecule. These initially calculated atomic charge densities are used to modify the coulomb integrals α_s and α_p , and the Slater exponents μ_s and μ_p for each atom in the molecule. The overlap matrix is then computed with this new set of parameters, using the computer program given in appendix VII, and the secular equation set up and solved. The MO's are then determined using the computer program for Hückel calculations, given in appendix VI. A new set of charge densities is calculated from this set of MO's, and then used to modify the coulomb and Slater parameters for each atom. This process is continued until the computed charge densities at the end of a given cycle are sufficiently close to the input charge densities, for that cycle. At this stage, self-consistency has been achieved.

The resulting SCF MO's can then be used to calculate the atomic charge densities for the positive and negative ions, in turn, and the process can be repeated for each of these in turn. In this manner, a self-consistent set of MO's is obtained for the positive ion, and a different set for the negative ion.

A similar allowance for the variation of the coulomb integrals with charge density and atomic configuration has recently been considered by Gray [43], in MO calculations for the permanganate ion. However, the method developed in this thesis appears to be the first attempt to allow for a systematic variation of the calculated overlap integrals with atomic charge density throughout the molecule. The method is practicable only with a computer program such as

that given in appendix VII.

Modification of the Slater parameters

The overlap integral is a function of the Slater exponents for the corresponding AO's, as discussed in appendix V. According to Slater's rules [29], the value of μ is given by Z^*/n , where Z^* is the effective nuclear charge. This can be simply related to the computed atomic charge densities.

A carbon atom in a molecule is initially assigned $Z^* = 3.25$, in accordance with Slater's rules, and is assumed electrically neutral, with a total electron density of 4.0 in the AO's with principal quantum number 2. If d_0 is the total electron density associated with this particular atom in the molecule, as determined from the initial MO calculation, then the value of Z^* for the second cycle is

$$Z_1^* = 3.25 + (4.0 - d_0) .$$

If d_1 is the charge density computed in the second cycle, using the above value of Z_1^* , then

$$Z_2^* = Z_1^* + (d_0 - d_1)$$

and so on.

For the hydrogen atoms, there is only one basis AO, and in this case,

$$Z_1^* = 1.0 + (1.0 - d_0),$$

$$Z_2^* = Z_1^* + (d_0 - d_1), \text{ and so on.}$$

Modification of the coulomb parameters

The coulomb integrals for the extended Hückel calculations are taken as the negative of the corresponding valence state ionisation energy (VSIE). VSIE's cannot be defined unambiguously, and several alternative methods of evaluating them from the experimental data have been used [43, 44].

For a neutral carbon atom, an average energy W is calculated from emission spectral data, for each configuration such as $2s2p^3$ or $2s^22p^2$. The average is taken over all spectroscopic terms, considering the J components of the terms separately, with each term weighted by the appropriate degeneracy. Similarly an average energy is calculated for each configuration such as $2s2p^2$ or $2s^22p$, of the positive ion C^+ . The ionisation potential for carbon relates the energy zeros of the two spectroscopic systems C and C^+ , and hence the appropriate VSIE under consideration can be evaluated. Two examples are given below. The VSIE's are evaluated for first the p electrons, and then the s electrons, for configurations sp^3 and s^2p^2 .

Similarly, the VSIE's of the s and p electrons for C^+ , $2s2p^2$, and $2s^22p$, are calculated. An experimental value for the electron affinity of carbon can be used to deduce values of the VSIE's for the negative ion, C^- , s^2p^3 .

From this data, graphs of the s and p VSIE's for both the configurations sp^n and s^2p^{n-1} can be constructed, as a function of the charge on the carbon atom. These graphs are then used to evaluate the s and p coulomb integrals, for a given configuration and charge density.

Calculated VSIE's

All experimental data employed, except for the electron affinity of carbon [45], are from Moore's tables [32].

For $C(2s^22p^2)$, the spectroscopic terms are 3P_2 , 3P_1 , 3P_0 , 1S_0 , 1D_2 . Hence the average energy for the configuration is

$$W(C\ 2s^22p^2) = \frac{1}{15} [5^3P_2 + 3^3P_1 + ^3P_0 + ^1S_0 + 5^1D_2]$$

$$= 4,858.9\ \text{cm}^{-1}.$$

For $C^+(2s^2 2p)$, the spectroscopic terms are $^2P_{3/2}$ and $^2P_{1/2}$, and

$$W(C^+ 2s^2 2p) = \frac{1}{6} [4 \ ^2P_{3/2} + 2 \ ^2P_{1/2}] = 42.7 \text{ cm}^{-1}.$$

The ionisation potential of carbon is $90,878.3 \text{ cm}^{-1}$.

Hence the p electron VSIE for $C(2s^2 2p^2)$ is

$$\begin{aligned} 90,878.3 + 42.7 - 4,858.9 &= 86,062.1 \text{ cm}^{-1} \\ &= 10.667 \text{ e.v.} \end{aligned}$$

For $C^+(2s 2p^2)$, the spectroscopic terms are 2S , 4P , 2P , 2D , so

$$\begin{aligned} W(C^+ 2s 2p^2) &= \frac{1}{28} [2 \ ^2S + 6 \ ^4P_{5/2} + 4 \ ^4P_{3/2} + 2 \ ^4P_{1/2} + 4 \ ^2P_{3/2} \\ &\quad + 2 \ ^2P_{1/2} + 6 \ ^2D_{5/2} + 4 \ ^2D_{3/2}] \\ &= 75,807.6 \text{ cm}^{-1}. \end{aligned}$$

$$\begin{aligned} \text{For } C^{2+}(2p^2), \quad W(C^{2+} 2p^2) &= \frac{1}{15} [5 \ ^3P_2 + 3 \ ^3P_1 + 3 \ ^3P_0 + 1 \ ^1S_0 + 5 \ ^1D_2] \\ &= 143,315.5 \text{ cm}^{-1}. \end{aligned}$$

The ionisation potential of C^+ is $196,666.3 \text{ cm}^{-1}$. Hence the s electron VSIE for $C^+(2s 2p^2)$ is

$$\begin{aligned} 196,666.3 + 143,315.5 - 75,807.6 &= 264,174.2 \text{ cm}^{-1} \\ &= 32.743 \text{ e.v.} \end{aligned}$$

The s and p type VSIE's for the configurations sp^n , $s^2 p^{n-1}$ and C^- , C , C^+ , are given in table 7.15.

Table 7.15 Calculated VSIE's for Carbon (in e.v.)

	configuration	C^-	C	C^+
s VSIE's	sp^n	-	21.586	32.743
	$s^2 p^{n-1}$	9.918	20.058	32.410
p VSIE's	sp^n	-	11.862	23.019
	$s^2 p^{n-1}$	1.723	10.667	24.371

Modified coulomb parameters

The charge densities for a particular cycle give an electron density $s^x p^y$ for each carbon atom in the molecule, where x and y are, in general, non-integral. The total electron density with principal quantum number 2, at that atom, is $x + y = d$, say. The configuration $s^x p^y$ is represented by the linear combination

$$a sp^{d-1} + b s^2 p^{d-2}$$

in order to recompute the coulomb parameters. Clearly

$$a + 2b = x$$

$$a(d-1) + b(d-2) = y$$

giving $a = 2-x$, $b = x-1$.

The modified VSIE's for the s and p type electrons are then given by the same linear combination of the appropriate VSIE's for the configurations sp^{d-1} , $s^2 p^{d-2}$, with the values appropriate for the charge density at that atom. Thus,

$$-\alpha_s = a \text{ VSIE}[s, sp^{d-1}, d] + b \text{ VSIE}[s, s^2 p^{d-2}, d]$$

$$-\alpha_p = a \text{ VSIE}[p, sp^{d-1}, d] + b \text{ VSIE}[p, s^2 p^{d-2}, d]$$

where $\text{VSIE}[s, sp^{d-1}, d]$ is the VSIE for an s electron, in the configuration sp^{d-1} , for the atomic charge density d . This is obtained graphically from the data given in table 7.15.

For hydrogen, no such analysis is possible, since hydrogen has only one electron. A linear relation between the hydrogen $1s$ VSIE and the atomic charge density is assumed, with a proportionality constant of 4 e.v. per electronic charge. Higher values of this constant appear to lead to divergence of the cyclic process, according to Lohr [46].

Results

Sufficient time was not available to perform all the necessary calculations for this section, but a preliminary study of pyracene was done, to obtain some estimate of the total electron density at the various atoms in the molecule, for the neutral case, and the positive and negative ions. This enables a deduction of the way in which the coulomb parameters should have been varied, systematically, in section 7.15. The computed charge densities, from the first cycle, are given in table 7.16

Table 7.16 Charge Densities for all the 2s, and 2p
Type AO's of Carbon, and 1s AO's of all the
Hydrogens, for Pyracene

atom	positive ion	neutral molecule	negative ion
CA	3.859	3.984	4.338
CB	4.050	4.127	4.238
CE	3.941	3.941	3.941
CK	4.111	4.134	4.146
HA	.941	.941	.941
HE	.893	.910	.927

According to the above discussions, the 1s coulomb integral for the pseudo AO's π_H (ie. for the C'-CH₂ 1s AO's)

should be significantly more negative than the value chosen initially, and the coulomb integral of the adjacent carbon $2p_{\pi}$ AO should also be slightly more negative than the value chosen originally. Furthermore, the value of the coulomb integral α_{π_H} should be more negative for the positive ion than for the negative ion. Thus, it would be permissible, in section 7.15, to use somewhat different sets of coulomb parameters to account for the experimental data for the positive and negative ions. This analysis has shown that the choice of larger numerical values for the coulomb integrals for π_H and for the adjacent carbon $2p_{\pi}$ AO appears reasonable.

The values given in the tables in section 7.15 are therefore seen to favour the calculated a'_H C'-CH₂ proton HFCC's, rather than the a_H values. This suggests that Slater AO's overestimate the amplitude of AO's at large distances, although other evidence, discussed in section 7.7, seemed to point to the opposite conclusion.

7.20 Conclusion

MO calculations in this chapter have shown that hyperconjugation leads to significantly greater values of the C'-CH₂ proton HFCC's in the pyracene and acenaphthene positive and negative ions, than does the spin polarisation mechanism considered in chapter 3.

Five different methods of calculating the π MO's have been considered; three of the methods accounted satisfactorily for the experimental data, provided suitable values were chosen for certain parameters in the calculations. A systematic method was later discussed for logically choosing the values of these parameters. However, the

π MO's calculated from two forms of Hückel theory considering only nearest neighbour interactions could not account satisfactorily for the experimental data. ESR data has been shown to be a convenient way of comparing different methods of calculating MO's for large molecules.

Hyperconjugation in three molecules containing C'-C-CH₂ fragments is now considered.

8.1 Introduction

Calculations in the preceding chapter have shown that hyperconjugation leads to significantly greater spin densities at C'-CH₂ protons than does spin polarisation in the σ bonds arising from spin density at C'. In chapter 4, spin polarisation in the σ bonds of a fragment C'-C-CH₂ was shown to give rise to only very small values for the terminal proton HFCC's, of about $+0.05 \rho$ gauss, where ρ is the spin density at C'.

In this chapter, hyperconjugation is considered in three molecules containing a fragment C'-C-CH₂. The molecules are perinaphthane [1,8-trimethylenenaphthalene], 3,4-aceperinaphthane, and pleiadane, all of which are shown in figure 8.1. Another molecule of the same type is 3,4,5,8,9,10-hexahydropyrene, which is also shown in figure 8.1. Since these molecules contain both C'-CH₂ and C'-C-CH₂ protons, a comparison of the values of the proton HFCC's for these two types of protons is possible. The molecule pleiadane is considered, as well as the other two, because of a subtle difference in the symmetry properties of this molecule compared with the other two. For perinaphthane and aceperinaphthane, group theory allows for the possibility of the coefficients of the AO's for atoms HI, HJ [see figure 8.1] being zero, in the MO's containing the unpaired electrons for the positive and negative ions. In pleiadane, however, the corresponding atoms HI, HJ do not lie in the reflection plane passing through atoms CE, CJ, and perpendicular to the aromatic plane. Consequently

Figure 8.1 LABELLING OF ATOMS

PERINAPHTHANE

HYDROPYRENE

ACEPERINAPHTHANE

PLEIADANE

there is no group theoretical reason for supposing the coefficients of the AO's associated with these atoms to be zero in any particular MO.

The six and seven membered non-aromatic rings in these molecules would not be expected to be planar. Consequently hydrogen atoms such as those bonded to carbon atom C1 are both on the same side of the aromatic plane, and the linear combination ($1s_u - 1s_1$) of the $1s$ AO's associated with these hydrogens does not have π -type symmetry with respect to the plane of the aromatic rings.

All three molecules studied in this chapter have C_s type symmetry. In all three cases there is no group theoretical factorisation of σ and π type electrons, so that the π electrons cannot be considered separately, as was possible for pyracene and acenaphthene, in the previous chapter. Instead, the MO calculations must be performed by including in the basis set all of the high energy AO's. The extended Hückel method, discussed in section 7.8 of the previous chapter, is used.

The secular equations are of order 64 for perinaphthane, 74 for ace-perinaphthane, and 70 for pleiadane. Group theory is used to reduce the order of these matrices, as explained in section 7.8; the largest matrix to be handled is then of order 41.

The calculations were performed with a modification of the overlap program, given in appendix VII. With this, sets of symmetry adapted linear combinations of the basis AO's are given, and the computer calculates the overlap matrix for each irreducible representation set, when supplied with the atomic coordinates. The program is arranged so that the matrix elements $S_{ij} = \langle \phi_i | \phi_j \rangle$ between the basis AO's are computed as required. Consequently, at

no stage is it necessary to compute or store the complete matrix, of order equal to the number of high energy AO's being considered in the molecule. In this manner, the method can be employed to perform MO calculations for giant molecules, with several hundred atoms, provided the molecule has reasonably high symmetry.

8.2 The Model

All aromatic carbon-carbon, aliphatic carbon-carbon, and carbon-hydrogen bond lengths are taken as 1.39, 1.54 and 1.08 Å, respectively. Tetrahedral angles ($109^{\circ}28'$) are assumed in the non-aromatic rings. The values given in section 7.8 are used for the Slater and coulomb parameters, and the constant k is taken as 1.75. The atoms are labelled in figure 8.1. The basis AO's are numbered so that all of the AO's for CA are given first, in the order $2s$, $2p_x$, $2p_y$, $2p_z$, then all of the AO's for CB, and so on. When all of the carbon AO's have been given, the hydrogen $1s$ AO's are listed. The z axis is chosen to be perpendicular to the aromatic plane, for purposes of comparison with the calculations for pyracene and acenaphthene, in the previous chapter. The atomic coordinates, required as input for the overlap program, are calculated from straightforward, but tedious, trigonometry.

The proton HFCC's for the positive and negative ions are evaluated for each of the four-non-equivalent types of hydrogens in the non-planar aliphatic rings. Slater AO's are used to calculate the amplitudes of the basis AO's at the coordinates of these protons. The proton HFCC's are then calculated as shown in section 7.7. Since it was found in the previous chapter that the most satisfactory agreement between the calculated and theoretical $C'-CH_2$

proton HFCC's was obtained by considering only those contributions to the HFCC from the hydrogen and carbon AO's associated with that particular CH_2 group, the values referred to as a'_H values in section 7.7 are used here. Because of the symmetry of the molecules studied here, the MO's containing the unpaired electrons in the positive and negative ions have components from the carbon 2s, $2p_x$ and $2p_y$ AO's of the carbon atom of the particular CH_2 group, as well as from the $2p_z$ AO for that carbon. Values are also calculated for the aromatic proton HFCC's, as shown in section 7.7.

8.3 Results

Table 8.1 gives the calculated binding energies, and atomic charge densities, for the neutral molecules. Table 8.2 gives the calculated proton HFCC's for the positive and negative ions. No experimental data is available at present on the ESR spectra of any of these molecules.

Table 8.1 Binding Energies and Atomic Charge Densities

molecule:	perinaphthane	aceperinaphthane	pleiadane
binding energy	234.492 e.v.	266.378	253.397
charge density			
at: CA	3.919	3.972	3.912
CB	4.137	4.102	4.148
CC	4.060	4.131	4.058
CD	4.126	3.974	4.137
CE	3.936	3.984	3.937
CJ	4.003	4.006	3.994
CK	4.147	4.148	4.231

CL	4.142	4.144	4.154
CN	-	4.132	-
HA	.939	.939	.939
HB	.941	.941	.942
HE	.940	.920	.940
HF	-	.910	-
HG	.920	.920	.921
HH	.910	.912	.818
HI	.932	.932	.925
HJ	.908	.908	.924

Table 8.2 Calculated Proton HFCC's for Positive Ions

	perinaphthane	aceperinaphthane	pleiadane
<u>non-aromatic</u> <u>protons:-</u>			
HG	4.37	3.12	14.25
HH	14.54	12.69	117.5
HI	0	0	8.52
HJ	0	0	0.27
HM	-	17.62	-
HN	-	17.06	-
<u>aromatic</u> <u>protons:-</u>			
HA	2.94	1.85	1.89
HB	1.29	2.50	0.32
HE	4.98	-	2.43

	<u>Negative Ions</u>		
	<u>perinaphthane</u>	<u>aceperinaphthane</u>	<u>pleiadane</u>
<u>non-aromatic</u>			
<u>protons</u>			
HG	1.14	0.97	0.02
HH	7.58	6.65	11.37
HI	0	0	0.004
HJ	0	0	1.44
HM	-	11.04	-
HN	-	11.07	-
<u>aromatic</u>			
<u>protons</u>			
HA	1.32	1.80	1.11
HB	2.32	1.41	2.44
HE	4.66	-	4.53

In all cases it is found that the MO's containing the unpaired electrons in the positive and negative ions are of A" symmetry. Consequently the coefficients of the 1s AO's of the atoms HI and HJ, for perinaphthane and aceperinaphthane, are rigorously zero, and the only non-zero AO coefficients for this C'-C-CH₂ group is for the 2p_y AO of carbon atom CL, where the y-axis points along CJ-CB. However, the amplitude of this AO at the coordinates of HI of HJ is zero. Furthermore, for any MO of A" symmetry, the contributions to the spin density at HI or HJ from atom pairs such as HG, HK or CK, CM always exactly cancel. Consequently, the proton HFCC's for the C'-C-CH₂ protons in perinaphthane and aceperinaphthane, are rigorously zero.

However, for pleiadane, the proton HFCC's for the C'-C-CH₂ protons are definitely non-zero, being as large as 8.52 gauss

for the positive ion. This is of the order of magnitude of the C'-CH₂ proton HFCC's for the pyracene and acenaphthene ions.

Table 8.2 shows that in all cases the HFCC's for a given non-aromatic proton in the positive ion is significantly larger than for the negative ion. The wide range of calculated values of the proton HFCC's in these three molecules suggests that they should make interesting experimental ESR studies.

Table 8.1 shows that the charge densities for perinaphthene and aceperinaphthene are very similar. These charge densities could be used as the basis for a SCF study of these molecules, as discussed in section 7.19. The C'-C-CH₂ and C'-CH₂ protons are seen to have charge densities significantly less than one. As explained in section 7.19, a coulomb integral of about -14.0 e.v., and a higher effective charge, would be more appropriate for these molecules.

8.4 Conclusion

Theoretical studies in this chapter, of three molecules containing C'-C-CH₂ fragments, have shown that, provided certain AO coefficients in the MO's housing the unpaired electrons are not rigorously zero, as a consequence of the symmetry of the molecule, hyperconjugation can lead to values of the C'-C-CH₂ proton HFCC's of about the same order of magnitude as for the C'-CH₂ proton HFCC's for the pyracene and acenaphthene ions.

The wide range of calculated values, and the lack of any experimental data at present, suggests that an ESR study of these radicals might yield valuable information.

Chapter 9

CONCLUSION

Two alternative theoretical mechanisms have been considered in this thesis, in interpreting experimental data on the hyperfine coupling constants of protons in fragments $C'-C_nH$ of organic molecules, for $n = 0, 1, 2$. For the $C'-H$ case, hyperconjugation does not occur, for reasons of symmetry, and in this case the spin polarisation mechanism appears to be able to account satisfactorily for the experimental data.

For the cases $C'-CH_2$ and $C'-C-CH_2$, spin polarisation was calculated to lead to only very small values of the HFCC a_H , for $C'-CH_2$, and minute values for the longer fragment.

In the second part of the thesis, molecular orbital calculations were performed to estimate the contribution of hyperconjugation to the $C'-CH_2$ and $C'-C-CH_2$ proton HFCC's. The calculated values for $C'-CH_2$ were found to be in good agreement with experiment, although a reasonably wide range of calculated values was obtained, depending on the method used to determine the MO's, and on certain assumptions made in evaluating the HFCC's from these MO's.

In the last chapter, values were predicted for the $C'-C-CH_2$ and $C'-CH_2$ proton HFCC's in three molecules containing these fragments. It appears that in certain cases, determined by the symmetry of the molecule, hyperconjugation can give rise to significant amounts of spin density even at the $C'-C-CH_2$ protons.

Appendix I THE CONSTRUCTION OF SPIN EIGENFUNCTIONS USING WIGNER COEFFICIENTS

AI.1 Introduction

Wigner coefficients provide a simple and convenient way of determining the eigenfunctions obtained by combining two angular momenta j_1 and j_2 , to give a resultant angular momentum j .

Wigner's formula is

$$|j_1 j_2 j m\rangle = \sum_{m_1, m_2} \langle j_1 j_2 m_1 m_2 | j_1 j_2 j m \rangle |j_1 j_2 m_1 m_2\rangle$$

where m_1, m_2 are the eigenvalues of the angular momenta j_1, j_2 respectively about a particular axis of quantisation, and m is the eigenvalue of j about this same axis.

$|j_1 j_2 m_1 m_2\rangle = |j_1 m_1\rangle |j_2 m_2\rangle$ is the product of the simultaneous eigenfunctions of the operators J_1^2, J_{z1} and J_2^2, J_{z2} for the two angular momenta j_1 and j_2 .

Wigner's formula then determines the simultaneous eigenfunctions of J^2 and J_z for the vector sum $j = j_1 + j_2$. The coefficients $\langle j_1 j_2 m_1 m_2 | j_1 j_2 j m \rangle$ are pure numbers, and are usually obtained from tables, such as those given by Condon and Shortley [36]; general expressions for these coefficients are available, but are extremely cumbersome. The summation in Wigner's formula is over all values of m_1, m_2 satisfying the restrictions $m_i = j_i, j_i - 1, \dots, -j_i$ and $m_1 + m_2 = m$.

To determine the simultaneous eigenfunctions of the operators S^2 and S_z for more than one electron, take $j_1 = S_1, j_2 = S_2$ where S_1 and S_2 are the resultant spins of a given number of electrons.

For example, by taking S_1 as two electrons, S_2 as three electrons:

$$\begin{aligned} S_1 &= 1, 0 & m_1 &= \pm 1, 0 \\ S_2 &= \frac{3}{2}, \frac{1}{2} & m_2 &= \frac{\pm 3}{2}, \pm \frac{1}{2} \end{aligned}$$

and by combining S_1 and S_2 according to Wigner's formula, the simultaneous eigenfunctions of S^2 and S_z for five electrons are obtained:

$$|j\ m\rangle = \sum_{m_1, m_2} \langle S_1 S_2 m_1 m_2 | S_1 S_2 j\ m\rangle |S_1 m_1\rangle |S_2 m_2\rangle$$

where $|S_1 m_1\rangle$, $|S_2 m_2\rangle$ are the simultaneous eigenfunctions of S^2 and S_z for two electrons and three electrons respectively. If these are not available, they may themselves be determined from Wigner's formula, as shown below.

The formula may thus be applied successively to obtain the eigenfunctions for 1, 2, 3, 4, 5, ... electrons. The results are tabulated below, where the symbol $|S\ M_s\rangle$ refers to the eigenvalues $S(S+1)$ of S^2 and M_s of S_z , for the total number of electrons.

AI.2 One Electron

$$|1/2\ 1/2\rangle = \alpha$$

$$|1/2\ -1/2\rangle = \beta$$

AI.3 Two Electrons

$$|0\ 0\rangle = 1/\sqrt{2}(\alpha\beta - \beta\alpha)$$

$$|1\ 1\rangle = \alpha\alpha$$

$$|1\ 0\rangle = 1/\sqrt{2}(\alpha\beta + \beta\alpha)$$

$$|1\ -1\rangle = \beta\beta$$

AI.4 Three Electrons

$$|3/2 \ 3/2\rangle = \alpha\alpha\alpha$$

$$|3/2 \ 1/2\rangle = 1/\sqrt{3}(\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha)$$

$$|3/2 \ -1/2\rangle = 1/\sqrt{3}(\beta\beta\alpha + \beta\alpha\beta + \alpha\beta\beta)$$

$$|3/2 \ -3/2\rangle = \beta\beta\beta$$

$$|1/2 \ 1/2\rangle = 1/\sqrt{2}(\alpha\beta\alpha - \beta\alpha\alpha)$$

$$|1/2 \ -1/2\rangle = 1/\sqrt{2}(\alpha\beta\beta - \beta\alpha\beta)$$

$$|1/2 \ 1/2\rangle = 1/\sqrt{6}(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)$$

$$|1/2 \ -1/2\rangle = 1/\sqrt{6}(\beta\alpha\beta + \alpha\beta\beta - 2\beta\beta\alpha)$$

Set 2

$$|1/2 \ 1/2\rangle = 1/\sqrt{2}(\alpha\alpha\beta - \alpha\beta\alpha)$$

$$|1/2 \ -1/2\rangle = 1/\sqrt{2}(\beta\alpha\beta - \beta\beta\alpha)$$

$$|1/2 \ 1/2\rangle = 1/\sqrt{6}(\alpha\alpha\beta + \alpha\beta\alpha - 2\beta\alpha\alpha)$$

$$|1/2 \ -1/2\rangle = 1/\sqrt{6}(2\alpha\beta\beta + \beta\beta\alpha + \beta\alpha\beta)$$

AI.5 Four Electrons

$$|2 \ 2\rangle = \alpha\alpha\alpha\alpha$$

$$|2 \ 1\rangle = 1/2(\alpha\alpha\alpha\beta + \alpha\alpha\beta\alpha + \alpha\beta\alpha\alpha + \beta\alpha\alpha\alpha)$$

$$|2 \ 0\rangle = 1/\sqrt{6}(\alpha\alpha\beta\beta + \beta\beta\alpha\alpha + \alpha\beta\alpha\beta + \alpha\beta\beta\alpha + \beta\alpha\alpha\beta + \beta\alpha\beta\alpha)$$

$$|2 \ -1\rangle = 1/2(\beta\beta\beta\alpha + \beta\beta\alpha\beta + \beta\alpha\beta\beta + \alpha\beta\beta\beta)$$

$$|2 \ -2\rangle = \beta\beta\beta\beta$$

$$|1 \ 1\rangle = 1/\sqrt{2}(\alpha\alpha\alpha\beta - \alpha\alpha\beta\alpha)$$

$$|1 \ 0\rangle = 1/2(\alpha\beta\alpha\beta - \alpha\beta\beta\alpha + \beta\alpha\alpha\beta - \beta\alpha\beta\alpha)$$

$$|1-1\rangle = 1/\sqrt{2}(\beta\beta\alpha\beta - \beta\beta\beta\alpha)$$

$$|1\ 1\rangle = 1/\sqrt{2}(\alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha)$$

$$|1\ 0\rangle = 1/2(\alpha\beta\alpha\beta + \alpha\beta\beta\alpha - \beta\alpha\alpha\beta - \beta\alpha\beta\alpha)$$

$$|1-1\rangle = 1/\sqrt{2}(\alpha\beta\beta\beta - \beta\alpha\beta\beta)$$

$$|1\ 1\rangle = 1/2(\alpha\alpha\alpha\beta + \alpha\alpha\beta\alpha - \alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha)$$

$$|1\ 0\rangle = 1/\sqrt{2}(\alpha\alpha\beta\beta - \beta\beta\alpha\alpha)$$

$$|1-1\rangle = 1/2(\alpha\beta\beta\beta + \beta\alpha\beta\beta - \beta\beta\beta\alpha - \beta\beta\alpha\beta)$$

$$|0\ 0\rangle = 1/2(\alpha\beta\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta + \beta\alpha\beta\alpha)$$

$$|0\ 0\rangle = 1/2\sqrt{3}(2\alpha\alpha\beta\beta + 2\beta\beta\alpha\alpha - \alpha\beta\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta - \beta\alpha\beta\alpha)$$

AI.6 Five Electrons

$$|5/2\ 5/2\rangle = \alpha\alpha\alpha\alpha\alpha$$

$$|5/2\ 3/2\rangle = 1/\sqrt{5}(\alpha\alpha\alpha\alpha\beta + \alpha\alpha\alpha\beta\alpha + \alpha\alpha\beta\alpha\alpha + \alpha\beta\alpha\alpha\alpha + \beta\alpha\alpha\alpha\alpha)$$

$$|5/2\ 1/2\rangle = 1/\sqrt{10}(\alpha\alpha\beta\beta\alpha + \alpha\alpha\beta\alpha\beta + \alpha\alpha\alpha\beta\beta + \beta\beta\alpha\alpha\alpha + \alpha\beta\alpha\alpha\beta + \alpha\beta\alpha\beta\alpha \\ + \alpha\beta\beta\alpha\alpha + \beta\alpha\alpha\alpha\beta + \beta\alpha\alpha\beta\alpha + \beta\alpha\beta\alpha\alpha)$$

$$|5/2-1/2\rangle = 1/\sqrt{10}(\beta\beta\alpha\alpha\beta + \beta\beta\alpha\beta\alpha + \beta\beta\beta\alpha\alpha + \alpha\alpha\beta\beta\beta + \beta\alpha\beta\beta\alpha + \beta\alpha\beta\alpha\beta \\ + \beta\alpha\alpha\beta\beta + \alpha\beta\beta\beta\alpha + \alpha\beta\beta\alpha\beta + \alpha\beta\alpha\beta\beta)$$

$$|5/2-3/2\rangle = 1/\sqrt{5}(\beta\beta\beta\beta\alpha + \beta\beta\beta\alpha\beta + \beta\beta\alpha\beta\beta + \beta\alpha\beta\beta\beta + \alpha\beta\beta\beta\beta)$$

$$|5/2-5/2\rangle = \beta\beta\beta\beta\beta$$

$$|3/2\ 3/2\rangle = 1/\sqrt{2}(\alpha\alpha\alpha\beta\alpha - \alpha\alpha\beta\alpha\alpha)$$

$$|3/2\ 1/2\rangle = 1/\sqrt{6}(\beta\alpha\alpha\beta\alpha + \alpha\beta\alpha\beta\alpha + \alpha\alpha\alpha\beta\beta - \beta\alpha\beta\alpha\alpha - \alpha\beta\beta\alpha\alpha - \alpha\alpha\beta\alpha\beta)$$

$$|3/2-1/2\rangle = 1/\sqrt{6}(\alpha\beta\alpha\beta\beta + \beta\alpha\alpha\beta\beta + \beta\beta\alpha\beta\alpha - \alpha\beta\beta\alpha\beta - \beta\alpha\beta\alpha\beta - \beta\beta\beta\alpha\alpha)$$

$$|3/2-3/2\rangle = 1/\sqrt{2}(\beta\beta\alpha\beta\beta - \beta\beta\beta\alpha\beta)$$

$$|3/2 \ 3/2\rangle = 1/\sqrt{6} (2\alpha\alpha\alpha\alpha\beta - \alpha\alpha\alpha\beta\alpha - \alpha\alpha\beta\alpha\alpha)$$

$$|3/2 \ 1/2\rangle = 1/3\sqrt{2} (2\beta\alpha\alpha\alpha\beta + 2\alpha\beta\alpha\alpha\beta + \alpha\alpha\beta\alpha\beta + \alpha\alpha\alpha\beta\beta - \beta\alpha\alpha\beta\alpha - \alpha\beta\alpha\beta\alpha - 2\alpha\alpha\beta\beta\alpha - \beta\alpha\beta\alpha\alpha - \alpha\beta\beta\alpha\alpha)$$

$$|3/2 - 1/2\rangle = 1/3\sqrt{2} (2\beta\beta\alpha\alpha\beta - 2\beta\alpha\beta\beta\alpha - 2\alpha\beta\beta\beta\alpha + \alpha\beta\beta\alpha\beta + \beta\alpha\beta\alpha\beta + \alpha\beta\alpha\beta\beta + \beta\alpha\alpha\beta\beta - \beta\beta\alpha\beta\alpha - \beta\beta\beta\alpha\alpha)$$

$$|3/2 - 3/2\rangle = 1/\sqrt{6} (\beta\beta\beta\alpha\beta + \beta\beta\alpha\beta\beta - 2\beta\beta\beta\beta\alpha)$$

$$|3/2 \ 3/2\rangle = 1/\sqrt{2} (\alpha\beta\alpha\alpha\alpha - \beta\alpha\alpha\alpha\alpha)$$

$$|3/2 \ 1/2\rangle = 1/\sqrt{6} (\alpha\beta\beta\alpha\alpha + \alpha\beta\alpha\beta\alpha + \alpha\beta\alpha\alpha\beta - \beta\alpha\alpha\alpha\beta - \beta\alpha\alpha\beta\alpha - \beta\alpha\beta\alpha\alpha)$$

$$|3/2 - 1/2\rangle = 1/\sqrt{6} (\alpha\beta\beta\beta\alpha + \alpha\beta\beta\alpha\beta + \alpha\beta\alpha\beta\beta - \beta\alpha\beta\beta\alpha - \beta\alpha\beta\alpha\beta - \beta\alpha\alpha\beta\beta)$$

$$|3/2 - 3/2\rangle = 1/\sqrt{2} (\alpha\beta\beta\beta\beta - \beta\alpha\beta\beta\beta)$$

$$|3/2 \ 3/2\rangle = 1/\sqrt{30} (2\alpha\alpha\alpha\alpha\beta + 2\alpha\alpha\alpha\beta\alpha + 2\alpha\alpha\beta\alpha\alpha - 3\alpha\beta\alpha\alpha\alpha - 3\beta\alpha\alpha\alpha\alpha)$$

$$|3/2 \ 1/2\rangle = 1/3\sqrt{10} (4\alpha\alpha\beta\beta\alpha + 4\alpha\alpha\beta\alpha\beta + 4\alpha\alpha\alpha\beta\beta - 6\beta\beta\alpha\alpha\alpha - \alpha\beta\alpha\alpha\beta - \alpha\beta\alpha\beta\alpha - \alpha\beta\beta\alpha\alpha - \beta\alpha\alpha\alpha\beta - \beta\alpha\alpha\beta\alpha - \beta\alpha\beta\alpha\alpha)$$

$$|3/2 - 1/2\rangle = 1/3\sqrt{10} (6\alpha\alpha\beta\beta\beta + \beta\alpha\beta\beta\alpha + \beta\alpha\beta\alpha\beta + \beta\alpha\alpha\beta\beta + \alpha\beta\beta\beta\alpha + \alpha\beta\beta\alpha\beta + \alpha\beta\alpha\beta\beta - 4\beta\beta\alpha\alpha\beta - 4\beta\beta\alpha\beta\alpha - 4\beta\beta\beta\alpha\alpha)$$

$$|3/2 - 3/2\rangle = 1/\sqrt{30} (3\beta\alpha\beta\beta\beta + 3\alpha\beta\beta\beta\beta - 2\beta\beta\beta\beta\alpha - 2\beta\beta\beta\alpha\beta - 2\beta\beta\alpha\beta\beta)$$

$$|a\rangle = |1/2 \ 1/2\rangle = 1/2\sqrt{3} (2\alpha\alpha\alpha\beta\beta - 2\alpha\alpha\beta\alpha\beta - \alpha\beta\alpha\beta\alpha + \alpha\beta\beta\alpha\alpha - \beta\alpha\alpha\beta\alpha + \beta\alpha\beta\alpha\alpha)$$

$$|1/2 - 1/2\rangle = 1/2\sqrt{3} (2\beta\beta\beta\alpha\alpha - 2\beta\beta\alpha\beta\alpha - \beta\alpha\beta\alpha\beta + \beta\alpha\alpha\beta\beta - \alpha\beta\beta\alpha\beta + \alpha\beta\alpha\beta\beta)$$

$$|b\rangle = |1/2 \ 1/2\rangle = 1/6 (2\alpha\alpha\beta\alpha\beta + 2\alpha\alpha\alpha\beta\beta - 4\alpha\alpha\beta\beta\alpha - 2\alpha\beta\alpha\alpha\beta - 2\beta\alpha\alpha\alpha\beta + \alpha\beta\alpha\beta\alpha + \alpha\beta\beta\alpha\alpha + \beta\alpha\alpha\beta\alpha + \beta\alpha\beta\alpha\alpha)$$

$$|1/2 - 1/2\rangle = 1/6 (2\beta\beta\alpha\beta\alpha + 2\beta\beta\beta\alpha\alpha - 4\beta\beta\alpha\alpha\beta - 2\beta\alpha\beta\beta\alpha + \beta\alpha\beta\alpha\beta + \beta\alpha\alpha\beta\beta - 2\alpha\beta\beta\beta\alpha + \alpha\beta\beta\alpha\beta + \alpha\beta\alpha\beta\beta)$$

$$|c\rangle = |1/2 \ 1/2\rangle = 1/2 (\alpha\beta\alpha\beta\alpha - \alpha\beta\beta\alpha\alpha - \beta\alpha\alpha\beta\alpha + \beta\alpha\beta\alpha\alpha)$$

$$|1/2 - 1/2\rangle = 1/2 (\beta\alpha\beta\alpha\beta - \beta\alpha\alpha\beta\beta - \alpha\beta\beta\alpha\beta + \alpha\beta\alpha\beta\beta)$$

$$|d\rangle = |1/2 \ 1/2\rangle = 1/2 \sqrt{3} (2\alpha\beta\alpha\alpha\beta - 2\beta\alpha\alpha\alpha\beta - \alpha\beta\alpha\beta\alpha - \alpha\beta\beta\alpha\alpha + \beta\alpha\alpha\beta\alpha + \beta\alpha\beta\alpha\alpha)$$

$$|1/2 - 1/2\rangle = 1/2 \sqrt{3} (2\beta\alpha\beta\beta\alpha - 2\alpha\beta\beta\beta\alpha - \beta\alpha\beta\alpha\beta - \beta\alpha\alpha\beta\beta + \alpha\beta\beta\alpha\beta + \alpha\beta\alpha\beta\beta)$$

$$|e\rangle = |1/2 \ 1/2\rangle = 1/3 \sqrt{2} (3\beta\beta\alpha\alpha\alpha + \alpha\alpha\beta\beta\alpha + \alpha\alpha\beta\alpha\beta + \alpha\alpha\alpha\beta\beta - \alpha\beta\alpha\alpha\beta - \alpha\beta\alpha\beta\alpha - \alpha\beta\beta\alpha\alpha - \beta\alpha\alpha\alpha\beta - \beta\alpha\alpha\beta\alpha - \beta\alpha\beta\alpha\alpha)$$

$$|1/2 - 1/2\rangle = 1/3 \sqrt{2} (3\alpha\alpha\beta\beta\beta + \beta\beta\alpha\alpha\beta + \beta\beta\alpha\beta\alpha + \beta\beta\beta\alpha\alpha - \beta\alpha\beta\beta\alpha - \beta\alpha\beta\alpha\beta - \beta\alpha\alpha\beta\beta - \alpha\beta\beta\beta\alpha - \alpha\beta\beta\alpha\beta - \alpha\beta\alpha\beta\beta)$$

Appendix II GENERAL SPIN DENSITY FORMULAE FOR USE
IN MO CALCULATIONS ON LINEAR SYSTEMS

AII.1 The General Formula

A general formula is developed for calculating the spin density at the proton in a linear fragment C_n-H , where the fragment is represented by a MO wave function obtained by mixing certain excited state configurations Ψ_i into the zero order representation Ψ_o of the ground state. This mixing must be considered when allowance is made for the electronic interaction term $H = \sum e^2/r_{ij}$. This gives a MO wave function of the form

$$\Psi = (1 + \sum \lambda_i^2)^{-1/2} (\Psi_o + \sum \lambda_i \Psi_i)$$

where, according to second order perturbation theory,

$$\lambda_i = - \frac{H_{oi}}{E_i} + \sum_{k \neq i} \frac{H_{ok} H_{ki}}{E_k E_i}$$

where H_{ik} is the matrix element $\langle \Psi_i | \sum e^2/r_{ij} | \Psi_k \rangle$ and E_i is the energy of state Ψ_i above state Ψ_o .

The general expression for the proton hyperfine coupling constant a_H is

$$a_H = \frac{8\pi}{3h} g\beta_N \beta_N Q(p)$$

where $Q(p)$ is the spin density at the coordinates of the proton. As shown in section 1.2, this is evaluated from

$$Q(p) = \frac{1}{\langle S_z \rangle} \langle \Psi | \sum_i \delta(r_i - r_H) s_{iz} | \Psi \rangle$$

where $\delta(r_i - r_H)$ is the Dirac delta function of the distance of the i 'th electron from the proton. As seen above, the wave function Ψ is usually expressed as a linear combination

of other MO wave functions; therefore it would be useful to have a general formula for $Q(p)$ in terms of the component functions of Ψ .

This problem is most satisfactorily approached through the formalism of density matrix theory [37]. Consider the general case of spin densities. The spin density is to be determined at a general position r in space, from a wave function Ψ that is given as a linear combination of other wave functions Ψ_i . One of the basic equations of density matrix theory [37] gives for the spin density function $Q(r)$, which is the density of spin angular momentum at the general point r in space,

$$Q(r) = \frac{1}{\langle \bar{S}_z \rangle} \sum' \langle \Psi | S_{kz} | \Psi \rangle_k .$$

The $\langle \Psi | S_{kz} | \Psi \rangle_k$ denotes a matrix element calculated by integrating over the spin and space coordinates of all the electrons except the space coordinates of electron k . The ' on the summation indicates that after the summation, the indices k are dropped.

An equivalent definition of the spin density function $Q(r)$ is

$$Q(r) = \frac{1}{\langle \bar{S}_z \rangle} \langle \Psi | \sum_i \delta(r_i - r) s_{iz} | \Psi \rangle$$

where $\delta(r_i - r)$ is the Dirac delta function of the distance between electron i and the general point r in space.

If the wave function Ψ representing the system is now expressed as a linear combination of other wave functions Ψ_i ,

$$\Psi = \sum_i a_i \Psi_i ,$$

the expression for $Q(r)$ may be split up into a sum of terms corresponding to the sum of the wave functions constituting Ψ :

$$\begin{aligned}
 Q(r) &= \sum_{i,j} a_i^* a_j Q_{ij}(r) \\
 &= \sum_{i,j} a_i a_j Q_{ij}(r) \quad \text{assuming the coefficients are real}
 \end{aligned}$$

where

$$Q_{ij}(r) = \left\langle \frac{1}{S_z} \right\rangle \langle \Psi_i | \sum_k \delta(r_k - r) s_{kz} | \Psi_j \rangle .$$

$\langle S_z \rangle$ is the expectation value of the total spin of the radical, and is the same for each Ψ_i , since only states with the same M_s value as Ψ_0 can be mixed into Ψ_0 .

The above expression for Ψ is now substituted into this formula, and throughout the derivation only terms up to second order are retained.

$$\Psi = \sum_i a_i \Psi_i = \left[1 - \frac{1}{2} \sum_i \frac{H_{0i}^2}{E_i} \right] \Psi_0 + \sum_i \left[-\frac{H_{0i}}{E_i} + \sum_{k \neq i} \frac{H_{0i} H_{ki}}{E_k E_i} \right] \Psi_i .$$

The $a_i a_j$ which appear in the expression for $Q(r)$ are, correct to second order:

$$\begin{aligned}
 a_0^2 &= 1 - \sum_i \frac{H_{0i}^2}{E_i} \\
 a_0 a_i &= -\frac{H_{0i}}{E_i} + \sum_{k \neq i} \frac{H_{0k} H_{ki}}{E_k E_i} \\
 a_i^2 &= \frac{H_{0i}^2}{E_i^2} \\
 a_i a_j &= \frac{H_{0i} H_{0j}}{E_i E_j} .
 \end{aligned}$$

This yields

$$Q(r) = \left[1 - \sum_i \frac{H_{0i}^2}{E_i^2} \right] Q_{00}(r) + 2 \sum_i \left[-\frac{H_{0i}}{E_i} + \sum_{k \neq i} \frac{H_{0k} H_{ki}}{E_k E_i} \right] Q_{0i}(r) \\ + \sum_i \frac{H_{0i}^2}{E_i^2} Q_{ii}(r) + 2 \sum_{i > j} \frac{H_{0i} H_{0j}}{E_i E_j} Q_{ij}(r) .$$

To calculate the spin density at the coordinates of the proton, say $Q(p)$, r is taken equal to p , and it is noted that $Q_{00}(p) = \pi^2(p) = 0$. Thus the general expression for the spin density at the coordinates of the proton is

$$Q(p) = 2 \sum_i \left[-\frac{H_{0i}}{E_i} + \sum_{k \neq i} \frac{H_{0k} H_{ki}}{E_k E_i} \right] Q_{0i}(p) + \sum_i \frac{H_{0i}^2}{E_i^2} Q_{ii}(p) \\ + 2 \sum_{i > j} \frac{H_{0j} H_{0i}}{E_j E_i} Q_{ij}(p)$$

III.2 Evaluation of Matrix Elements

To facilitate calculations, a brief discussion is given on the method of calculating the $Q_{ij}(p)$ matrix elements. These are the matrix elements of the one electron operator

$$\sum_i \delta(r_i - r_H) s_{iz} .$$

Consequently, these matrix elements must obey the general rules given by Condon and Shortley [38] for any one electron operator. To standardise the notation used in this thesis with that of Condon and Shortley, the wave functions Ψ_i are written as

$$\Psi_i = |u_1(a^1)u_2(a^2)u_3(a^3)\dots u_n(a^n)|$$

where the a^j are the individual sets of one electron quantum numbers, such as b_1^β , etc. If the operator given above is denoted by δ , then from the general results for one electron operators, the matrix elements $\langle \Psi_i | \delta | \Psi_j \rangle$ are zero if Ψ_i and Ψ_j differ in more than one of their individual sets of quantum numbers. It should be noted that permutations of the quantum numbers in Ψ_j are permitted, to bring as many as possible of the a^j for Ψ_j to be the same as those for Ψ_i .

If Ψ_i and Ψ_j differ in regard to just the k 'th individual quantum numbers, after the rearrangement, then

$$\begin{aligned} \langle \Psi_i | \delta | \Psi_j \rangle &= \pm \langle u_i(a^k) | \delta | u_i(b^k) \rangle \\ &= \pm \left(\pm \frac{1}{2} \right) [u_i(a^k) u_i(b^k)]_{\text{at } r=p} . \end{aligned}$$

Here the $\pm$ sign refers to the sign of the permutation required to reorder the one electron quantum numbers in Ψ_j , so that Ψ_i and Ψ_j differ in only one of their one electron quantum numbers. The $\pm \frac{1}{2}$ arises from the spin part of (b^k) : $+\frac{1}{2}$ arises from an α spin function for (b^k) and $-\frac{1}{2}$ for a β spin function. The "at $r=p$ " refers to the values of the wave functions $u_i(a^k)$, $u_i(b^k)$ at the space coordinates $r=p$. This arises from the "spotlighting" property of the Dirac delta function $\delta(x-x_0)$ when multiplied by a function of x and integrated over the complete range of the x variable [4].

Appendix III

EVALUATION OF ELECTROSTATIC

MATRIX ELEMENTS

In using perturbation theory to set up approximate eigenfunctions of hyperfine interaction for simple organic fragments, the matrix elements of electrostatic interaction between two states A and B, represented by wave functions Ψ_A and Ψ_B , are required. These matrix elements, written

$$\langle A | \sum_{i>j=1}^N e^2/r_{ij} | B \rangle ,$$

are readily evaluated from the general rules given by Condon and Shortley [38] for any two electron operator, such as $\sum e^2/r_{ij}$.

The wave functions are written as determinants, to satisfy Fermi-Dirac statistics. The Pauli principle is then automatically satisfied. For convenience, a shorthand notation is employed :

$$\Psi_A = | a^1 a^2 a^3 \dots a^N | \quad \text{is short for}$$

$$\Psi_A = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(a^1) & u_1(a^2) & . & . & u_1(a^N) \\ u_2(a^1) & u_2(a^2) & . & . & u_2(a^N) \\ . & . & . & . & . \\ u_N(a^1) & u_N(a^2) & . & . & u_N(a^N) \end{vmatrix}$$

which may also be written as

$$\Psi_A = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P \phi(A) .$$

In these expressions, the a^i are the individual one electron

quantum numbers. For the C_n-H fragments, they are the π^α , a_2^β , etc.

$$\begin{array}{lcl} \text{For two states A and B,} & A: & a^1 a^2 \dots a^N \\ & B: & b^1 b^2 \dots b^N \end{array}$$

the general expression for the electrostatic matrix element is

$$\langle A | \sum e^2/r_{ij} | B \rangle = \frac{1}{N!} \sum_{i>j} \sum_{P P'} (-1)^{P+P'} \prod_{k=1}^N \delta(Pa^k, P'b^k) \times$$

$$\langle Pa^i Pa^j | e^2/r_{ij} | P'b^i P'b^j \rangle$$

where the continued product of Kronecker delta functions contains a term for each index except i and j . Note that this Kronecker delta function is quite distinct from the Dirac delta function discussed in chapter 1 and in appendix II. The Kronecker delta function is defined by

$$\begin{array}{ll} \delta(i, j) = 0 & i \neq j \\ \delta(i, j) = 1 & i = j. \end{array}$$

For this matrix element to be non-zero, it is seen from the delta function terms that B can differ from A by at most two of the individual sets of one electron quantum numbers. There are therefore three cases which can give rise to non-zero electrostatic matrix elements: when A and B differ in regard to two, one and none, of the individual sets of one electron quantum numbers. These three cases are considered separately.

(i) A and B differ by two individual sets

For convenience, a permutation is taken of the quantum numbers in B to give a representation B' where $(N-2)$ of the sets correspond with those in A with the latter in conventional

order:

$$\begin{aligned} A: & a^1 a^2 \dots a^k \dots a^t \dots a^N \\ B': & a^1 a^2 \dots b^k \dots b^t \dots a^N \end{aligned}$$

In general, B' is not in its conventional order, so the matrix element must be multiplied by plus or minus one, according to the parity of the permutation from the conventional order of B to this order B' . The above general expression for the matrix element is thus reduced to

$$\langle A | \sum e^{2/r_{ij}} | B \rangle = \pm \left[\langle a^k a^t | e^{2/r_{ij}} | b^k b^t \rangle - \langle a^k a^t | e^{2/r_{ij}} | b^t b^k \rangle \right]$$

where the $\pm$ refers to the sign of the permutation $B \rightarrow B'$.

(ii) A and B differ by only one set

In the same way as above, the representations are chosen as

$$\begin{aligned} A: & a^1 a^2 \dots a^k \dots a^N \\ B': & a^1 a^2 \dots b^k \dots a^N \end{aligned}$$

and the general expression is reduced to

$$\langle A | \sum e^{2/r_{ij}} | B \rangle = \pm \sum_{a^t} \left[\langle a^k a^t | e^{2/r_{ij}} | b^k a^t \rangle - \langle a^k a^t | e^{2/r_{ij}} | a^t b^k \rangle \right]$$

where a^t runs over the $(N-1)$ individual sets which are common to A and B .

(iii) A identical with B

The general expression is reduced to

$$\langle A | \sum e^{2/r_{ij}} | B \rangle = \sum_{k>t=1}^N \left[\langle a^k a^t | e^{2/r_{ij}} | a^k a^t \rangle - \langle a^k a^t | e^{2/r_{ij}} | a^t a^k \rangle \right] .$$

Any of the integrals $\langle ab | e^2/r_{ij} | cd \rangle$, which throughout this thesis is abbreviated to (ab, cd) , is zero if $m_s^a \neq m_s^c$ and/or $m_s^b \neq m_s^d$, where m_s is the spin quantum number.

Thus each of these integrals should be written as

$$\delta(m_s^a, m_s^c) \cdot \delta(m_s^b, m_s^d) (ab, cd) .$$

Two examples are given, to illustrate the use of these formula: -

$$(i) \quad \Psi_A = |\pi b_1 b_1 b_2 b_2 | \alpha \alpha \beta \alpha \beta$$

$$\Psi_B = |\pi b_1 b_1 b_2 a_2 | \alpha \alpha \beta \beta \alpha .$$

Here $a^1 = \pi^\alpha$, $a^2 = b_1^\alpha$, etc. The representation B can be reordered by a permutation of odd parity to give B', which differs from A in regard to only b^4 :

$$\begin{array}{l} A : \quad \pi^\alpha \quad b_1^\alpha \quad b_1^\beta \quad b_2^\alpha \quad b_2^\beta \\ B' : \quad \pi^\alpha \quad b_1^\alpha \quad b_1^\beta \quad a_2^\alpha \quad b_2^\beta \end{array} .$$

Thus

$$\begin{aligned} \langle A | \sum e^2/r_{ij} | B \rangle = & - [(b_2 \pi, a_2 \pi) - (b_2 \pi, \pi a_2) + (b_2 b_1, a_2 b_1) \\ & - (b_2 b_1, b_1 a_2) + (b_2 b_1, a_2 b_1) + (b_2 b_2, a_2 b_2)] \end{aligned}$$

Note that there is no term $(b_2 b_1, b_1 a_2)$ arising from a^3 , since $m_s(a^3) \neq m_s(a^4)$.

$$(ii) \quad \Psi_A = |\pi b_1 b_1 b_2 b_2 | \alpha \alpha \beta \alpha \beta$$

$$\Psi_B = |\pi b_1 a_1 b_2 b_2 | \beta \alpha \alpha \alpha \beta .$$

Here A and B differ by two of their quantum numbers, and no reordering of B can reduce this number. Thus

$$\langle A | \sum e^2/r_{ij} | B \rangle = - (\pi b_1, a_1 \pi)$$

There is no term $(\pi b_1, \pi a_1)$ since $m_s(a^1) \neq m_s(b^1)$.

Appendix IV THE EIGENVALUES AND EIGENFUNCTIONS FOR
A NON-ORTHOGONAL BASIS

AIV.1 Derivation of Equation

Löwdin's method [27] is used to obtain the eigenfunctions and eigenvalues for a non-orthogonal basis. The usual case in which a non-orthogonal basis arises is when MO's are being constructed by LCAO, and when overlap between adjacent AO's cannot be neglected.

A set of basis AO wave functions $\{\psi_1, \psi_2, \dots, \psi_n\}$ is taken, from which it is desired to construct MO's Ψ_j by LCAO:

$$\Psi_j = \sum_i c_{ij} \psi_i \quad .$$

The coefficients c_{ij} must now be determined. Two matrices H and S are constructed:

$$H_{ij} = \langle \psi_i | H | \psi_j \rangle$$

$$S_{ij} = \langle \psi_i | \psi_j \rangle$$

where H is the Hamiltonian operator of which the MO's Ψ_j are to be approximate eigenfunctions.

The coefficients are determined by two conditions, the variation principle and the normalisation condition:

$$E_j = \frac{\langle \Psi_j | H | \Psi_j \rangle}{\langle \Psi_j | \Psi_j \rangle} = \text{a minimum} \quad \dots(1)$$

$$\langle \Psi_j | \Psi_j \rangle = 1 \quad \dots(2) \quad .$$

The condition for E_j to be a minimum is $\partial E_j / \partial c_i = 0$ for $i = 1, 2, \dots, n$. Now from (1),

$$E_j \left\langle \sum_i c_{ij} \psi_i \middle| \sum_k c_{kj} \psi_k \right\rangle = \left\langle \sum_i c_{ij} \psi_i \middle| H \middle| \sum_k c_{kj} \psi_k \right\rangle$$

$$\text{ie } E_j \left[c_{ij}^2 S_{ii} + 2 \sum_{i>k}^n \sum_{k=1}^n c_{ij} c_{kj} S_{ik} \right] = c_{ij}^2 H_{ii} + 2 \sum_{i>k=1}^n c_{ij} c_{kj} H_{ik} .$$

This relation is differentiated with respect to c_i , and the result set equal to zero. Thus

$$E_j \left[2c_{ij} S_{ii} + 2 \sum_k' c_{kj} S_{ik} \right] = 2 c_{ij} H_{ii} + 2 \sum_k' c_{kj} H_{ik}$$

$$\text{ie } \sum_{k=1}^n c_{kj} [H_{ik} - E_j S_{ik}] = 0 \quad \dots(3)$$

Condition (2) gives

$$\left\langle \sum_{i=1}^n c_{ij} \psi_i \middle| \sum_{k=1}^n c_{kj} \psi_k \right\rangle = \sum_{i=1}^n \sum_{k=1}^n c_{ij}^* S_{ik} c_{kj} = 1 \quad \dots(4)$$

The relations (3) and (4) for the coefficients may be written in matrix form as

$$H C = S C E \quad \dots(5)$$

$$C^\dagger S C = 1 \quad \dots(6)$$

where † stands for the Hermitian transpose.

AIV.2 Method of Solution

To determine the AO coefficients in the MO's, the matrix C must be found, where C satisfies conditions (5) and (6). To determine the order in which electrons should be fed into these MO's, the matrix E must be found.

Equation (5) is not an eigenvalue equation. It may be written as $(S^{-1}H)C = CE$, which is equivalent to the

determination of the eigenvalues E_i and eigenvectors C_i of the matrix $(S^{-1}H)$. Unfortunately, the matrix S^{-1} , and therefore $(S^{-1}H)$, is not symmetric; consequently the eigenvalues and eigenfunctions of $(S^{-1}H)$ may not be real. This problem could, in principle, be solved using the algebra of complex matrices, but would require a considerable amount of work, and has not as yet been programmed for a computer.

Instead, a transformation is applied to equation (5), to reduce the problem to the determination of the eigenvalues and eigenfunctions of a symmetric matrix, whose eigenvalues and eigenfunctions are real. With this method, equation (6) is automatically satisfied. This is a method developed by Löwdin [27]. Equation (5) is multiplied on the left with $S^{-1/2}$, to give

$$(S^{-1/2}HS^{-1/2})(S^{1/2}C) = (S^{1/2}C)E$$

which is equivalent to

$$H'C' = C'E \quad \dots(7)$$

where

$$H' = S^{-1/2}HS^{-1/2}$$

$$C' = S^{1/2}C .$$

Equation (7) is then an eigenvalue equation, with H' a symmetric matrix.

The matrix C whose column vectors give the coefficients of the AO's in the MO's is thus determined by computing the matrix $S^{-1/2}$, taking the product $H' = S^{-1/2}HS^{-1/2}$, finding the eigenvalues E_H , and eigenfunctions C' of H' , and reversing the transformation to give C : $C = S^{-1/2}C'$. These operations are performed on a high speed digital computer. The only difficult part is the computation of the matrix $S^{-1/2}$.

AIV.3 Computation of Matrix $S^{-1/2}$

Two methods were used, an iterative process and a finite method. For small matrices, of order less than ten, an iterative process is fast and accurate. The matrix S is inverted, and a Newton-Raphson square root iteration on S^{-1} performed, to give $S^{-1/2}$. A check matrix $S^{-1/2}SS^{-1/2}$, which should be the unit matrix, is computed. Five iterations usually gave off-diagonal elements of this matrix of less than 10^{-6} .

For larger matrices, a finite process using unitary transforms is more suitable. The eigenfunctions of S , when arranged as a row of column vectors, form a unitary matrix U , which transforms S to diagonal form,

$$U^{-1}SU = S_D = \text{diag}[\lambda_1, \lambda_2, \dots, \lambda_n]$$

where $\lambda_1, \lambda_2, \dots, \lambda_n$ are the eigenvalues of S . The matrix S is positive definite [36] and consequently all of the eigenvalues of S are greater than zero. The real matrix $S_D^{-1/2}$ is therefore computed by taking the inverse square root of the diagonal elements of S_D , which are simply the eigenvalues of S . The required matrix $S^{-1/2}$ is then found by reversing the unitary transform,

$$S^{-1/2} = U S_D^{-1/2} U^{-1}.$$

Furthermore, since U is unitary, $U^{-1} = U^T$, where T stands for transposition, and therefore

$$S^{-1/2} = U S_D^{-1/2} U^T.$$

It is much more convenient from a computing viewpoint, to use U^T than U^{-1} , since U^T is merely the matrix U with rows and columns interchanged, whereas U^{-1} is a different matrix, in general, and must be computed and stored separately.

An ALGOL-503 program, i.e. one written in ALGOL-60 for an Elliott 503 computer, to perform Hückel calculations using Löwdin's method, is given in appendix VI. This program was written for this thesis by Mr Keith Morris, of Applied Mathematics Division, Department of Scientific and Industrial Research.

The input is the upper triangle of the overlap matrix S , followed by the diagonal elements of the matrix H . The matrix $S^{-1/2}$ is computed, using the unitary transform method discussed above. The matrix H is then set up, using one of three options for calculating the off diagonal elements:

$$(a) H_{ij} = \beta_{ij} = 4 S_{ij}$$

$$(b) H_{ij} = \beta_{ij} = k \frac{1}{2}(H_{ii} + H_{jj}) S_{ij} = k \frac{1}{2}(\alpha_i + \alpha_j) S_{ij}$$

$$(c) H_{ij} = \beta_{ij} = -k [H_{ii} \cdot H_{jj}]^{1/2} S_{ij} = -k[\alpha_i \cdot \alpha_j]^{1/2} S_{ij}$$

where k is a positive constant, read from the data tape.

The matrix $H' = S^{-1/2} H S^{-1/2}$ is then set up, and the eigenvalues E and eigenfunctions C' , of H' evaluated, using Householder's method. The matrix C' of orthogonal vectors, and the matrix $C = S^{-1/2} C'$ of the MO vectors, are printed. For convenience, the vectors are arranged in order of increasing energy for the associated eigenvalue.

This program can handle matrices of up to order 50; for larger matrices, it is necessary to rewrite this ALGOL program in machine code. This enables an extension to matrices of up to order 76.

Approximate computation times are 75 seconds for a matrix of order 18, 5 minutes for one of order 30, and 25 minutes for one of order 48.

Appendix V

SLATER WAVE FUNCTIONS AND

OVERLAP INTEGRALS

AV.1 Slater Wave Functions

These are simple analytic expressions used to represent AO's, of the form

$$|n \ l \ m \ \mu\rangle = N_r r^{n^*-1} e^{-\mu r} S_{lm}(\theta, \phi)$$

where

N_r is a radial normalising factor

n^* is an effective principal quantum number

$\mu = Z^*/n^*$, where Z^* is an effective nuclear charge

$S_{lm}(\theta, \phi)$ is a normalised real spherical harmonic, defined by

$$S_{lm}(\theta, \phi) = \begin{cases} Y_{1,0}(\theta, \phi) \\ \frac{1}{\sqrt{2}} [Y_{1,-|m|}(\theta, \phi) \begin{Bmatrix} + \\ - \end{Bmatrix} Y_{1,|m|}(\theta, \phi)] \end{cases} \begin{cases} \text{if } m = 0 \\ \text{if } m > 0 \\ \text{if } m < 0 \end{cases}$$

$$= \begin{cases} \left[\frac{2l+1}{4\pi} \right]^{1/2} P_l(\cos \theta) \\ \left[\frac{2l+1}{4\pi} \frac{(1-|m|)!}{(1+|m|)!} \right]^{1/2} P_l^{|m|}(\cos \theta) \begin{cases} \cos(|m|\phi) \\ \sin(|m|\phi) \end{cases} \end{cases} \begin{cases} \text{if } m = 0 \\ \text{if } m > 0 \\ \text{if } m < 0 \end{cases}.$$

$P_l^{|m|}(\cos \theta)$ is the associated Legendre polynomial of order l and degree $|m|$.

The normalising factor N_r is evaluated using the integral $\int_0^\infty r^k e^{-qr} dr = k!/q^{k+1}$, to give

$$N_r = (2\mu)^{n^*+1/2} [\Gamma(2n^*+1)]^{-1/2}$$

$$= (2\mu)^{n^*+1/2} [(2n^*)!]^{-1/2} \text{ for } n^* \text{ integral.}$$

The numerical values of the parameters μ and n^* are chosen to minimise the energy, and are readily determined from the rules given by Slater [29]. These are as follows.

principal quantum number	1	2	3	4	5	6
n^*	1	2	3	3.7	4.0	4.2

$\mu = Z^*/n^*$, where $Z^* = Z - S$ and Z is the actual nuclear charge. The screening constant S is determined by dividing the electrons into groups:

1s, 2s 2p, 3s 3p, 3d, 4s 4p, 4d 4f, etc.

For any group of electrons, S is formed from

- (a) nothing from any shell outside the one considered;
- (b) an amount 0.35 from each other electron in the group considered, except for the 1s, where 0.30 is used;
- (c) if the orbital considered is of s or p type, an amount 0.85 from each electron with principal quantum number less by one, an amount 1.00 for each electron still further in, but if the orbital is of d or f type, an amount 1.00 from each electron inside it.

Thus for carbon 2s and 2p AO's, $\mu = 1.625$ and so

$$\psi(\text{C } 2p_z) = 1.899 \text{ re}^{-1.625r} \cos \theta = 1.899 \text{ ze}^{-1.625r}.$$

Slater AO's do not provide the best AO's, either for free atoms or atoms in molecules. The best available AO's are SCF AO's obtained by the Hartree-Fock procedure. However, these are usually obtained as numerical tables, and are therefore not very convenient to use. Slater AO's offer a reasonable compromise, being easy to handle with their simple analytic form. Furthermore, SCF AO's can be closely approximated by a sum of Slater type AO's. For molecules, neither SCF free atom nor Slater AO's are best, but it is

possible to express the best AO's for molecules as a sum of Slater type AO's [39].

AV.2 Overlap Integrals

These are expressions $S_{ij} = \langle n_i l_i m_i \mu_i | n_j l_j m_j \mu_j \rangle$ and are readily evaluated using Slater wave functions.

The integration over all space is performed with spheroidal coordinates (sometimes known as prolate spheroidal coordinates),

$$\xi = \frac{r_a + r_b}{R} \quad \eta = \frac{r_a - r_b}{R} \quad \phi = \phi_a = \phi_b$$

where R is the internuclear distance. The limits of integration are 1 to ∞ for ξ , -1 to 1 for η and 0 to 2π for ϕ .

Although $S_{ij} = S_{ji}$, it is necessary to make a convention as to which orbital is referred to first, ie as to which of i and j is labelled a, to avoid ambiguity in the formulae.

Mulliken et al [35], who have given master formulae for many of the required overlap integrals, take the convention that the orbital with smaller n^* , or if $n_i^* = n_j^*$, the one with larger μ , is orbital a. For convenience, the formulae are expressed in terms of two auxiliary parameters p and t, defined by

$$p = \frac{1}{2}(\mu_a + \mu_b)R/a_0$$

$$t = \frac{\mu_a + \mu_b}{\mu_a - \mu_b}$$

where distances are measured in Å, and a_0 is the Bohr radius, which has the value 0.529172 Å.

To evaluate the integrals, the following standard integrals are used:

$$A_k(p) = \int_1^\infty x^k e^{-px} dx = e^{-p} \sum_{j=1}^{k+1} [k! / p^j (k-j+1)!]$$

$$B_k(pt) = \int_{-1}^1 x^k e^{-ptx} dx$$

$$= -e^{-pt} \sum_{j=1}^{k+1} [k!/(pt)^j (k-j+1)!] - e^{pt} \sum_{j=1}^{k+1} [k!/(pt)^j (k-j+1)!].$$

These formulae are valid only for integral k ; when k is non-integral, the $A_k(p)$ and $B_k(pt)$ must be expressed in terms of the incomplete gamma function. The calculations in this thesis do not require values for k non-integral.

The Hückel calculations in chapters 7 and 8 require values for the overlap integrals between the following AO pairs:

- (a) two H 1s AO's
- (b) two C 2s AO's
- (c) two C 2p_σ AO's
- (d) two C 2p_π AO's
- (e) a H 1s AO and a C 2s AO
- (f) a H 1s AO and a C 2p_σ AO
- (g) a C 2s AO and a C 2p_σ AO
- (h) the H pseudo AO π_H and a C 2p_π AO.

Formulae for cases (a) to (g) can be obtained directly from Mulliken's tables [35]. The formula for case (h) is expressed in terms of those for (a) and (f).

The formulae for cases (a) to (f) are given below, in terms of the parameters p and t defined above. Some additional formulae are given for such cases as the overlap of two hydrogen 1s AO's, when the hydrogen atoms have different effective nuclear charges, giving a non-zero value of t for the AO pair. These additional formulae are required for the general overlap program.

$$S(1s, 1s, t=0) = 6^{-1} p^3 [3A_2 - A_0]$$

$$S(1s, 1s, t>0) = 4^{-1} p^3 (1-t^2)^{3/2} [A_2 B_0 - A_0 B_2]$$

$$S(1s, 2s, t \neq 0) = 8^{-1} 3^{-1/2} p^4 (1+t)^{3/2} (1-t)^{5/2} [A_3 B_0 - A_2 B_1 - A_1 B_2 + A_0 B_3]$$

$$S(1s, 2p_\sigma, t \neq 0) = 8^{-1} p^4 (1+t)^{3/2} (1-t)^{5/2} [-A_3 B_1 + A_2 B_0 + A_1 B_3 - A_0 B_2]$$

$$S(2s, 2s, t=0) = (360)^{-1} p^5 [15A_4 - 10A_2 + 3A_0]$$

$$S(2s, 2s, t > 0) = (48)^{-1} p^5 (1-t^2)^{5/2} [A_4 B_0 - 2A_2 B_2 + A_0 B_4]$$

$$S(2s, 2p_\sigma, t=0) = (60)^{-1} 3^{-1/2} p^5 [5A_3 - A_1]$$

$$S(2s, 2p_\sigma, t \neq 0) = (16)^{-1} 3^{-1/2} p^5 (1-t^2)^{5/2} [A_3 (B_0 - B_2) + A_1 (B_4 - B_2) + B_1 (A_2 - A_4) + B_3 (A_2 - A_0)]$$

$$S(2p_\sigma, 2p_\sigma, t=0) = (120)^{-1} p^5 [5A_4 - 18A_2 + 5A_0]$$

$$S(2p_\sigma, 2p_\sigma, t > 0) = (16)^{-1} p^5 (1-t^2)^{5/2} [B_2 (A_0 + A_4) - A_2 (B_0 + B_4)]$$

$$S(2p_\pi, 2p_\pi, t=0) = (120)^{-1} p^5 [5A_4 - 6A_2 + A_0]$$

$$S(2p_\pi, 2p_\pi, t > 0) = (32)^{-1} p^5 (1-t^2)^{5/2} [A_4 (B_0 - B_2) + A_2 (B_4 - B_0) + A_0 (B_2 - B_4)]$$

When the parameter t is zero, it is more convenient in computation to use the special formulae given by Mulliken for these cases:

For $t = 0$:-

$$S(1s, 1s) = e^{-p} [1 + p + p^2/3]$$

$$S(2s, 2s) = e^{-p} [1 + p + 4p^2/9 + p^3/9 + p^4/45]$$

$$S(2p_\sigma, 2p_\sigma) = e^{-p} [-1 - p - p^2/5 + 2p^3/15 + p^4/15]$$

$$S(2p_\pi, 2p_\pi) = e^{-p} [1 + p + 2p^2/5 + p^3/15]$$

$$S(2s, 2p_\sigma) = S(2p_\sigma, 2s) = 6^{-1} 3^{1/2} e^{-p} [p + p^2 + 7p^3/15 + 2p^4/15]$$

These master formulae were used to compute the tables of numerical values for cases (a) to (g), given below.

Table AV.1 Overlap Between Two Hydrogen 1s AO's

$$\mu_a = \mu_b = 1.0$$

R (Å)	S	R	S
1.0	.61655	1.8	.27518
1.1	.56529	1.9	.24516
1.2	.51587	2.0	.21786
1.3	.46875	2.5	.11685
1.4	.42425	3.0	.05998
1.5	.38258	3.5	.02977
1.6	.34383	4.0	.01439
1.7	.30805	4.5	.00681

Table AV.2 Overlap Integrals Between Two Carbon Atoms

$$\mu_a = \mu_b = 1.625$$

R (Å)	S(2s, 2s)	S(2s, 2p _σ)	S(2p _σ , 2p _σ)	S(2p _π , 2p _π)
1.3	.45762	.44490	.31819	.28815
1.35	.43169	.42948	.32630	.26553
1.39	.41148	.41654	.33031	.24843
1.40	.40650	.41323	.33099	.24430
1.45	.38213	.39637	.33263	.22442
1.50	.35861	.37907	.33158	.20587
1.60	.31429	.34386	.32276	.17251
1.70	.27374	.30878	.30708	.14381
1.80	.23703	.27472	.28672	.11931
1.90	.20410	.24238	.26351	.09854
2.0	.17483	.21220	.23892	.08105
2.5	.07522	.09910	.12577	.02892
3.0	.02942	.04088	.05561	.00961
4.5	.00120	.00181	.00272	.00027
5.0	.00038	.00058	.00089	.00008

Table AV.3 Overlap of Hydrogen 1s AO with Carbon
2s and Carbon 2p_σ AO's

R (Å)	S(1s, 2s)	S(1s, 2p _σ)
1.0	.61922	.48255
1.08	.57573	.46804
1.10	.56498	.46379
1.2	.51221	.43956
1.3	.46165	.41159
1.4	.41381	.38138
1.5	.36907	.35014
1.75	.27187	.27341
2.0	.19551	.20539
2.5	.09556	.10657
3.0	.04416	.05114
3.5	.01961	.02329
4.0	.00846	.01022
5.0	.00148	.00183

AV.3 Overlap of the Pseudo AO π_H with a Carbon 2p_z AO

Consider first the overlap between a carbon 2p_z AO and a hydrogen 1s AO centred in a plane above the nodal plane of the 2p_z. This overlap S is a function of the distance R

and the angle β . Since p AO's transform as the components of a vector, the carbon 2p_z AO can be expressed as the linear combination

$$|2p_z\rangle = \sin \beta |2p_\sigma\rangle + \cos \beta |2p_\pi\rangle$$

where $|2p_\sigma\rangle$ is a carbon 2p AO directed towards H and $|2p_\pi\rangle$ is a carbon 2p AO with its nodal plane along the line

joining C to H. Then $\langle 1s | 2p_z \rangle = 0$ by symmetry, and so

$$S(1s, 2p_z; R, \beta) = \sin \beta \ S(1s, 2p_\sigma; R).$$

The pseudo AO π_H is given in normalised form as

$$\pi_H = [2(1-S_H)]^{-1/2} (1s_u - 1s_l)$$

where $S_H = \langle 1s_u | 1s_l \rangle$ is given as a function of the distance R, in table AV.1. From above, it follows that

$$S(\pi_H, C 2p_z; R, \beta) =$$

$$[2/(1-S_H)]^{1/2} \sin \beta \ S(1s, 2p_\sigma; R).$$

Values of this function are tabulated below for R between 0.90 and 1.20 Å, and 2β between 95° and 120° .

Table AV.4 Overlap Between Pseudo AO π_H and Adjacent Carbon $2p_z$ AO

$R(\text{\AA})$	$2\beta = 95^\circ$	$2\beta = 109^\circ 28'$	$2\beta = 120^\circ$
0.90	.69841	.73306	.75573
1.00	.64573	.68156	.70498
1.08	.60370	.63993	.66356
1.14	.57260	.60876	.63234
1.20	.54196	.57785	.60144

Appendix VI ALGOL-503 PROGRAM FOR HUCKEL CALCULATIONS

```

HUCKEL;
begin integer n;
  begin integer array title[1:999];
    n := 1;
    instring(title, n);
    print $R99L9??;
    n := 1;
    outstring(title, n);
    print $L??
  end;
  prefix($ ?);
  digits(2);
  read n;
  begin real work, k, sumh;
    integer i, j, n2, bl1, bl2, a, b, s, l;
    array S[1:n,1:n], A[0:n], B[1:n];
    switch ss := 11, 12, 13, 14, 15;
    procedure BSWRITE(block, size, main, back);
    value block, size, main, back;
    integer block, size, main, back;
    begin elliott(7, 6, 5121, 0, 3, 0, size);
      elliott(5, 5, 20, 0, 0, 4, block);
      elliott(0, 4, back, 0, 6, 7, main);
      elliott(7, 7, 0, 0, 0, 0, 0)
    end;
    procedure BSREAD(block, size, main, back);
    value block, size, main, back;
    integer block, size, main, back;
    begin elliott(7, 6, 5120, 0, 3, 0, size);
      elliott(5, 5, 20, 0, 0, 4, block);
      elliott(0, 4, back, 0, 6, 7, main);
      elliott(7, 7, 0, 0, 0, 0, 0)
    end;
    procedure SQR2BS(n, g, bl);
    value n, bl;
    integer n, bl;
    array g;
    begin real t, norm, eps, sine, cosine, lambda, mu, a0, a1,
      b0, beta, x0, x1;
      integer k, m, m1;
      array a, x[1:n], b[0:n], c[0:n-1], cs, sn[1:n-1];
      switch s := insp, ret;
      real procedure sum(i, m, n, a);
      value m, n;
      real a;
      integer i, m, n;

```

```

begin work := 0.0;
  for i := m step 1 until n do
    work := work+a;
    sum := work
  end;
real procedure max(a, b);
value a, b;
real a, b;
max := if a>b then a else b;
real procedure rx(i, j);
value i, j;
integer i, j;
begin i:= n*(i-1)+j+1;
  elliot(3, 0, i, 0, 7, 2, 5120);
  elliot(7, 5, 5122, 0, 2, 0, work);
  rx := work
end;
procedure wx(i, j, a);
value i, j, a;
real a;
integer i, j;
begin i := n*(i-1)+j+1;
  elliot(3, 0, a, 0, 7, 2, 5122);
  elliot(3, 0, i, 0, 7, 2, 5121)
end;
procedure HOUSEHOLDER2(n, g, a, b, x, norm);
comment This subroutine calculates the eigenvalues
and eigenfunctions of a symmetric matrix, using
Householders method;
value n;
real norm;
integer n;
array g, a, b, x;
begin real t, sigma, alpha, beta, gamma, absb;
  array p[2:n];
  norm := absb := 0.0;
  for k := 1 step 1 until n-2 do
    begin a[k]:= g[k,k];
      sigma := sum(i, k+1, n, g[i,k]2);
      t := absb+abs(a[k]);
      absb := sqrt(sigma);
      norm := max(norm, t+absb);
      alpha := g[k+1,k];
      b[k] := beta := if alpha<0.0 then absb else -absb;
      if sigma≠0.0 then
        begin gamma := 1.0/(sigma-alpha*beta);
          g[k+1,k] := alpha-beta;
          for i := k+1 step 1 until n do
            p[i] := gamma*(sum(j, k+1, i, g[i,j]*g[j,k])
              +sum(j, i+1, n, g[j,i]*g[j,k]));
            t := 0.5*gamma*sum(i, k+1, n, g[i,k]*p[i]);
            for i := k+1 step 1 until n do
              p[i] := p[i]-t*g[i,k];

```

```

        for i := k+1 step 1 until n do
        for j := k+1 step 1 until i do
        g[i,j] := g[i,j]-g[i,k]*p[j]-p[i]*g[j,k];
        for i := 2 step 1 until n do
        begin BSREAD(bl, n-k, address(x)+k, n*(i-1)+k+1);
        p[i] := gamma*sum(j, k+1, n, x[j]*g[j,k])
        end;
        for i := 2 step 1 until n do
        begin BSREAD(bl, n-k, address(x)+k, n*(i-1)+k+1);
        for j := k+1 step 1 until n do
        x[j] := x[j]-p[i]*g[j,k];
        BSWRITE(bl, n-k, address(x)+k, n*(i-1)+k+1)
        end
        end
    end;
    a[n-1] := g[n-1,n-1];
    a[n] := g[n,n];
    b[n-1] := g[n,n-1];
    t := abs(b[n-1]);
    norm := max(norm, absb+abs(a[n-1])+t);
    norm := max(norm, t+abs(a[n]))
end;
for i := 1 step 1 until n do
begin for j := 1 step 1 until n do
x[j] := 0.0;
x[i] := 1.0;
BSWRITE(bl, n, address(x), n*(i-1)+1)
end;
HOUSEHOLDER2(n, g, a, b, x, norm);
eps := norm*210-9;
b[0] := mu := 0.0;
m := n;
insp: if m=0 then goto ret else i := k := m1 := m-1;
if abs(b[k])<eps then
begin g[m,m] := a[m];
mu := 0.0;
m := k;
goto insp
end;
for i := i-1 while abs(b[i])>eps do
k := i;
lambda := if abs(a[m]-mu)<0.5*abs(a[m]) or m1=k then
a[m]+0.5*b[m1] else 0.0;
mu := a[m];
a[k] := a[k]-lambda;
beta := b[k];
for j := k step 1 until m1 do
begin a0 := a[j];
a1 := a[j+1]-lambda;
b0 := b[j];
t := sqrt(a0*a0+beta*beta);

```

```

        cosine := cs[j] := a0/t;
        sine := sn[j] := beta/t;
        a[j] := cosine*a0+sine*beta;
        a[j+1] := -sine*b0+cosine*a1;
        b[j] := cosine*b0+sine*a1;
        beta := b[j+1];
        b[j+1] := cosine*beta;
        c[j] := sine*beta
    end;
    b[k-1] := c[k-1] := 0.0;
    for j:= k step 1 until m1 do
    begin sine := sn[j];
        cosine := cs[j];
        a0 := a[j];
        b0 := b[j];
        b[j-1] := b[j-1]*cosine+c[j-1]*sine;
        a[j] := a0*cosine+b0*sine+lambda;
        b[j] := -a0*sine+b0*cosine;
        a[j+1] := a[j+1]*cosine;
        for i := 1 step 1 until n do
        begin x0 := rx(i, j);
            x1 := rx(i, j+1);
            wx(i, j, x0*cosine+x1*sine);
            wx(i, j+1, -x0*sine+x1*cosine)
        end
    end;
    a[m] := a[m]+lambda;
    goto insp;
ret:
end;
procedure MMMULT(b11, b12);
value b11, b12;
integer b11, b12;
for i := 1 step 1 until n do
begin BSREAD(b11, n, a, n*(i-1)+1);
    for j := 1 step 1 until n do
    begin work := 0.0;
        for l := 1 step 1 until n do
        work := work+A[l]*S[l,j];
        B[j] := work
    end;
    BSWRITE(b12, n, b, n*(i-1)+1)
end;
Boolean procedure on;
on := 1<i+8 and 1<n;
procedure PRINT(head);
string head;
for i := 1 step 8 until n do
for j := 1 step 1 until n do
begin if j=1 or j=41 then
    begin print f$HL9?MO numberf$LS??;
        prefix(f ?);
        for l := i, l+1 while on do
        print f$S5??, l;
    end
end

```

```

        print 'Energy Levels';
        aligned(3, 3);
        for l := i, l+1 while on do
            print A[l];
            print ' ', head
        end;
        prefix(' ');
        aligned(1, 4);
        print ' ', j;
        for l := i, l+1 while on do
            begin work := 10-4*(entier(104*S[j,l]+0.5));
                if work ≠ 0.0 then print work else print 'S9'
            end
        end;
    end;
    procedure SWOP(x, y);
    real x, y;
    begin work := x;
        x := y;
        y := work
    end;
    n2 := n*n;
    a := address(A)+1;
    b := address(B);
    s := address(S);
    b11 := 0;
    b12 := n2;
    for i := 1 step 1 until n do
        begin S[i,i] := 1.0;
            for j := i+1 step 1 until n do
                S[i,j] := S[j,i] := 0.0
            end;
        11: read i, j;
        12: read work;
            S[i,j] := S[j,i] := work;
            if buffer(1, ' ') then goto 11;
            if buffer(1, ' ') then goto 13;
            j := j+1;
            goto 12;
        13: for i := 1 step 1 until n do
            B[i] := S[i,i];
            SQR2BS(n, S, b11);
            for i := 1 step 1 until n do
                begin A[i] := 1.0/sqrt(S[i,i]);
                    S[i,i] := B[i]
                end;
            BSWRITE(b12, n2, s, 1);
            BSREAD(b11, n2, s, 1);
            for i := 1 step 1 until n do
                begin S[i,i] := A[i]*S[i,i];
                    for j := i+1 step 1 until n do
                        begin work := S[i,j];

```

```

        S[i,j] := A[i]*S[j,i];
        S[j,i] := A[j]*work
    end
end;
MXMULT(b11, b11);
BSREAD(b12, n2, s, 1);
for i := 1 step 1 until n do
    A[i] := 0.0;
14: read work;
15: read i;
    A[i] := work;
    if buffer(1, £,?) then goto 14;
    if not buffer(1, £;?) then goto 15;
    read k;
    if k<0.0 then for i := 1 step 1 until n do
        B[i] := sqrt(abs(A[i]));
        sumh := 0.0;
        for i := 1 step 1 until n do
            begin S[i,i] := A[i]*(1.0+k*(S[i,i]-1.0));
                comment This method of setting up the
                diagonal elements of matrix H permits the
                use of group theory reduction of matrices,
                in which cases the diagonal elements of the
                overlap matrix submatrices are not necessarily
                one;
                sumh := sumh+A[i];
                for j := i+1 step 1 until n do
                    S[i,j] := S[j,i] := if k>0.0 then 0.5*k*(A[i]+A[j])*S[i,j] else
                        if k=0.0 then 4.0*S[i,j] else k*B[i]*B[j]*S[i,j]
                end;
            MXMULT(b11, b12);
            BSREAD(b11, n2, s, 1);
            MXMULT(b12, b12);
            BSREAD(b12, n2, s, 1);
            SQR2BS(n, S, b12);
            A[0] := if k=0.0 then 75 else -75;
            for i := 1 step 1 until n do
                A[i] := S[i,i];
            BSREAD(b12, n2, s, 1);
            for i := 2 step 1 until n do
                if A[i-1]<A[i]=k=0.0 then
                    for j := i, j-1 while A[j-1]<A[j]=k=0.0 do
                        begin SWOP(A[j-1], A[j]);
                            for l := 1 step 1 until n do
                                SWOP(S[l,j-1], S[l,j])
                            end;
                        PRINT(£Orthogonal Vectors?);
                        l := n div 2;
                        k := 0.0;
                        for i := 1 step 1 until l do
                            k := k+2.0*A[i];
                        if n#2*1 then k := k+A[l+1];
                        aligned(2, 4);
                    end
                end
            end
        end
    end

```

```

for i := 1 step 1 until n do
begin if i=1 or i=41 then
    print aligned(4, 3), ££HL9?Sum of diagonals of H£L??, sumh,
    ££L2?Total energy of molecule£L??, k,
    ££L2?Binding energy£L??, sumh-k,
    ££L2?Charge densities£L??;
    work := 0.0;
    for j := 1 step 1 until 1 do
    work := work+2.0*S[i,j]↑2;
    if n÷2*1 then work := work+S[i,1+1]↑2;
    print i, work, ££L??
end;
begin array C[1:n];
    for i:= 1 step 1 until n do
    C[i] := A[i];
    MXMULT(b11, b12);
    BSREAD(b12, n2, s, 1);
    for i := 1 step 1 until n do
    A[i] := C[i];
    PRINT(£Molecular Orbital coefficients?)
end
end;
print ££L9HR99??;
wait;
restart

```

end;

Appendix VII COMPUTER PROGRAM FOR OVERLAP MATRICES

The extended Hückel calculations in chapters 7 and 8 necessitated the development of a computer program to handle the calculation of the overlap integrals between the s and p type AO's associated with any given number of atoms, situated at arbitrary positions in space.

When there are non-planar atoms with p type AO's, the evaluation of the overlap integrals by hand is considerably more tedious than for the case when all atoms with p type AO's are planar. The calculation is tractable, and sufficiently accurate, only if programmed for an electronic computer.

When two p AO's, located in the same plane, are not directed along the line joining their centres, or perpendicular to this line, the overlap integral between these two AO's is evaluated by resolving each p AO into two mutually perpendicular components. Each p AO can be represented by a vector perpendicular to the nodal plane and pointing in the direction of the positive values of the wave function. Thus,

$$|p_1\rangle = |p_\sigma^A\rangle \cos\delta + |p_\pi^A\rangle \sin\delta$$

$$|p_2\rangle = |p_\sigma^B\rangle \cos\beta + |p_\pi^B\rangle \sin\beta$$

where $|p_\sigma^A\rangle$, $|p_\pi^A\rangle$ are p AO's centred at A and pointing towards B and perpendicular to AB, respectively. The required overlap integral is then given by

$\langle p_1 | p_2 \rangle = \langle p_{\sigma}^A | p_{\sigma}^B \rangle \cos \delta \cos \beta + \langle p_{\pi}^A | p_{\pi}^B \rangle \sin \delta \sin \beta$
 since, by symmetry, $\langle p_{\sigma}^A | p_{\pi}^B \rangle = \langle p_{\pi}^A | p_{\sigma}^B \rangle = 0$. $\langle p_{\sigma}^A | p_{\sigma}^B \rangle$
 and $\langle p_{\pi}^A | p_{\pi}^B \rangle$ are found either from the general formulae
 or the numerical tables given in Appendix V.

When the initial p AO's are not planar, each p AO must be resolved into three mutually perpendicular components, one along the line joining their centres, and the other two mutually perpendicular to this line. This leads to an immense amount of calculation for a molecule as large as perinaphthane.

The method developed here uses parallel axes at each atom, with one p AO pointing along the positive direction of each of the axes. Hoffmann [34] gives a brief outline of the method of resolving the basis p AO's. Let

$\underline{P}_i = \underline{i}, \underline{j}, \underline{k}$ be cartesian unit vectors

$\underline{R}_{ij}$ = the unit vector along the interatomic distance vector for an atom pair (i,j).

Then, the overlap integrals between the s and p type AO's on atoms i and j are:-

$$\begin{aligned} \langle ns_i | n's_j \rangle &= 1. S(ns_i, n's_j) \\ \langle ns_i | n'p_j \rangle &= - \underline{R}_{ij} \cdot \underline{P}_j S(ns_i, n'p_{\sigma j}) \\ \langle np_i | n'p_j \rangle &= -(\underline{R}_{ij} \cdot \underline{P}_i)(\underline{R}_{ij} \cdot \underline{P}_j) S(np_{\sigma i}, n'p_{\sigma j}) + \\ &\quad [\underline{P}_i - (\underline{R}_{ij} \cdot \underline{P}_i)\underline{R}_{ij}][\underline{P}_j - (\underline{R}_{ij} \cdot \underline{P}_j)\underline{R}_{ij}] S(np_{\pi i}, n'p_{\pi j}) \\ &= -(\underline{R}_{ij} \cdot \underline{P}_i)(\underline{R}_{ij} \cdot \underline{P}_j) S(np_{\sigma i}, n'p_{\sigma j}) + \\ &\quad [\underline{P}_i \cdot \underline{P}_j - (\underline{R}_{ij} \cdot \underline{P}_i)(\underline{R}_{ij} \cdot \underline{P}_j)] S(np_{\pi i}, n'p_{\pi j}) \end{aligned}$$

where formulae for $S(ns_i, n's_j)$, $S(ns_i, n'p_{\sigma j})$, $S(np_{\sigma i}, n'p_{\sigma j})$, $S(np_{\pi i}, n'p_{\pi j})$ are given in appendix V as functions of the parameters p and t, which characterise the atom pair (i,j) and the distance between the two atoms.

An ALGOL-503 program, i.e. an ALGOL-60 program for an Elliott 503 computer, is given on the next page. This program was written for this thesis by Mr Keith Morris, of the Applied Mathematics Division, Department of Scientific and Industrial Research. The input for the program consists of the atomic number of the atom, followed by the cartesian coordinates of that atom. The atomic numbers identify each atom, and so determine n , the principal quantum number of the high energy electrons, $\mu(s)$, $\mu(p)$, $\alpha_i(p)$ and $\alpha_i(s)$. $\mu(s)$ and $\mu(p)$ are the exponents in the s and p Slater AO's, as defined in appendix V; $\alpha_i(s)$ and $\alpha_i(p)$ are the coulomb integrals for the s and p electrons.

If in a particular calculation, alternative values are to be used for these parameters, the program is arranged such that a new set of parameters can be specified at any stage, which will then apply to all subsequent atoms with that particular atomic number. This can be done as many times as desired, in a given calculation, and can be used, for example, to give each carbon atom in a particular molecule a different set of Slater and Coulomb parameters.

The program presented below can handle the overlap matrix for molecules with up to 250 high energy basis AO's, although this limit can easily be extended if required. The computation time is controlled completely by the speed at which the computer can punch the matrix elements on tape, ready for input to the Hückel program given in appendix VI.

ALGOL-503 PROGRAM TO CALCULATE OVERLAP MATRICES

OVERLAP;

```

begin real x, y, z, mu, hi, k, work;
integer i, j, orbs, ni, posn, atom;
Boolean blc;
array X, Y, Z, MU, H[1:250], SMUS, SHS, SMUP, SHP[1:100];
integer array D, N[1:250], SN[1:100];
switch s := 11, 12, 13, 1err;
procedure TEST(lcom, lsem);
label lcom, lsem;
if buffer(1, £,?) then goto lcom else if buffer(1, £;?)
then goto lsem;
procedure PUT;
begin i := i+1;
      orbs := orbs+1;
      D[orbs] := i;
      X[orbs] := x;
      Y[orbs] := y;
      Z[orbs] := z;
      N[orbs] := ni;
      MU[orbs] := mu;
      H[orbs] := hi

```

end;

comment The following are the assumed values for the Slater exponents and coulomb integrals. The subscripted variable is the atomic number. SMUS[i], SMUP[i] are the Slater exponents for the s and p type AOs. SHS[i], SHP[i] are the coulomb integrals for the s and p type AOs;

```

SN[1] := 1;
SMUS[1] := 1.0;
SHS[1] := -13.6;
SN[5] := 2;
SMUS[5] := 1.3;
SHS[5] := -15.2;
SMUP[5] := 1.3;
SHP[5] := -8.5;
SN[6] := 2;
SMUS[6] := 1.625;
SHS[6] := -21.4;
SMUP[6] := 1.625;
SHP[6] := -11.4;
SN[7] := 2;
SMUS[7] := 1.95;
SHS[7] := -26.0;
SMUP[7] := 1.95;
SHP[7] := -13.4;

```

```

SN[8] := 2;
SMUS[8] := 2.275;
SHS[8] := -35.6;
SMUP[8] := 2.275;
SHP[8] := -18.0;
orbs := 0;
begin integer array title[1:999];
    i := 1;
    instring(title, i);
    print ££R99L9Q??;
    i := 1;
    outstring(title, i);
    print ££UL??
end;
11: read atom;
    if buffer(1, £*) then
        begin read ni, mu, hi;
            SN[atom] := ni;
            SMUS[atom] := mu;
            SHS[atom] := hi;
            if ni≠1 then
                begin read mu, hi;
                    SMUP[atom] := mu;
                    SHP[atom] := hi
                end;
                comment This makes provision for the Slater and
                coulomb parameters to be given values other than
                the assumed ones;
                TEST(11, 13);
                goto lerr
            end else
            begin x := y := z := 0.0;
                i := 0;
                TEST(12, 12);
                read x;
                TEST(12, 12);
                read y;
                TEST(12, 12);
                read z;
                TEST(12, 12);
            lerr: print ££L?INPUT ERROR£L??, punch(3), ££L?INPUT ERROR£L??;
                wait;
                restart;
                12: ni := SN[atom];
                    mu := SMUS[atom];
                    hi := SHS[atom];
                    PUT;
                    if ni≠1 then
                        begin mu := SMUP[atom];
                            hi := SHP[atom];
                            for j := 1 step 1 until 3 do
                                PUT
                            end;

```

```

        TEST(11, 13)
    end;
13: read k;
    prefix(? ?);
    aligned(0, 6);
    digits(2);
    posn := 5;
    print orbs;
    for i := 1 step 1 until orbs-1 do
    begin j := i+1;
        blc := false;
        for ni := ni while D[j]≠1 and j<orbs do
        j := j+1;
        if D[j]=1 then
        for j := j step 1 until orbs do
        begin real p, q, r, t, q2;
            integer k, n;
            Boolean blw;
            array A, B[0:4], DOT[2:];
            switch overlap := S1s1s, S1s2st, S1s2pt, S2s2s, S2s2p, S2p2p,
            S2s2st, S2s2pt, S2p2pt, S1s1st, lend;
            procedure SWOP;
            begin k := i;
                i := j;
                j := k
            end;
            real procedure C(i, j);
            comment This is a subroutine for calculating the quantity
            C(i,j) = Ai(p) times Bj(pt) in Mullikens notation. The
            procedures for calculating the Ai(p) and Bj(pt) are
            given below;

            value i, j;
            integer i, j;
            C := A[i]*B[j];
            r := sqrt((X[i]-X[j])2+(Y[i]-Y[j])2+(Z[i]-Z[j])2);
            blw := N[i]>N[j];
            if blw then SWOP else
            begin if N[i]=N[j] then
                begin blw := MU[i]<MU[j];
                    if blw then SWOP
                end
            end;
            DOT[2] := (X[j]-X[i])/r;
            DOT[3] := (Y[j]-Y[i])/r;
            DOT[4] := (Z[j]-Z[i])/r;
            p := .9448723*(MU[i]+MU[j])*r;
            t := (MU[i]-MU[j])/(MU[i]+MU[j]);
            q := p*t;
            A[0] := exp(-p)/p;
            for n := 1 step 1 until 4 do
            A[n] := A[0]+n*A[n-1]/p;
        end
    end

```

```

if q=0.0 then
begin B[1] := B[3] := 0.0;
      B[0] := 2.0;
      B[2] := 2/3;
      B[4] := .4
end else
if abs(q)<8.0 then
begin for n := 0 step 1 until 4 do
      if n=2*(n div 2) then
begin switch s := 11;
      r := 2.0/(n+1);
      y := r*10-8;
      x := r;
      k := 0;
      q2 := q*q;
11: k := k+2;
      r := r*q2*(n+k-1)/(k*(k-1)*(n+k+1));
      x := x+r;
      if r>y then goto 11;
      B[n] := x+r
end else
begin switch s := 11;
      r := 2.0*q/(n+2);
      y := abs(r*10-8);
      x := r;
      k := 1;
      q2 := q*q;
11: k := k+2;
      r := r*q2*(n+k-1)/(k*(k-1)*(n+k+1));
      x := x+r;
      if abs(r)>y then goto 11;
      B[n] := -(x+r)
end
end
end else
begin x := 1.0/q;
      y := x*exp(q);
      z := (x*x)/y;
      B[0] := y-z;
      mu := -1.0;
      hi := 1.0;
      for n := 1 step 1 until 4 do
begin B[n] := mu*y-z+hi*x*B[n-1];
      mu := -mu;
      hi := hi+1.0
end
end;
if N[i] = 1 then
begin k := if N[j] = 1 then
      (if k=0.0 then 1 else 10) else if D[j] = 1 then 2 else 3
end else
begin k := if t = 0.0 then 4 else 7;
      k := k+(if D[i] = 1 then

```

```

        (if D[j] = 1 then 0 else 1) else
        if D[j] = 1 then 1 else 2)
    end;
    goto overlap[k];
    comment The following are the formulae for the various
    types of overlap integrals. A subroutine has been
    given earlier for the C(i,j);
S1s1s: work := exp(-p)*(1.0+p*(1.0+p*(1/3)));
    goto lend;
S1s1st: work := 0.25*p†3*(1.0-t*t)†1.5*(C(2,0)-C(0,2));
    goto lend;
S1s2st: work := .72168783510-1*p†4*(1.0+t)†1.5*(1.0-t)†2.5
    *(C(3,0)-C(2,1)-C(1,2)+C(0,3));
    goto lend;
S1s2pt: work := -DOT[D[j]]*.125*p†4*(1.0+t)†1.5*(1.0-t)†2.5
    *(-C(3,1)+C(2,0)+C(1,3)-C(0,2));
    goto lend;
S2s2s: work := exp(-p)*(1.0+p*(1.0+p*(4/9+p*(1/9+p*(1/45)))));
    goto lend;
S2s2p: work := -DOT[if D[j]=1 then D[i] else D[j]].288675134
    *exp(-p)*p*(1.0+p*(1.0+p*(7/15+p*(2/15))))*
    (if D[i]=1 then 1.0 else -1.0);
    goto lend;
S2p2p: work := exp(-p)*(-DOT[D[i]]*DOT[D[j]]
    *(-1.0+p*(-1.0+p*(-.2+p*(2/15+p*(1/15))))))
    +((if D[i] = D[j] then 1.0 else 0.0)-DOT[D[i]]*DOT[D[j]])
    *(1.0+p*(1.0+p*(.4+p*(1/15)))));
    goto lend;
S2s2st: work := 1/48*p†5*(1.0-t*t)†2.5*(C(4,0)-2.0*C(2,2)+C(0,4));
    goto lend;
S2s2pt: work := -DOT[if D[j]=1 then D[i] else D[j]].36084391810-1*
    p†5*(1.0-t*t)†2.5
    *(C(3,0)-C(3,2)+C(1,4)-C(1,2)+C(2,1)-C(4,1)+C(2,3)-C(0,3))
    *(if D[i]=1 then 1.0 else -1.0);
    goto lend;
S2p2pt: work := .03125*p†5*(1.0-t*t)†2.5*(2.0*DOT[D[i]]*DOT[D[j]]
    *(C(0,2)+C(4,2)-C(2,0)-C(2,4))
    +((if D[i] = D[j] then 1.0 else 0.0)-DOT[D[i]]*DOT[D[j]])
    *(C(4,0)-C(4,2)+C(2,4)-C(2,0)+C(0,2)-C(0,4)));
lend: if blw then SWOP;
    ni := 106*work;
    work := 10-6*ni;
    if work≠0.0 then
    begin if blc then
        begin posn := posn+9;
            if posn>75 then
            begin print ££L??;
                posn := 9
            end;
            print work
        end else
        begin posn := posn+18;

```

```

        print £,?;
        if posn>75 then
            begin print ££L??;
                  posn := 18
            end;
        print i, j, work;
        blc := true
    end
end else
    blc := false
end
end;
print £;£L??;
blc := false;
scaled(8);
posn := 0;
for i := 1 step 1 until orbs do
    if H[i]≠0.0 then
        begin work := H[i];
            print £,?;
            posn := posn+15;
            if posn>75 then
                begin print ££L??;
                      posn := 15
                end;
            print work;
            for j := i step 1 until orbs do
                begin if H[j]=work then
                    begin posn := posn+4;
                          if posn>75 then
                              begin print ££L??;
                                    posn := 4
                              end;
                          print j;
                          H[j] := 0.0
                    end
                end
            end;
        end
    end;
    blc := true
end;
if blc then print £;? else
print 0, 1, £;?;
print k, £;£L9HR99??;
wait;
restart
end;

```


Appendix VIII

PYRACENE π ELECTRONS MO COEFFICIENTS

PYRACENE π MO's from method (1)

The basis AO's are numbered as in section 7.4, page 83.

MO coefficients

symmetry	energy	c ₁	c ₂	c ₅	c ₆	c ₈
1b _{1u}	2.963	.2590	.3505	.1845	.1862	.0931
1b _{2g}	2.883	.2877	.3802	.1378	.0707	.0353
1b _{3g}	2.115	.3007	.3072	.1911	0	-.1694
2b _{1u}	2.109	.1678	.1710	-.2385	-.4254	-.2127
1a _u	2.047	.3365	.3348	.1493	0	-.0488
2b _{3g}	1.471	.1917	.1477	-.1894	0	.3944
2b _{2g}	1.185	.1291	.0850	-.3731	-.3404	-.1702
3b _{1u}	.994	0	0	0	.4082	-.4082
2a _u	.530	.1520	.0612	-.3956	0	.2581
3b _{3g}	-.607	-.1230	.0052	.4117	0	.2556
3b _{2g}	-.994	0	0	0	.4082	-.4082
4b _{1u}	-1.241	.1445	-.0418	-.3778	.3360	.1680
3a _u	-1.579	-.0847	.0357	.2493	0	.4236
4b _{2g}	-2.129	-.2281	.1452	.2315	-.4054	-.2027
5b _{1u}	-2.669	.3659	-.3101	.1280	-.0694	-.0347
5b _{2g}	-2.765	.3139	-.2778	.1954	-.2194	-.1097
4b _{3g}	-3.353	.3282	-.3658	.0898	0	.0205
4a _u	-3.359	.3263	-.3645	.0951	0	.0400

PYRACENE π MO's from method (2)

symmetry	energy	MO coefficients				
		c_1	c_2	c_5	c_6	c_8
$1b_{1u}$	4.029	.2661	.3100	.2111	.2282	.1121
$1b_{2g}$	3.746	.3063	.3524	.1606	.0949	.0414
$1b_{3g}$	2.198	.1942	.2015	-.2101	-.3810	-.2345
$2b_{1u}$	2.026	.1870	.2032	.2669	0	-.3202
$1a_u$	1.579	.3002	.3191	.2234	0	-.0900
$2b_{3g}$	1.018	.2770	.2822	-.0460	0	.3026
$2b_{2g}$	.791	-.1346	-.1143	.3641	.3295	.1787
$3b_{1u}$	.717	-.0222	-.0108	.0225	.4288	-.3962
$2a_u$	-.006	.1767	.1536	-.3464	0	.2742
$3b_{3g}$	-.936	.1181	.0691	-.4189	0	-.2363
$3b_{2g}$	-1.097	-.0189	.0041	.0144	.4013	-.4110
$4b_{1u}$	-1.374	.0815	.0169	-.3981	.3446	.1588
$3a_u$	-1.562	-.0676	-.0178	.2805	0	.4080
$4b_{2g}$	-1.985	.0659	-.0104	-.2975	.4700	.2158
$5b_{1u}$	-2.736	.3666	-.3361	.0479	-.0145	-.0164
$5b_{2g}$	-2.739	.3652	-.3356	.0540	-.0222	-.0291
$4b_{3g}$	-3.034	.3526	-.3526	.0349	0	.0113
$4a_u$	-3.035	.3522	-.3525	.0372	0	.0174

PYRACENE π MO's from method (3)

		MO coefficients				
symmetry	energy	c_1	c_2	c_5	c_6	c_8
$1b_{1u}$	1.662	.1752	.2532	.1567	.1685	.0843
$1b_{2g}$	1.624	.2061	.2879	.1139	.0607	.0304
$2b_{1u}$	1.364	.1448	.1601	-.1797	-.3319	-.1659
$1b_{3g}$	1.340	.2165	.2339	.1717	0	-.1673
$1a_u$	1.297	.2591	.2693	.1307	0	-.0446
$2b_{3g}$	1.058	.1787	.1479	-.1446	0	.3235
$2b_{2g}$	.908	.1144	.0814	-.3246	-.2976	-.1488
$3b_{1u}$	.796	0	0	0	.3654	-.3654
$2a_u$	.463	.1441	.0613	-.3683	0	.2413
$3b_{3g}$	-.710	.1325	-.0092	-.4448	0	-.2769
$3b_{2g}$	-1.323	0	0	0	.4709	-.4709
$4b_{1u}$	-1.771	.1809	-.0623	-.4470	.4001	.2000
$3a_u$	-2.593	-.1109	.0550	.3164	0	.5431
$4b_{2g}$	-4.252	.3719	-.2642	-.2830	.5273	.2636
$5b_{1u}$	-6.561	.5514	-.4946	.2325	-.1328	-.0664
$5b_{2g}$	-7.724	.4424	-.4260	.3943	-.4776	-.2388
$4b_{3g}$	-14.750	.6619	-.7861	.2075	0	.0498
$4a_u$	-14.942	.6598	-.7862	.2237	0	.1029

PYRACENE π MO's from method (4)

symmetry	energy	MO coefficients				
		c_1	c_2	c_5	c_6	c_8
$1b_{1u}$	1.966	.1706	.2112	.1589	.1770	.0879
$1b_{2g}$	1.879	.2076	.2528	.1220	.0733	.0322
$2b_{1u}$	1.397	.1585	.1731	-.1598	-.2965	-.1850
$1b_{3g}$	1.328	.1349	.1532	.2203	0	-.2719
$1a_u$	1.090	.2409	.2651	.1952	0	-.0802
$2b_{3g}$	.782	.2436	.2548	-.0302	0	.2586
$2b_{2g}$	.655	-.1226	-.1075	.3302	.2995	.1626
$3b_{1u}$	.608	.0205	.0106	-.0208	-.3951	.3646
$2a_u$	-.006	.1753	.1523	-.3436	0	.2719
$3b_{3g}$	-1.210	.1341	.0716	-.4767	0	-.2701
$3b_{2g}$	-1.510	.0230	-.0061	-.0169	-.4703	.4826
$4b_{1u}$	-2.081	.1054	.0125	-.4889	.4248	.1953
$3a_u$	-2.552	.0886	.0137	-.3567	0	-.5228
$4b_{2g}$	-3.921	.1106	-.0358	-.4137	.6607	.3011
$5b_{1u}$	-6.964	.5701	-.5488	.0961	-.0341	-.0326
$5b_{2g}$	-6.996	.5657	-.5473	.1168	-.0672	-.0661
$4b_{3g}$	-9.659	.6056	-.6511	.0774	0	.0247
$4a_u$	-9.675	.6047	-.6511	.0836	0	.0408

PYRACENE π MO's from method (5), with $k=1.75$

and taking $\alpha_H = -13.6$, $\alpha_C = -11.4$

symmetry	energy	MO coefficients				
		c_1	c_2	c_5	c_6	c_8
$1b_{1u}$	-16.165	.2014	.2445	.1162	.1079	.0509
$1b_{2g}$	-16.087	.2145	.2609	.0973	.0532	.0228
$2b_{1u}$	-14.538	.1102	.1304	-.1917	-.3298	-.1971
$2b_{3g}$	-14.433	.1674	.2103	.2065	0	-.2212
$1a_u$	-14.114	.2315	.2912	.1760	0	-.0666
$2b_{3g}$	-13.287	.1948	.2421	-.0726	0	.3042
$2b_{2g}$	-12.832	-.0959	-.1008	.3382	.3050	.1651
$3b_{1u}$	-12.699	.0158	.0093	-.0208	-.3945	.3652
$2a_u$	-11.388	.1418	.1599	-.3524	0	.2790
$3b_{3g}$	-8.749	.1111	.0936	-.4806	0	-.2693
$3b_{2g}$	-8.169	.0181	-.0024	-.0171	-.4721	.4820
$4b_{1u}$	-6.895	.0796	.0337	-.4934	.4249	.1964
$3a_u$	-5.899	.0718	.0348	-.3618	0	-.5215
$4b_{2g}$	-2.943	.0722	.0005	-.4220	.6614	.3054
$5b_{1u}$	7.292	.5758	-.5459	.0728	-.0216	-.0257
$5b_{2g}$	7.331	.5746	-.5459	.0820	-.0326	-.0455
$4b_{3g}$	13.960	.6197	-.6370	.0617	0	.0206
$4a_u$	13.986	.6192	-.6372	.0661	0	.0324

PYRACENE π MO's from method XR5, with $k = 1.75$.

CH_2 parameters taken as $1.08 \text{ \AA}$, $109^\circ 28'$

MO coefficients						
symmetry	energy	c_1	c_2	c_5	c_6	c_8
$1b_{1u}$	-16.109	.2012	.2447	.1194	.1094	.0544
$1b_{2g}$	-16.029	.2152	.2622	.0999	.0500	.0254
$2b_{1u}$	-14.555	.1123	.1331	-.1869	-.3395	-.1892
$2b_{3g}$	-14.472	.1778	.2239	.2008	0	-.2025
$1a_u$	-14.212	.2307	.2907	.1702	0	-.0682
$2b_{3g}$	-13.304	.1846	.2292	-.0965	0	.3131
$2b_{2g}$	-12.848	.0964	.1019	-.3375	-.2844	-.1816
$3b_{1u}$	-12.622	.0086	.0022	-.0015	-.3995	.3666
$2a_u$	-11.558	.1376	.1556	-.3425	0	.2874
$3b_{3g}$	-8.571	.1066	.0855	-.4814	0	-.2820
$3b_{2g}$	-8.196	.0212	.0005	-.0500	-.4743	.4776
$4b_{1u}$	-7.066	.0840	.0351	-.4930	.3964	.2115
$3a_u$	-5.942	.0738	.0347	-.3759	0	-.5098
$4b_{2g}$	-2.921	.0770	-.0013	-.4166	.6812	.2901
$5b_{1u}$	7.561	.5772	-.5498	.0764	-.0247	-.0272
$5b_{2g}$	7.600	.5757	-.5497	.0870	-.0426	-.0467
$4b_{3g}$	13.590	.6179	-.6313	.0639	0	.0219
$4a_u$	13.614	.6175	-.6315	.0681	0	.0333

ACENAPHTHENE π MOs from method (3)

MO number																	
1		2		3		4		5		6		7		8			
1b1		2b1		1a2		2a2		3b1		4b1		3a2		4a2			
Energy Levels		1.646		1.410		1.322		1.101		0.941		0.796		0.496		-0.718	
Molecular Orbital coefficients																	
1		-0.2633		-0.1517		-0.3263		-0.1942		-0.1218				-0.1490		-0.1347	
2		-0.3751		-0.1748		-0.3470		-0.1676		-0.0896				-0.0662		0.0097	
3		-0.3751		-0.1748		0.3470		0.1676		-0.0896				0.0662		-0.0097	
4		-0.2633		-0.1517		0.3263		0.1942		-0.1218				0.1490		0.1347	
5		-0.1964		0.1498		-0.2188		0.1186		0.3369				0.3719		0.4522	
6		-0.1753		0.3087						0.3240		0.3654					
7		-0.1964		0.1498		0.2188		-0.1186		0.3369				-0.3719		-0.4522	
8		-0.0876		0.1543		0.1668		-0.3105		0.1620		-0.3654		-0.2630		0.2842	
9		-0.0502		0.1882		0.1124		-0.3557		-0.1364		-0.3654		0.2220		0.2782	
10		-0.0535		0.2578		0.0566		-0.2329		-0.3308				0.3895		-0.4545	
11		-0.1003		0.3764						-0.2729		0.3654					
12		-0.0535		0.2578		-0.0566		0.2329		-0.3308				-0.3895		0.4545	
13		-0.0502		0.1882		-0.1124		0.3557		-0.1364		-0.3654		-0.2220		-0.2782	
14		-0.0876		0.1543		-0.1668		0.3105		0.1620		-0.3654		0.2630		-0.2842	
MO number																	
9		10		11		12		13		14							
5b1		6b1		5a2		7b1		8b1		6a2							
Energy Levels		-1.323		-1.837		-2.641		-4.688		-7.262		-14.846					
Molecular Orbital coefficients																	
1				-0.1927		-0.1096		0.4485		0.6577		0.9346					
2				0.0690		0.0552		-0.3378		-0.6171		-1.1118					
3				0.0690		-0.0552		-0.3378		-0.6171		1.1118					
4				-0.1927		0.1096		0.4485		0.6577		-0.9346					
5				0.4667		0.3106		-0.2281		0.4691		0.3049					
6		0.4709		-0.4295				0.5041		-0.4939							
7				0.4667		-0.3106		-0.2281		0.4691		-0.3049					
8		-0.4709		-0.2148		0.5398		0.2520		-0.2469		0.1081					
9		0.4709		-0.1948		-0.5533		-0.3192		0.1716		-0.0379					
10				0.4614		0.3457		0.4410		-0.1984		0.0120					
11		-0.4709		-0.3895				-0.6383		0.3433							
12				0.4614		-0.3457		0.4410		-0.1984		-0.0120					
13		0.4709		-0.1948		0.5533		-0.3192		0.1716		0.0379					
14		-0.4709		-0.2148		-0.5398		0.2520		-0.2469		-0.1081					

ACENAPHTHENE π MOs from method (3)ORTHOGONAL VECTOR COEFFICIENTS

MO number

1	2	3	4	5	6	7	8
1b1	2b1	1a2	2a2	3b1	4b1	3a2	4a2

Energy Levels

1.646	1.410	1.322	1.101	0.941	0.796	0.496	-0.718
-------	-------	-------	-------	-------	-------	-------	--------

Orthogonal Vectors

1	-0.3676	-0.2017	-0.4269	-0.2441	-0.1488		-0.1700	-0.1321
2	-0.4924	-0.2182	-0.4253	-0.1967	-0.1024		-0.0696	0.0108
3	-0.4924	-0.2182	0.4253	0.1967	-0.1024		0.0696	-0.0108
4	-0.3676	-0.2017	0.4269	0.2441	-0.1488		0.1700	0.1321
5	-0.2561	0.1861	-0.2677	0.1391	0.3851		0.3972	0.4161
6	-0.2285	0.3836			0.3705	0.4082		
7	-0.2561	0.1861	0.2677	-0.1391	0.3851		-0.3972	-0.4161
8	-0.1142	0.1918	0.2038	-0.3647	0.1853	-0.4082	-0.2811	0.2617
9	-0.0654	0.2339	0.1374	-0.4178	-0.1560	-0.4082	0.2372	0.2562
10	-0.0697	0.3204	0.0692	-0.2735	-0.3783		0.4162	-0.4185
11	-0.1308	0.4677			-0.3120	0.4082		
12	-0.0697	0.3204	-0.0692	0.2735	-0.3783		-0.4162	0.4185
13	-0.0654	0.2339	-0.1374	0.4178	-0.1560	-0.4082	-0.2372	-0.2562
14	-0.1142	0.1918	-0.2038	0.3647	0.1853	-0.4082	0.2811	-0.2617

MO number

9	10	11	12	13	14
5b1	6b1	5a2	7b1	8b1	6a2

Energy Levels

-1.323	-1.837	-2.641	-4.688	-7.262	-14.846
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Orthogonal Vectors

1		-0.1693	-0.0903	0.3213	0.4125	0.4513
2		0.0594	0.0446	-0.2347	-0.3752	-0.5229
3		0.0594	-0.0446	-0.2347	-0.3752	0.5229
4		-0.1693	0.0903	0.3213	0.4125	-0.4513
5		0.3862	0.2409	-0.1542	0.2803	0.1416
6	0.4082	-0.3555		0.3418	-0.2946	
7		0.3862	-0.2409	-0.1542	0.2803	-0.1416
8	-0.4082	-0.1778	0.4189	0.1709	-0.1473	0.0500
9	0.4082	-0.1612	-0.4294	-0.2166	0.1023	-0.0175
10		0.3820	0.2683	0.2992	-0.1183	0.0055
11	-0.4082	-0.3225		-0.4331	0.2046	
12		0.3820	-0.2683	0.2992	-0.1183	-0.0055
13	0.4082	-0.1612	0.4294	-0.2166	0.1023	0.0175
14	-0.4082	-0.1778	-0.4189	0.1709	-0.1473	-0.0500

ACENAPHTHENE - π MOs from method (4)

MO number	1	2	3	4	5	6	7	8
	1b1	2b1	1a2	2a2	3b1	4b1	3a2	4a2
Energy Levels	1.932	1.523	1.284	0.930	0.762	0.608	0.145	-1.106
Molecular Orbital coefficients								
1	0.2564	0.1661	0.1829	-0.3057	0.1352	-0.0310	-0.1920	-0.1409
2	0.3154	0.1871	0.2067	-0.3281	0.1234	-0.0197	-0.1740	-0.0795
3	0.3154	0.1871	-0.2067	0.3280	0.1234	-0.0197	0.1740	0.0795
4	0.2564	0.1661	-0.1829	0.3057	0.1352	-0.0310	0.1920	0.1410
5	0.2036	-0.1053	0.2699	-0.0938	-0.3403	0.0500	0.3196	0.4889
6	0.1939	-0.2492			-0.3105	0.4189		
7	0.2036	-0.1053	-0.2699	0.0938	-0.3403	0.0500	-0.3196	-0.4889
8	0.0945	-0.1520	-0.3045	-0.1514	-0.2199	-0.3494	-0.3314	0.2317
9	0.0582	-0.2029	-0.2616	-0.2933	0.0915	-0.3790	0.1833	0.3299
10	0.0627	-0.2685	-0.1552	-0.2248	0.3320	-0.0088	0.4048	-0.4560
11	0.1105	-0.3583			0.2743	0.3646		
12	0.0627	-0.2685	0.1552	0.2248	0.3320	-0.0088	-0.4048	0.4560
13	0.0582	-0.2029	0.2616	0.2933	0.0915	-0.3790	-0.1833	-0.3299
14	0.0945	-0.1520	0.3045	0.1514	-0.2199	-0.3494	0.3314	-0.2317

MO number	9	10	11	12	13	14
	5b1	6b1	5a2	7b1	8b1	6a2
Energy Levels	-1.512	-2.008	-2.519	-3.899	-6.983	-9.666
Molecular Orbital coefficients						
1	0.0217	0.1047	-0.0920	-0.1129	-0.8032	0.8558
2	-0.0066	0.0141	-0.0151	0.0361	0.7751	-0.9208
3	-0.0066	0.0141	0.0151	0.0361	0.7751	0.9208
4	0.0217	0.1047	0.0920	-0.1129	-0.8031	-0.8559
5	-0.0108	-0.4851	0.3705	0.4237	-0.1508	0.1138
6	-0.4741	0.4006		-0.6726	0.0721	
7	-0.0108	-0.4851	-0.3705	0.4237	-0.1509	-0.1137
8	0.4812	0.1899	0.5371	-0.3075	0.0702	0.0463
9	-0.4870	0.2066	-0.5216	0.3029	-0.0240	-0.0114
10	0.0221	-0.4862	0.3275	-0.4022	0.0146	0.0042
11	0.4620	0.4644		0.6602	-0.0237	
12	0.0221	-0.4862	-0.3275	-0.4022	0.0146	-0.0042
13	-0.4870	0.2066	0.5216	0.3029	-0.0240	0.0114
14	0.4812	0.1899	-0.5371	-0.3075	0.0702	-0.0463

REFERENCES

- [1] Griffith, J.S., 1961, The Theory of Transition-metal Ions, Cambridge, p.325;
Bleaney, B., and Stevens, K., 1953, Rep. Prog. Phys., 16, 131
- [2] Bloembergen, N., and Dickinson, W., 1950, Phys. Rev., 79, 179
- [3] Golding, R.M., 1964, Mol. Phys., 8, 561
- [4] Mackie, A.G., 1965, Boundary Value Problems, Oliver and Boyd, pp 12, 159
- [5] Hoffmann, R., 1963, J. Chem. Phys., 39, 1397
- [6] Lipkin et al, 1953, Science, 117, 534
- [7] Fraenkel, G.K., 1956, J. Chem. Phys., 24, 737
- [8] McConnell, H.M., 1956, J. Chem. Phys., 24, 764
- [9] Weissman, S.I., 1956, J. Chem. Phys., 25, 890
- [10] McConnell, H.M., and Chesnut, R., 1958, J. Chem. Phys., 28, 107
- [11] Colpa, J.P., and Bolton, J.R., 1963, Mol. Phys., 6, 273
- [12] Carrington, A., 1963, Quart. Rev., 17, 66
- [13] Colpa, J.P., and de Boer, E., 1964, Mol. Phys., 7, 333
- [14] McLachlan, A., 1958, Mol. Phys., 1, 233
- [15] Altmann, S.L., 1952, Proc. Roy. Soc., A210, 327
- [16] Condon, E.U., and Shortley, G.H., 1963, The Theory of Atomic Spectra, Cambridge, p.177
- [17] Hinze, J., and Jaffe, H.H., 1963, J. Chem. Phys., 38, 1834
- [18] Voge, H.H., 1948, J. Chem. Phys., 16, 984
- [19] McConnell, H.M., 1958, J. Chem. Phys., 28, 115
- [20] Fraenkel, G.K., and Karplus, M., 1961, J. Chem. Phys., 35, 1312
- [21] Weissman, S.I., 1957, J. Chem. Phys., 28, 61

- [22] Kotani, M., et al, 1955, Table of Molecular Integrals, Maruzen Co., Tokyo
- [23] Silbey, R., et al, 1965, J. Chem. Phys., 42, 444
- [24] Trotter, J., 1964, Crystal Structure Studies of Aromatic Hydrocarbons, Royal Institute of Chemistry
- [25] Bolton, J.R., 1965, to be published
- [26] Golding, R.M., private communication
- [27] Lowdin, P.O., 1950, J. Chem. Phys., 18, 365
- [28] Lohr, L.L., and Lipscomb, W.N., 1963, J. Chem. Phys., 38, 1607
- [29] Slater, J.C., 1930, Phys. Rev., 36, 57; Appendix V, this thesis
- [30] Simmons, G.L., and Lingafelter, E.C., 1961, Acta. Cryst., 14, 872
- [31] Coulson, C.A., and Crawford, V.A., 1953, J. Chem. Soc., 2052
- [32] Moore, C.E., 1949, Atomic Energy Levels, Nat. Bur. Stnds circular no. 467
- [33] Muller, N., Pickett, and Mulliken, 1954, J. Am. Chem. Soc., 76, 4770
- [34] Hoffmann, R., and Lipscomb, W., 1962, J. Chem. Phys., 36, 2179
- [35] Mulliken, R.S., Rieke, Orloff, and Orloff, 1949, J. Chem. Phys., 17, 1248
- [36] Condon, E.U., and Shortley, G.H., 1963, *ibid*, p. 76
- [37] McWeeny, R., 1954, Proc. Roy. Soc., A223, 63, 306
- [38] Condon, E.U., and Shortley, G.H., 1963, *ibid*, p.169
- [39] Parr, Craig, and Ross, 1950, J. Chem. Phys., 18, 1561; McConnell, H.M., 1958, J. Chem. Phys., 28, 1190
- [40] Mulliken, R.S., 1955, J. Chem. Phys., 23, 1833, 1841
- [41] Ballhausen, C.J., and Gray, H.B., 1964, Molecular Orbital Theory, Benjamin
- [42] Danenberg et al, 1956, Chem. Ber., 89, 1326

- [43] Viste, A., and Gray, H.B., 1964, Inorg. Chem, 3, 1113
- [44] Hinze, J., and Jaffe, H.H., 1962, J. Am. Chem. Soc.,
84, 540
- [45] Branscomb, L.M., et al, 1958, Phys. Rev., 111, 504
- [46] Lohr, L.L, and Lipscomb, W.N., 1963, J. Chem. Phys.,
38, 1607