# THEORETICAL STUDIES IN NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

A Thesis submitted by

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## Abstract

In Part I the analysis of spin-spin multiplets encountered in nuclear magnetic resonance spectra is presented with particular reference to the programming of $A_2B_2$ and ABC systems. Applications to practical spectra are given.

Part II describes theoretical studies of the ring current contribution to the chemical shift and diamagnetic anisotropy. The factors influencing the shielding of protons in aromatic systems are reviewed. A new perturbation theory for a self-consistent field treatment is presented, results for a number of molecules are obtained and compared with those of a more approximate theory developed by McWeeny. It is shown that the new theory improves appreciably the value for the ring current contribution to these two quantities, when heteroatoms are present in the molecule. The method has been applied to naphthalene, azulene, 1-Me-2-pyridone, 1-Me-4-pyridone, 1-Me-2-cyclopentadienyl-1,2—dihydropyridine, 1-Me-4-cyclopentadienyl-1,4-dihydropyridine, 4-(1-Indenylidene)-1-Me--1,4-dihydropyridine, cyclazine, pyridine, pyrimidine, S-triazine, cyclopentadienyl ion, tropilium ion, and where possible compared with experiment.

This theory is developed in a general form, based on Schrödinger formulation, which should be applicable to molecules where the $\sigma$- and $\pi$-electronic systems are not separable.

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# Analysis of Spin-Spin Multiplets

## I. Introduction

The mathematical theory of spin-spin coupling is well developed[1,2,3,4].

The Hamiltonian of a system of nuclei is built up from two terms

$$\underline{H}^{(o)} = (2\pi)^{-1} \sum_i \gamma_i H_i I_z (i)$$

$$\underline{H}^{(1)} = \sum_{i<j} J_{ij} \underline{I}(i) \cdot \underline{I}(j)$$

where $\gamma_i$ is the magnetogyric ratio of nucleus i, $H_i$ is the magnetic field experienced by nucleus i, and the direction of the applied magnetic field $H_o$ is considered as the negative $\underline{z}$ direction. $I_z$ is the component of the spin in the $\underline{z}$ direction. $J_{ij}$ are the coupling constants. We can put

$$H_i = H_o (1 - \sigma_i)$$

$\sigma_i$ being the shielding constant.

The simplest set of functions describing this many-spin system would be the $2^p$ basic product spin functions

$\psi_n = \alpha(1)\,\beta(2)\,\alpha(3)\,\ldots\,\beta(p)$ and the Hamiltonian can be simplified if the molecule possesses elements of symmetry, using a linear combination of basic product function $\psi_n$.

It can also be shown[2] that for nuclei with $I = \frac{1}{2}$

1) $\underline{H}^{(o)}$ is a diagonal matrix with elements

$$\langle \psi_m | \underline{H}^{(o)} | \psi_m \rangle = (2\pi)^{-1} \sum_i \gamma_i H_i \langle I_z(i) \rangle_m$$

where $|I_z^{(i)}|_m$ is $\frac{1}{2}$ if nucleus i has $\alpha$ spin in $\psi_m$ and $-\frac{1}{2}$ if it has $\beta$ spin.

2) The matrix elements of $\underline{H}^{(1)}$ are,

$$\langle \psi_m | \underline{H}^{(1)} | \psi_m \rangle = \tfrac{1}{4} \sum_{i<j} J_{ij} T_{ij}$$

$$\langle \psi_m | \underline{H}^{(1)} | \psi_n \rangle = \tfrac{1}{2} \mathcal{V} J_{ij}$$

where $T_{ij} = \pm 1$ depending on whether spins i and j are parallel or antiparallel in $\psi_m$, and $\mathcal{V} = 1$ if $\psi_m$ differs from $\psi_n$ by an interchange of spins i and j, and zero if otherwise.

3) No mixing occurs between functions with different values of the total spin component $F_z$ neither between

functions of different symmetry.

4) The number of possible transitions is limited by the selection rule $\Delta F_z = \pm 1$.

With these rules, the Hamiltonian can be constructed, and the eigenvalues, and hence transition energies, and eigenvectors found by solving the secular equation

$$| \underline{H}_{mn} - E\delta_{mn} | = 0$$

The eigenvectors of the Hamiltonian yield the intensities of the transitions since the intensities of the lines are proportional to the transition probability in the x direction:

$$\hbar^2 \left| \langle q | \sum_i \gamma_i I_x(i) | q' \rangle \right|^2 \qquad (1)$$

for the $q \longrightarrow q'$ transition.

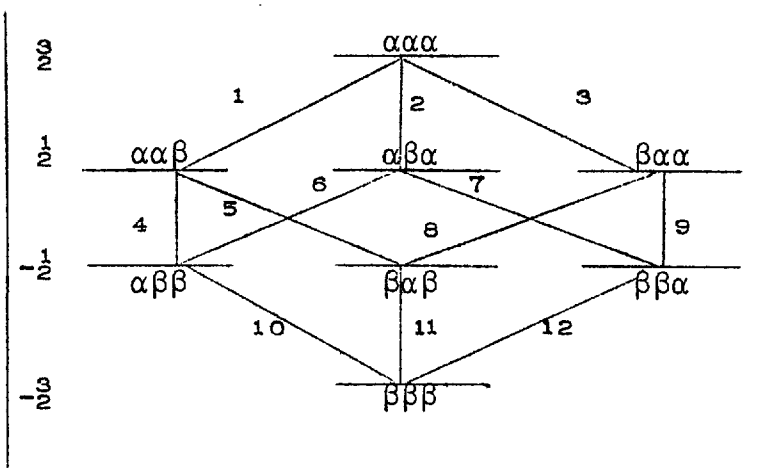
Returning to the Hamiltonian $\underline{H}$, it can be seen that the problem of the analysis of spectra can be divided into two main categories:

a) The Hamiltonian is such that explicit expressions for the energies can be derived.

b) No explicit expressions can be derived and solution of the problem involves iterative methods.

In the last case the technique developed by Reilly and Swalen[5] has been followed.

Estimates are made of the spectral parameters, and the corresponding Hamiltonian is built up. The eigenvalues and eigenvectors of this Hamiltonian, $\underline{H}$, are found. From the experimental spectrum, a transition energy diagram is constructed, from which the experimental energy levels, i.e. the experimental eigenvalues




Numbers refer to transitions in table 6

$\Lambda_{iexp}$, are derived. The iterative process consists of applying the following transformation to the diagonal matrix $\Lambda_{exp}$.

$$V . \Lambda_{exp} . V^{-1} = \underline{H}_1$$

where $V$ is the matrix, the columns of which are the eigenvectors of the approximate Hamiltonian $\underline{H}$. $\underline{H}_1$ is a better approximation. From $\underline{H}_1$ improved values of the parameters are obtained, a new Hamiltonian is formed, and the process is repeated.

In connection with certain chemical and stereochemical problems it was necessary to analyse $A_2B_2$ * and ABC spectra. The problem investigated here consists essentially of rewriting Reilly's method in a form which allows the matrix interpretive Scheme B programme of DEUCE computer to be used.

The Scheme B programme is a form of orthocode which enables nearly all operations with matrices to be performed.

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* Groups of equivalent nuclei for which the chemical shifts and coupling constants are of the same order are symbolized by $A_n B_m$ ....., where the subscripts refer to the number of nuclei in the group and A,B ... are in order of increasing $\tau = 10 - \frac{\Delta(Me_{14}Si) \cdot 10^6}{\text{oscillator frequency}(c/s)}$ (6) where $\Delta$ in c/s is the difference in chemical shift between the proton and the proton of $Me_{14}Si$ being considered + if the latter is at higher field.

## II. COMPUTATIONAL PROCEDURES FOR A THREE SPIN AND A FOUR SPIN SYSTEM.

### 1) $A_2B_2$ SPIN SYSTEM.

The $A_2B_2$ spin system consists of two pairs of equivalent protons in which the chemical shift between the pairs is of the same order as the coupling constants for the interaction between them.

The resonance frequency of the two groups in the absence of spin coupling, are

$$\nu_A = (2\pi)^{-1} \gamma_A H_o (1 - \sigma_A)$$

$$\nu_B = (2\pi)^{-1} \gamma_B H_o (1 - \sigma_B)$$

Following Pople et al.[2] we suppose $\nu_A > \nu_B$ and define

$$K = J_A + J_B$$
$$M = J_A - J_B$$
$$L = J - J'$$
$$N = J + J'$$

in which the J's are given in fig. I, and where

$$\nu_o \delta = \nu_o (\sigma_A - \sigma_B) = \nu_A - \nu_B$$

$\cos 2\theta_a$: $\sin 2\theta_a$: $1 = K : L : (K^2 + L^2)^{\frac{1}{2}}$

$\cos 2\phi$ : $\sin 2\phi$ : $1 = \nu_o\delta : N : [(\nu_o\delta)^2 + N^2]^{\frac{1}{2}}$

$\cos 2\psi_{\pm}$: $\sin 2\psi_{\pm}$: $1 = (\nu_o\delta \pm M) : L : [(\nu_o\delta \pm M)^2 + L^2]^{\frac{1}{2}}$

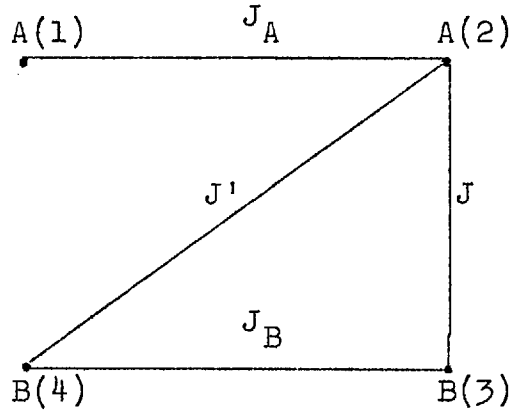



Fig. I.

Tables 1, 2, 3 give the matrix elements, explicit eigenvalues, and explicit transition frequencies respectively.

TABLE 1. BASIC FUNCTIONS AND COMPLETE MATRIX OF HAMILTONIAN H FOR FOUR NUCLEI $A_2B_2$

| 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|
| $s_2$ | $\alpha\alpha$ | $\alpha\alpha$ | $\mathcal{V}_A + \mathcal{V}_B + \frac{1}{2}N$ | |
| $1s_1$ | $2^{-\frac{1}{2}}(\alpha\beta+\beta\alpha)$ | $\alpha\alpha$ | $\mathcal{V}_B$ | $\langle 1s_1\|H\|2s_1\rangle = \frac{1}{2}N$ |
| $2s_1$ | $\alpha\alpha$ | $2^{-\frac{1}{2}}(\alpha\beta+\beta\alpha)$ | $\mathcal{V}_A$ | |
| $1s_0$ | $\beta\beta$ | $\alpha\alpha$ | $-\mathcal{V}_A + \mathcal{V}_B - \frac{1}{2}N$ | $\langle 1s_0\|H\|2s_0\rangle = 0$ $\langle 2s_0\|H\|3s_0\rangle = \frac{1}{2}L$ |
| $2s_0$ | $\alpha\alpha$ | $\beta\beta$ | $\mathcal{V}_A - \mathcal{V}_B - \frac{1}{2}N$ | $\langle 1s_0\|H\|3s_0\rangle = \frac{1}{2}L$ $\langle 2s_0\|H\|4s_0\rangle = \frac{1}{2}N$ |
| $3s_0$ | $2^{-\frac{1}{2}}(\alpha\beta-\beta\alpha)$ | $2^{-\frac{1}{2}}(\alpha\beta-\beta\alpha)$ | $-K$ | $\langle 1s_0\|H\|4s_0\rangle = \frac{1}{2}N$ $\langle 3s_0\|H\|4s_0\rangle = \frac{1}{2}L$ |
| $4s_0$ | $2^{-\frac{1}{2}}(\alpha\beta+\beta\alpha)$ | $2^{-\frac{1}{2}}(\alpha\beta+\beta\alpha)$ | 0 | |
| $1s_{-1}$ | $2^{-\frac{1}{2}}(\alpha\beta+\beta\alpha)$ | $\beta\beta$ | $-\mathcal{V}_B$ | $\langle 1s_{-1}\|H\|2s_{-1}\rangle = \frac{1}{2}N$ |
| $2s_{-1}$ | $\beta\beta$ | $2^{-\frac{1}{2}}(\alpha\beta+\beta\alpha)$ | $-\mathcal{V}_A$ | |
| $s_{-2}$ | $\beta\beta$ | $\beta\beta$ | $-\mathcal{V}_A - \mathcal{V}_B + \frac{1}{2}N$ | |
| $1a_1$ | $2^{-\frac{1}{2}}(\alpha\beta-\beta\alpha)$ | $\alpha\alpha$ | $\mathcal{V}_B - \frac{1}{2}K - \frac{1}{2}M$ | $\langle 1a_1\|H\|2a_1\rangle = -\frac{1}{2}L$ |
| $2a_1$ | $\alpha\alpha$ | $2^{-\frac{1}{2}}(\alpha\beta-\beta\alpha)$ | $\mathcal{V}_A - \frac{1}{2}K + \frac{1}{2}M$ | |
| $1a_0$ | $2^{-\frac{1}{2}}(\alpha\beta+\beta\alpha)$ | $2^{-\frac{1}{2}}(\alpha\beta-\beta\alpha)$ | $-\frac{1}{2}K + \frac{1}{2}M$ | $\langle 1a_0\|H\|2a_0\rangle = -\frac{1}{2}L$ |
| $2a_0$ | $2^{-\frac{1}{2}}(\alpha\beta-\beta\alpha)$ | $2^{-\frac{1}{2}}(\alpha\beta+\beta\alpha)$ | $-\frac{1}{2}K - \frac{1}{2}M$ | |
| $1a_{-1}$ | $2^{-\frac{1}{2}}(\alpha\beta-\beta\alpha)$ | $\beta\beta$ | $-\mathcal{V}_B - \frac{1}{2}K - \frac{1}{2}M$ | $\langle 1a_{-1}\|H\|2a_{-1}\rangle = -\frac{1}{2}L$ |
| $2a_{-1}$ | $\beta\beta$ | $2^{-\frac{1}{2}}(\alpha\beta-\beta\alpha)$ | $-\mathcal{V}_A - \frac{1}{2}K + \frac{1}{2}M$ | |

1.- Function $\alpha\alpha\beta\beta$ means $\alpha(1)\alpha(2)\beta(3)\beta(4)$, the numbering being as in Fig.I

2.- Nuclei A. 3.- Nuclei B.

4.- Diagonal matrix elements, from which $\frac{1}{4}K$ has been subtracted.

5.- Off-diagonal matrix elements.

TABLE 2. EXPLICIT EXPRESSION FOR ENERGIES AND WAVE FUNCTIONS FOR FOUR NUCLEI $A_2B_2$.

| State | Energy | Wave Function |
|---|---|---|
| $s_2$ | $\nu_A+\nu_B+\frac{1}{2}N$ | $s_2$ |
| $1s_{1,1}$ | $\frac{1}{2}(\nu_A+\nu_B)-\frac{1}{2}[(\nu_0\delta)^2+N^2]^{\frac{1}{2}}$ | $(1s_1)\cos\phi-(2s_1)\sin\phi$ |
| $2s_{1,1}$ | $\frac{1}{2}(\nu_A+\nu_B)+\frac{1}{2}[(\nu_0\delta)^2+N^2]^{\frac{1}{2}}$ | $(1s_1)\sin\phi+(2s_1)\cos\phi$ |
| $1s_{1,-1}$ | $-\frac{1}{2}(\nu_A+\nu_B)+\frac{1}{2}[(\nu_0\delta)^2+N^2]^{\frac{1}{2}}$ | $(1s_{-1})\cos\phi+(2s_{-1})\sin\phi$ |
| $2s_{1,-1}$ | $-\frac{1}{2}(\nu_A+\nu_B)-\frac{1}{2}[(\nu_0\delta)^2+N^2]^{\frac{1}{2}}$ | $-(1s_{-1})\sin\phi+(2s_{-1})\cos\phi$ |
| $s_{-2}$ | $-(\nu_A+\nu_B)+\frac{1}{2}N$ | $s_{-2}$ |
| $1a_{1,1}$ | $\frac{1}{2}(\nu_A+\nu_B)-\frac{1}{2}K-\frac{1}{2}[(\nu_0\delta+M)^2+L^2]^{\frac{1}{2}}$ | $(1a_1)\cos\psi_+ + (2a_1)\sin\psi_+$ |
| $2a_{1,1}$ | $\frac{1}{2}(\nu_A+\nu_B)-\frac{1}{2}K+\frac{1}{2}[(\nu_0\delta+M)^2+L^2]^{\frac{1}{2}}$ | $-(1a_1)\sin\psi_+ + (2a_1)\cos\psi_+$ |
| $1a_{1,0}$ | $-\frac{1}{2}K+\frac{1}{2}(M^2+L^2)^{\frac{1}{2}}$ | $(1a_0)\cos\theta_a-(2a_0)\sin\theta_a$ |
| $2a_{1,0}$ | $-\frac{1}{2}K-\frac{1}{2}(M^2+L^2)^{\frac{1}{2}}$ | $(1a_0)\sin\theta_a+(2a_0)\cos\theta_a$ |
| $1a_{1,-1}$ | $-\frac{1}{2}(\nu_A+\nu_B)-\frac{1}{2}K+\frac{1}{2}[(\nu_0\delta-M)^2+L^2]^{\frac{1}{2}}$ | $(1a_{-1})\cos\psi_- -(2a_{-1})\sin\psi_-$ |
| $2a_{1,-1}$ | $-\frac{1}{2}(\nu_A+\nu_B)-\frac{1}{2}K-\frac{1}{2}[(\nu_0\delta-M)^2+L^2]^{\frac{1}{2}}$ | $(1a_{-1})\sin\psi_-+(2a_{-1})\cos\psi_-$ |

TABLE 3. ENERGIES AND INTENSITIES OF A TRANSITIONS FOR FOUR NUCLEI $A_2B_2$.

| Transition | Energy relative to $\frac{1}{2}(\nu_A+\nu_B)$ | Intensity |
|---|---|---|
| 1*. $1s_{,1} \longrightarrow s_2$ | $\frac{1}{2}N+\frac{1}{2}\sqrt{(\nu_0\delta)^2+N^2}$ | $1 - \sin 2\phi$ |
| 2*. $1s_{,0} \longrightarrow 1s_{,1}$ | | |
| 3*. $s_{-2} \longrightarrow 1s_{,-1}$ | $-\frac{1}{2}N+\frac{1}{2}\sqrt{(\nu_0\delta)^2+N^2}$ | $1 + \sin 2\phi$ |
| 4*. $1s_{,-1} \longrightarrow 2s_{,0}$ | | |
| 5*. $3s_{,0} \longrightarrow 2s_{,1}$ | | |
| 6*. $2s_{,-1} \longrightarrow 4s_{,0}$ | | |
| 7*. $4s_{,0} \longrightarrow 2s_{,1}$ | | |
| 8*. $2s_{,-1} \longrightarrow 3s_{,0}$ | | |
| 9*. $2a_{,0} \longrightarrow 2a_{,1}$ | $\frac{1}{2}\sqrt{(\nu_0\delta+M)^2+L^2}+\frac{1}{2}(M^2+L^2)^{\frac{1}{2}}$ | $\sin^2(\theta_a-\psi_+)$ |
| 10*. $2a_{,-1} \longrightarrow 1a_{,0}$ | $\frac{1}{2}\sqrt{(\nu_0\delta-M)^2+L^2}+\frac{1}{2}(M^2+L^2)^{\frac{1}{2}}$ | $\cos^2(\theta_a+\psi_-)$ |
| 11*. $1a_{,0} \longrightarrow 2a_{,1}$ | $\frac{1}{2}\sqrt{(\nu_0\delta+M)^2+L^2}-\frac{1}{2}(M^2+L^2)^{\frac{1}{2}}$ | $\cos^2(\theta_a-\psi_+)$ |
| 12*. $2a_{,-1} \longrightarrow 2a_{,0}$ | $\frac{1}{2}\sqrt{(\nu_0\delta-M)^2+L^2}-\frac{1}{2}(M^2+L^2)^{\frac{1}{2}}$ | $\sin^2(\theta_a+\psi_-)$ |

From these expressions it follows that:

$$N = 1^* - 3^*$$

$$\nu_0\delta = (1^* \times 3^*)^{\frac{1}{2}} + \left\{\tfrac{1}{2}(9^* \times 11^* + 10^* \times 12^*)\right\}^{\frac{1}{2}}$$

$$M = (9^* \times 11^* - 10^* \times 12^*)/\nu_0\delta$$

$$L = \tfrac{1}{2}\left[\left\{(9^* - 11^*)^2 - M^2\right\}^{\frac{1}{2}} + \left\{(10^* - 12^*)^2 - M^2\right\}^{\frac{1}{2}}\right]$$

$$1s_{1,0} = -\tfrac{1}{2}\left[(\nu_0\delta)^2 + N^2\right]^{\frac{1}{2}} - 2^*$$

$$2s_{1,0} = \tfrac{1}{2}\left[(\nu_0\delta)^2 + N^2\right]^{\frac{1}{2}} + 4^*$$

$$3s_{1,0} = \tfrac{1}{2}(8^* - 5^*)$$

$$4s_{1,0} = \tfrac{1}{2}(6^* - 7^*)$$

Although it has been stated[2] that the transition involving $S_0$ states can only be investigated by iterative methods, inspection of the eigenvalues and observable transition energies show that all of the former can be evaluated from the latter.

It is seen that the eigenvalues and eigenvectors corresponding to the states labelled $1s_0$, $2s_0$, $3s_0$, $4s_0$ in Table 1, require solution of a 4th order problem However an expression for K has been derived taking into account the diagonal sum rule:

$$K = 2^* + 3^* - 1^* - 4^* + \tfrac{1}{2}(5^* + 7^* - 6^* - 8^*)$$

In this way it is possible to circumvent the iterative procedure in cases where all transitions are separately resolved in the experimental spectrum.

The energies for the lines 2*, 4*, 5*, 6*, 7*, 8*, are found:

$$\underline{\text{Energy}} \quad 2^* = {}^1s_1 - {}^1s_0$$

$$4^* = {}^2s_0 - {}^1s_{-1}$$

$$5^* = {}^2s_1 - {}^3s_0$$

$$6^* = {}^4s_0 - {}^2s_{-1}$$

$$7^* = {}^2s_1 - {}^4s_0$$

$$8^* = {}^3s_0 - {}^2s_{-1}$$

where $${}^1s_1 = -\tfrac{1}{2}\left[(\nu\delta)^2 + N^2\right]^{\frac{1}{2}}$$

$${}^1s_{-1} = \tfrac{1}{2}\left[(\nu\delta)^2 + N^2\right]^{\frac{1}{2}}$$

Applying formula (1), the expressions for the intensities of the lines 2*, 4*, 5*, 6*, 7*, 8*, are derived:

$$\underline{\text{Intensity}} \quad 2^* = \left[\cos\phi.(a_1+a_4) - \sin\phi.(a_2+a_4)\right]^2$$

$$4^* = \left[\cos\phi.(b_2+b_4) + \sin\phi.(b_1+b_4)\right]^2$$

$$5^* = \left[\cos\phi.(c_2+c_4) + \sin\phi.(c_1+c_4)\right]^2$$

$$6^* = \left[\cos\phi.(d_1+d_4) - \sin\phi.(d_2+d_4)\right]^2$$

$$7^* = \left[\cos\phi.(d_2+d_4) + \sin\phi.(d_1+d_4)\right]^2$$

$$8^* = \left[\cos\phi.(c_1+c_4) - \sin\phi.(c_2+c_4)\right]^2$$

where

$$\begin{vmatrix} a_1 & a_2 & a_3 & a_4 \\ b_1 & b_2 & b_3 & b_4 \\ c_1 & c_2 & c_3 & c_4 \\ d_1 & d_2 & d_3 & d_4 \end{vmatrix}$$

is the matrix of the eigenvectors corresponding to the 4 x 4 determinant in the secular equation.

Corresponding programmes for these arithmetic operations have been written for the DEUCE computer in Alpha-code and the diagonalization of the 4th order matrix has been carried out with the Givens programme of the DEUCE library. This method consists of applying successive plane rotations to a symmetric matrix to form a codiagonal matrix, roots of which are the same as those of the original matrix. These roots are found one by one, by bisection, starting with the algebraically largest. The vectors, if required, are then found.

## 2) ABC SPIN SYSTEM

No elements of symmetry are present in this system of 3-non-equivalent nuclei each of spin $\frac{1}{2}$. Table 4 gives the Hamiltonian of the system.[2]

TABLE 4. BASIC FUNCTIONS AND MATRIX OF HAMILTONIAN H FOR THREE NUCLEI ABC.

| Basic function | $F_z$ | Diagonal Matrix Elements | Off-diagonal Elements |
|---|---|---|---|
| 1. $\alpha\alpha\alpha$ | 3/2 | $\frac{1}{2}(\nu_A+\nu_B+\nu_C)+1/4(J_{AB}+J_{BC}+J_{CA})$ | |
| 2. $\alpha\alpha\beta$ | 1/2 | $\frac{1}{2}(\nu_A+\nu_B-\nu_C)+1/4(J_{AB}-J_{BC}-J_{CA})$ | $\langle 2\|H\|3\rangle = \frac{1}{2}J_{BC}$ |
| 3. $\alpha\beta\alpha$ | 1/2 | $\frac{1}{2}(\nu_A-\nu_B+\nu_C)+1/4(-J_{AB}-J_{BC}+J_{CA})$ | $\langle 3\|H\|4\rangle = \frac{1}{2}J_{AB}$ |
| 4. $\beta\alpha\alpha$ | 1/2 | $\frac{1}{2}(-\nu_A+\nu_B+\nu_C)+1/4(-J_{AB}+J_{BC}-J_{CA})$ | $\langle 2\|H\|4\rangle = \frac{1}{2}J_{CA}$ |
| 5. $\alpha\beta\beta$ | -1/2 | $\frac{1}{2}(\nu_A-\nu_B-\nu_C)+1/4(-J_{AB}+J_{BC}-J_{CA})$ | $\langle 5\|H\|6\rangle = \frac{1}{2}J_{AB}$ |
| 6. $\beta\alpha\beta$ | -1/2 | $\frac{1}{2}(-\nu_A+\nu_B-\nu_C)+1/4(-J_{AB}-J_{BC}+J_{CA})$ | $\langle 6\|H\|7\rangle = \frac{1}{2}J_{BC}$ |
| 7. $\beta\beta\alpha$ | -1/2 | $\frac{1}{2}(-\nu_A-\nu_B+\nu_C)+1/4(J_{AB}-J_{BC}-J_{CA})$ | $\langle 5\|H\|7\rangle = \frac{1}{2}J_{CA}$ |
| 8. $\beta\beta\beta$ | -3/2 | $\frac{1}{2}(-\nu_A-\nu_B-\nu_C)+1/4(J_{AB}+J_{BC}+J_{CA})$ | |

If the eigenvalues and eigenvectors of this Hamiltonian are:

TABLE 5. EIGENVALUES AND EIGENVECTORS FOR THREE NUCLEI ABC

| Basic function | Eigenvalue | Eigenvector |
|---|---|---|
| 1. ααα | $L_1$ | 1 |
| 2. ααβ | $L_2$ | $c_{22}$ $c_{23}$ $c_{24}$ |
| 3. αβα | $L_3$ | $c_{32}$ $c_{33}$ $c_{34}$ |
| 4. βαα | $L_4$ | $c_{42}$ $c_{43}$ $c_{44}$ |
| 5. αββ | $L_5$ | $c_{55}$ $c_{56}$ $c_{57}$ |
| 6. βαβ | $L_6$ | $c_{65}$ $c_{66}$ $c_{67}$ |
| 7. ββα | $L_7$ | $c_{75}$ $c_{76}$ $c_{77}$ |
| 8. βββ | $L_8$ | 1 |

The transition lines and intensities are calculated following the rules given above. For example, the calculation of the intensity for the transition $2 \longrightarrow 5$ is performed as follows. After diagonalisation, the eigenfunctions 2 and 5 are respectively:

2. $c_{22}\alpha\alpha\beta + c_{23}\alpha\beta\alpha + c_{24}\beta\alpha\alpha$

5. $c_{55}\alpha\beta\beta + c_{56}\beta\alpha\beta + c_{57}\beta\beta\alpha$

Applying the formula (1) for the intensity, and ignoring constants:

$$I_{2\rightarrow 5} = \left|\left(c_{22}\alpha\alpha\beta + c_{23}\alpha\beta\alpha + c_{24}\beta\alpha\alpha\right|\sum \gamma_i I_x(i)\left|\, c_{55}\alpha\beta\beta + c_{56}\beta\alpha\beta + c_{57}\beta\beta\alpha\right\rangle\right|^2$$

$$= \left\{c_{22}c_{55} + c_{22}c_{56} + c_{23}c_{55} + c_{23}c_{57} + c_{24}c_{56} + c_{24}c_{57}\right\}^2$$

$$= \left\{c_{22}(c_{55}+c_{56}) + c_{23}(c_{55}+c_{57}) + c_{24}(c_{56}+c_{57})\right\}^2$$

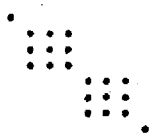
where the probability of the transition $c_{23}\alpha\alpha\beta \rightarrow c_{57}\beta\beta\alpha$ is zero, because from $\alpha\alpha\beta$ to $\beta\beta\alpha$ involves more than one change of spin, and U = 0 (rule 2). Table 6 gives the transition energies and relative intensities for three nuclei ABC.

TABLE 6. TRANSITION ENERGIES AND RELATIVE INTENSITIES FOR THREE NUCLEI ABC.

| | Transition | Origin* | Energy | Relative Intensity |
|---|---|---|---|---|
| 1 | $1 \rightarrow 2$ | C | $L_1 - L_2$ | $(c_{22}+c_{23}+c_{24})^2$ |
| 2 | $1 \rightarrow 3$ | B | $L_1 - L_3$ | $(c_{32}+c_{33}+c_{34})^2$ |
| 3 | $1 \rightarrow 4$ | A | $L_1 - L_4$ | $(c_{42}+c_{43}+c_{44})^2$ |
| 4 | $2 \rightarrow 5$ | B | $L_2 - L_5$ | $[c_{22}(c_{55}+c_{56}) + c_{23}(c_{55}+c_{57}) + c_{24}(c_{56}+c_{57})]^2$ |
| 5 | $2 \rightarrow 6$ | A | $L_2 - L_6$ | $[c_{22}(c_{65}+c_{66}) + c_{23}(c_{65}+c_{67}) + c_{24}(c_{66}+c_{67})]^2$ |
| | $2 \rightarrow 7$ | Comb. | $L_2 - L_7$ | $[c_{22}(c_{75}+c_{76}) + c_{23}(c_{75}+c_{77}) + c_{24}(c_{76}+c_{77})]^2$ |
| 6 | $3 \rightarrow 5$ | C | $L_3 - L_5$ | $[c_{32}(c_{55}+c_{56}) + c_{33}(c_{55}+c_{57}) + c_{34}(c_{56}+c_{57})]^2$ |
| | $3 \rightarrow 6$ | Comb. | $L_3 - L_6$ | $[c_{32}(c_{65}+c_{66}) + c_{33}(c_{65}+c_{67}) + c_{34}(c_{66}+c_{67})]^2$ |
| 7 | $3 \rightarrow 7$ | A | $L_3 - L_7$ | $[c_{32}(c_{75}+c_{76}) + c_{33}(c_{75}+c_{77}) + c_{34}(c_{76}+c_{77})]^2$ |
| | $4 \rightarrow 5$ | Comb. | $L_4 - L_5$ | $[c_{42}(c_{55}+c_{56}) + c_{43}(c_{55}+c_{57}) + c_{44}(c_{56}+c_{57})]^2$ |
| 8 | $4 \rightarrow 6$ | C | $L_4 - L_6$ | $[c_{42}(c_{65}+c_{66}) + c_{43}(c_{65}+c_{67}) + c_{44}(c_{66}+c_{67})]^2$ |
| 9 | $4 \rightarrow 7$ | B | $L_4 - L_7$ | $[c_{42}(c_{75}+c_{76}) + c_{43}(c_{75}+c_{77}) + c_{44}(c_{76}+c_{77})]^2$ |
| 10 | $5 \rightarrow 8$ | A | $L_5 - L_8$ | $(c_{55}+c_{56}+c_{57})^2$ |
| 11 | $6 \rightarrow 8$ | B | $L_6 - L_8$ | $(c_{65}+c_{66}+c_{67})^2$ |
| 12 | $7 \rightarrow 8$ | C | $L_7 - L_8$ | $(c_{75}+c_{76}+c_{77})^2$ |

* The various transitions may be classified according to the first-order transitions that they reduce to as the chemical shift is steadily increased. In this limit, the so-called combinations lines are forbidden.

In the ABC case, the form of H is

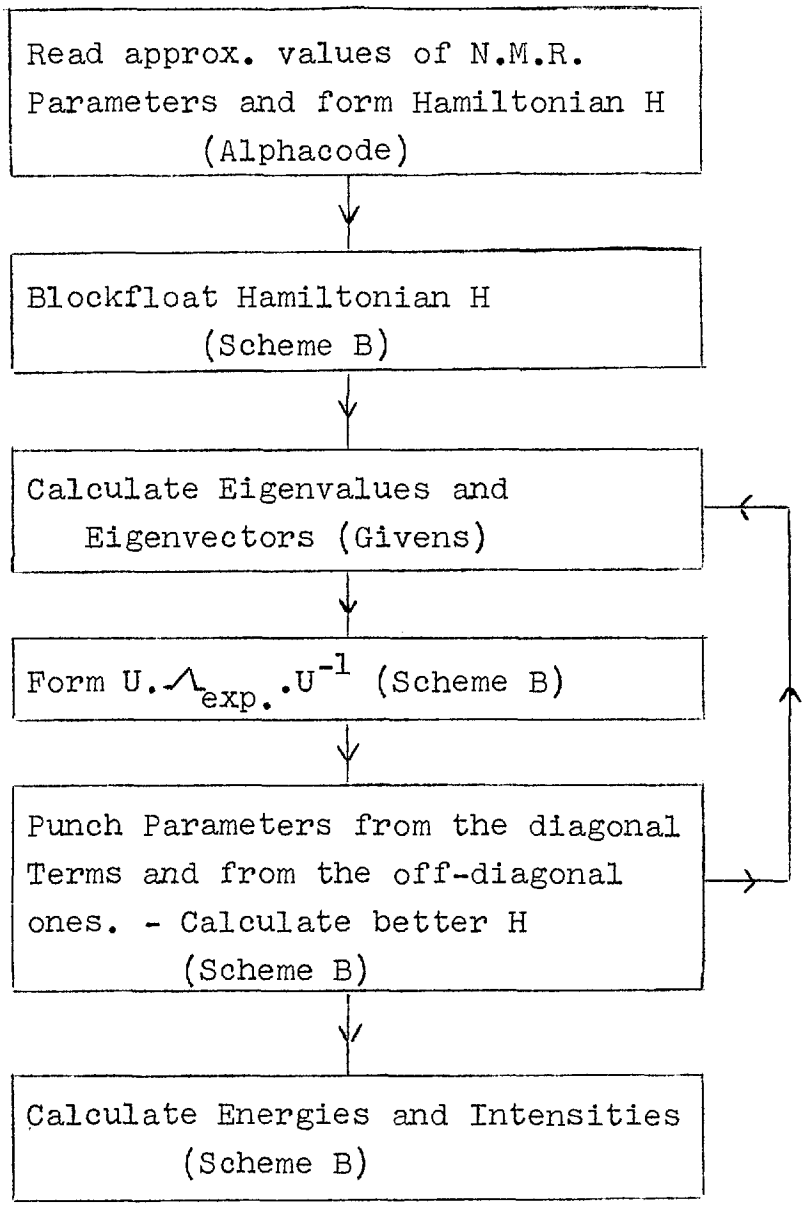


The diagonalisation process is performed by means of the Givens programme used twice for the two 3 x 3 matrices. The transformation $U.\Lambda_{exp}.U^{-1}$ is performed by a Scheme B programme, from which two matrices 3 x 3 are obtained. In the first approximation, the values of $J_{AB}$, $J_{BC}$, $J_{CA}$ obtained from the diagonal elements are not consistent with the values derived from the off-diagonal ones. In practice we have used the values from the diagonal elements and iterated until values consistent with the off-diagonal ones were obtained. This choice speeds convergence as it has been observed that if mean values of the J's are used for the iterations, the process leads to the diagonal values. The construction of the new H matrices (3 x 3) from $H_1$ is done by another Scheme B programme which first punches the J's from the off--diagonal and diagonal elements in decimal, in order to facilitate testing of the consistency of the different J's. Punching of results in decimal proceeds at the middle of the programme, and at the end the H's matrices for the next iteration are produced.

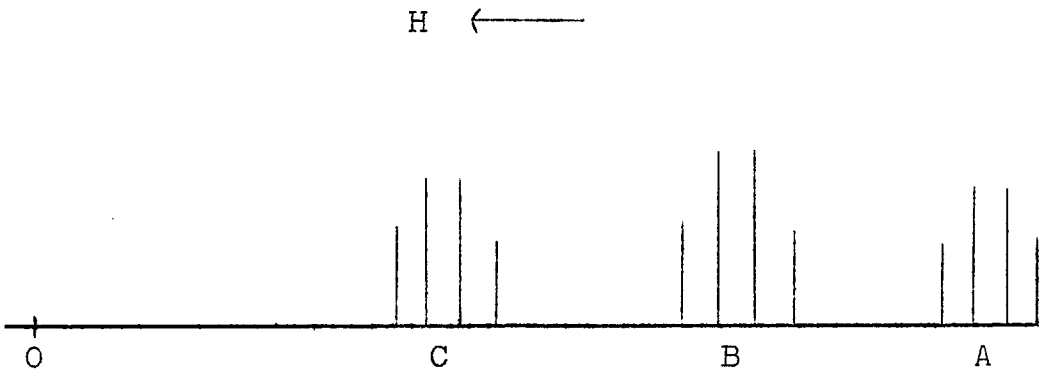
When consistency of the J's is achieved, another Scheme B programme is used for computing the energies and intensities. If the theoretical spectrum is not consistent with the practical one, the original transition energy diagram is known to be incorrect and alternative assignment has then to be investigated.

The annexed block diagram explains the sequence of these operations.

BLOCK DIAGRAM FOR THREE NUCLEI ABC



The values of the N.M.R. parameters are taken from the practical spectrum, where the following notation and origin are supposed:




It is convenient for the purpose of the calculation to set up the origin at 100 c/s on the high field side C, in order to weight the diagonal elements in preference to the off-diagonal ones.

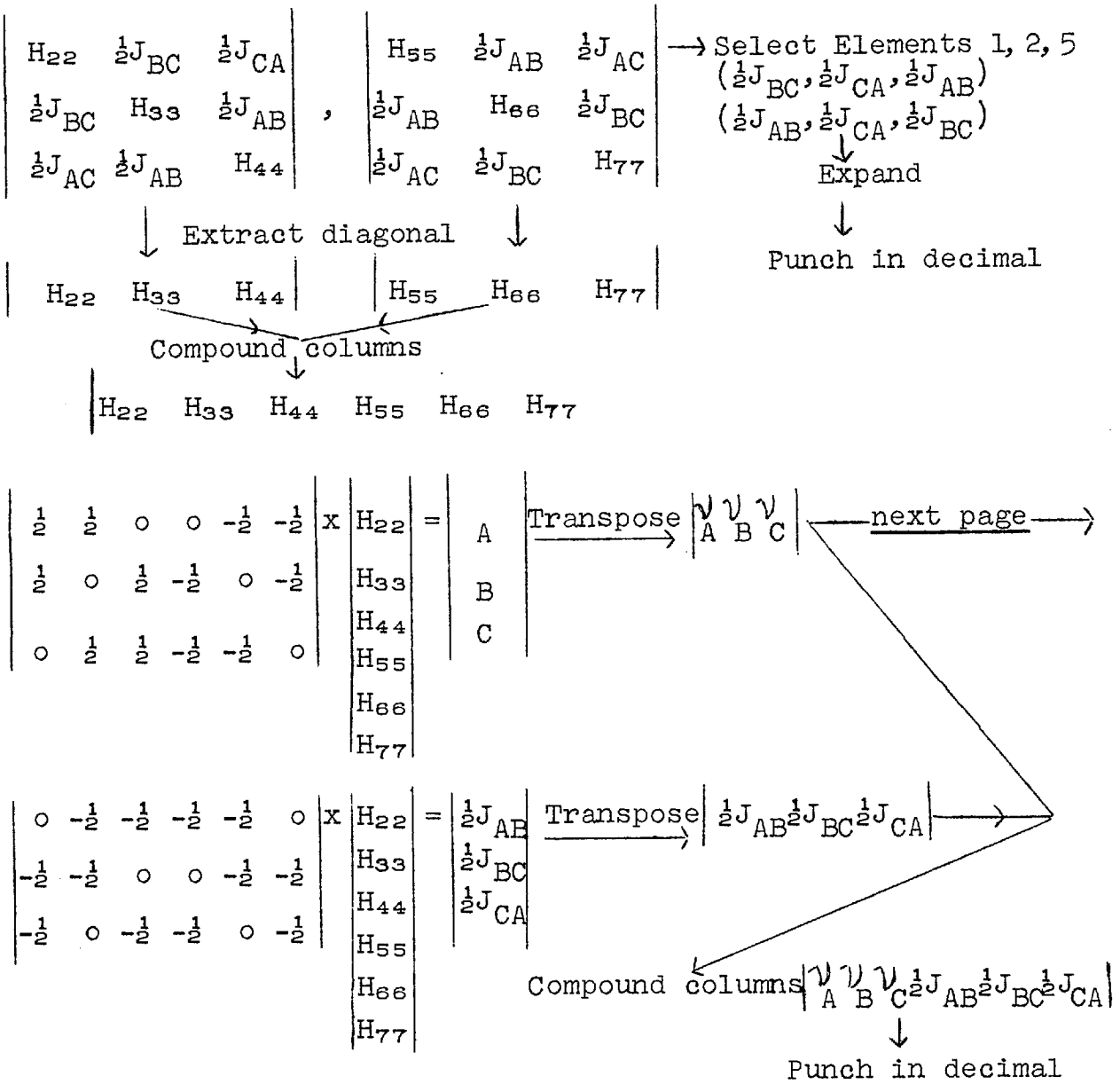
The Alphacode programme accepts the approximate values of $\nu_A, \nu_B, \nu_C$ and $J_{AB}, J_{BC}, J_{CA}$ and forms the Hamiltonian matrix. This Hamiltonian is punched out in fully-floating form (binary). It is then converted to block-floating form, and read into the Givens programme for the eigenvalues and eigenvectors. In fact, the Alphacode programme forms the Hamiltonian in four matrices, two 1 x 1 and two 3 x 3. The last are put into the Givens programme consecutively to give two eigenvector's matrices $U_1$ and $U_2$.

The operation $U.\Lambda_{exp.}.U^{-1}$ is performed separately for each U ($U_1$ and $U_2$) with two $\Lambda_{exp.}$, $\Lambda_{exp._1}$ and $\Lambda_{exp._2}$, by a Scheme B programme which has to be read only once by the computer.

The Givens programme does not give the matrix U, but U', the transpose, and the eigenvectors are not normalized, so the Scheme B programme carried out the following operations: read U' - normalize U' - transpose - etc.

Now the results $H_1$ and $H_2$ are read in another Scheme B programme which punches the values $J_{AB}$, $J_{BC}$, $J_{CA}$ and $\nu_A, \nu_B, \nu_C$ from the diagonal and off-diagonal elements directly in decimal, and while the computer is calculating a better H from these values, these values are read on an off-line printer in order to decide if it is necessary to iterate, or to go to the next programme and calculate the intensities.

A scheme of the arithmetic is given below.


Select Elements 1, 2, 5
(½J_BC, ½J_CA, ½J_AB)
(½J_AB, ½J_CA, ½J_BC)
Expand
Punch in decimal
Extract diagonal
Compound columns
Transpose
next page
Transpose
Compound columns
Punch in decimal

$$\left|\begin{matrix} \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{matrix}\right| \times \left|\begin{matrix} A \\ B \\ C \\ \frac{1}{2}J_{AB} \\ \frac{1}{2}J_{BC} \\ \frac{1}{2}J_{CA} \end{matrix}\right| = \left|\begin{matrix} L_1 \\ L_8 \end{matrix}\right|$$

Shift down 3 places

Punch in binary

From page(23)

$\left|\frac{1}{2}J_{AB}\ \frac{1}{2}J_{BC}\ \frac{1}{2}J_{CA}\right|$ → Select elements 0, 1, 2 → Expand

Form $\left|0\right|$ → Compound rows and columns and form

$$\left|\begin{matrix} 0 & \frac{1}{2}J_{BC} & \frac{1}{2}J_{CA} \\ \frac{1}{2}J_{BC} & 0 & \frac{1}{2}J_{AB} \\ \frac{1}{2}J_{CA} & \frac{1}{2}J_{AB} & 0 \end{matrix}\right| \quad (+)^* \quad \left|\begin{matrix} 0 & \frac{1}{2}J_{AB} & \frac{1}{2}J_{CA} \\ \frac{1}{2}J_{AB} & 0 & \frac{1}{2}J_{BC} \\ \frac{1}{2}J_{CA} & \frac{1}{2}J_{BC} & 0 \end{matrix}\right|$$

$\left|H_{22}\ H_{33}\ H_{44}\right|$ → Expand diagonal

$\left|H_{55}\ H_{66}\ H_{77}\right|$ ↗

$$\left|\begin{matrix} H_{22} & 0 & 0 \\ 0 & H_{33} & 0 \\ 0 & 0 & H_{44} \end{matrix}\right| \qquad \left|\begin{matrix} H_{55} & 0 & 0 \\ 0 & H_{66} & 0 \\ 0 & 0 & H_{77} \end{matrix}\right|$$

New H's

$$\left|\begin{matrix} H_{22} & \frac{1}{2}J_{BC} & \frac{1}{2}J_{CA} \\ \frac{1}{2}J_{BC} & H_{33} & \frac{1}{2}J_{AB} \\ \frac{1}{2}J_{CA} & \frac{1}{2}J_{AB} & H_{44} \end{matrix}\right| \qquad \left|\begin{matrix} H_{55} & \frac{1}{2}J_{AB} & \frac{1}{2}J_{CA} \\ \frac{1}{2}J_{AB} & H_{66} & \frac{1}{2}J_{BC} \\ \frac{1}{2}J_{CA} & \frac{1}{2}J_{BC} & H_{77} \end{matrix}\right|$$

Shift down 3 places

Punch in binary

* The signs (+), (-), (x), (:) mean term by term sum difference, multiplication and division, respectively.

The next programme in Scheme B punches out the energies and intensities from the eigenvalues and eigenvectors. The arithmetic is:

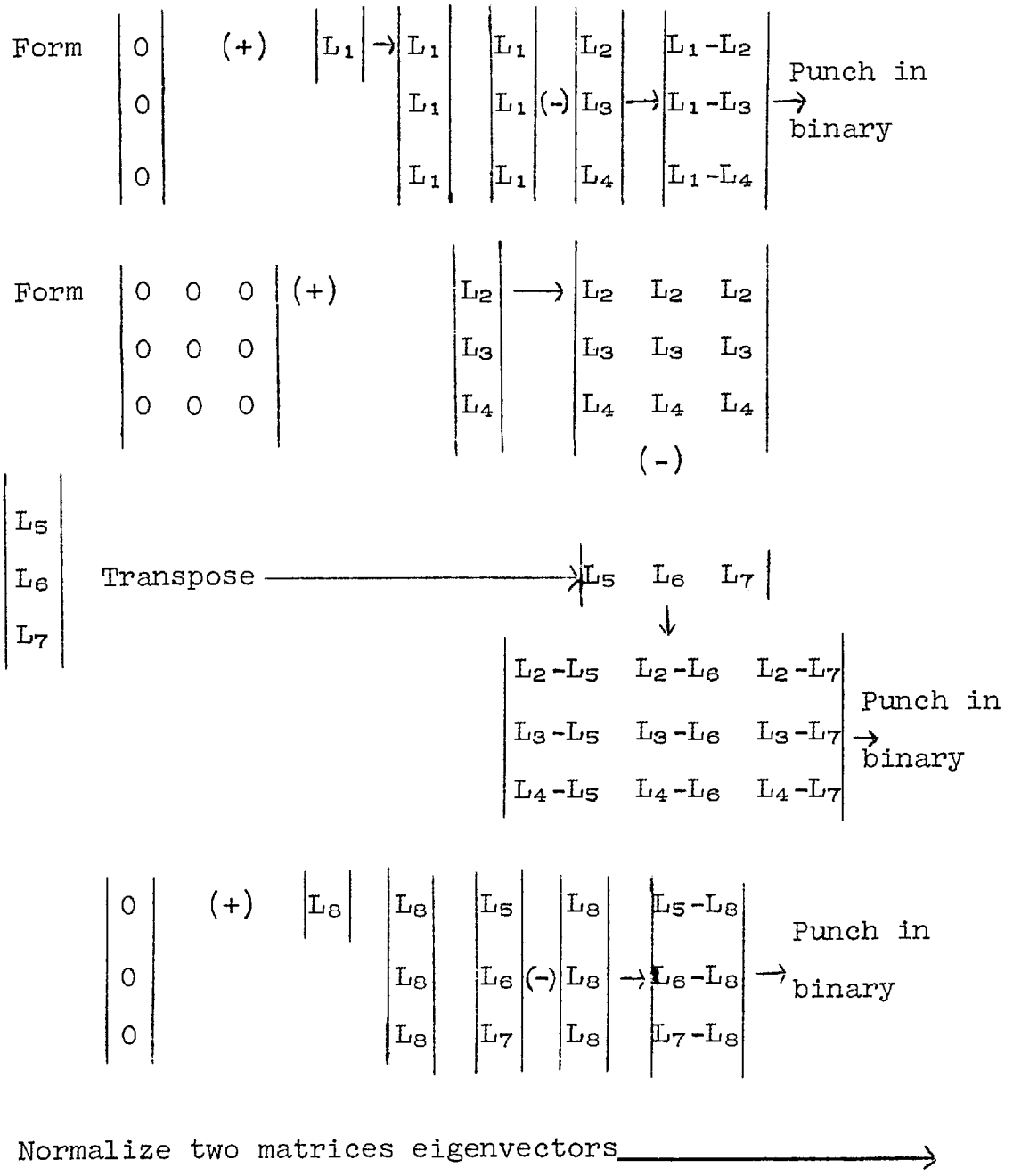
Read $\left|L_1\right|$

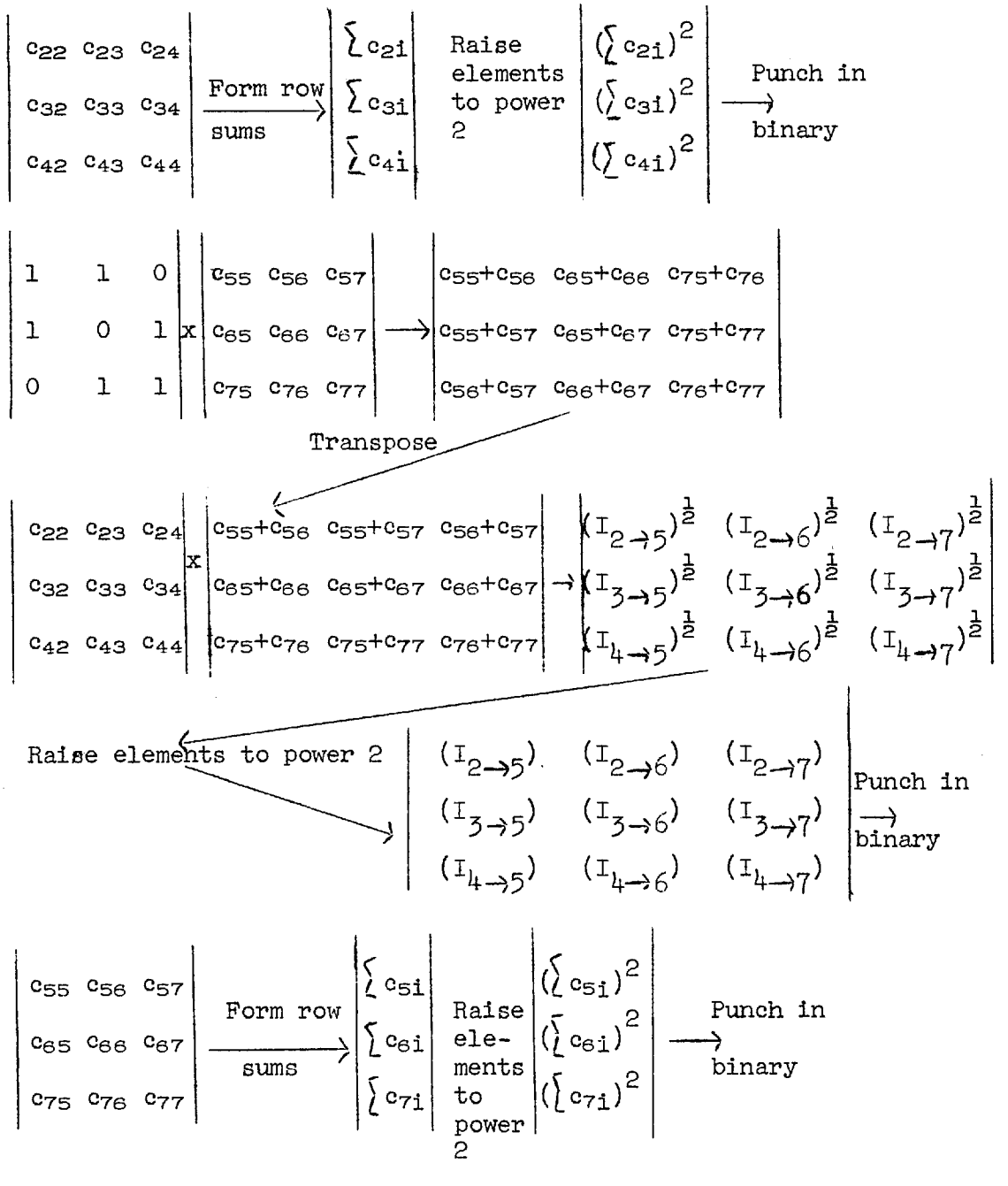
$\left|L_8\right|$

$$\left|\begin{matrix} L_2 \\ L_3 \\ L_4 \end{matrix}\right| \qquad \left|\begin{matrix} c_{22} & c_{23} & c_{24} \\ c_{32} & c_{33} & c_{34} \\ c_{42} & c_{43} & c_{44} \end{matrix}\right|$$

$$\left|\begin{matrix} L_5 \\ L_6 \\ L_7 \end{matrix}\right| \qquad \left|\begin{matrix} c_{55} & c_{56} & c_{57} \\ c_{65} & c_{66} & c_{67} \\ c_{75} & c_{76} & c_{77} \end{matrix}\right|$$

Auxiliary matrix $\left|\begin{matrix} 1 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 1 \end{matrix}\right|$


Form
0
0
0
(+)
$L_1$
$L_1$
$L_1$
$L_1$
$L_1$
$L_1$
$L_1$
(-)
$L_2$
$L_3$
$L_4$
$L_1-L_2$
$L_1-L_3$
$L_1-L_4$
Punch in
binary
Form
0 0 0
0 0 0
0 0 0
(+)
$L_2$
$L_3$
$L_4$
$L_2$ $L_2$ $L_2$
$L_3$ $L_3$ $L_3$
$L_4$ $L_4$ $L_4$
(-)
$L_5$
$L_6$
$L_7$
Transpose
$L_5$ $L_6$ $L_7$
$L_2-L_5$ $L_2-L_6$ $L_2-L_7$
$L_3-L_5$ $L_3-L_6$ $L_3-L_7$
$L_4-L_5$ $L_4-L_6$ $L_4-L_7$
Punch in
binary
0
0
0
(+)
$L_8$
$L_8$
$L_8$
$L_8$
$L_5$
$L_6$
$L_7$
(-)
$L_8$
$L_8$
$L_8$
$L_5-L_8$
$L_6-L_8$
$L_7-L_8$
Punch in
binary
Normalize two matrices eigenvectors


Form row sums
Raise elements to power 2
Punch in binary
Transpose
Raise elements to power 2
Punch in binary
Form row sums
Raise elements to power 2
Punch in binary

There is not necessarily a unique solution[5,7] for a given spectrum and it is possible that the iterative method could converge on an incorrect set of parameters. However, the intensities are very sensitive to the choice of parameters, and in general a correct solution is recognisable from empirical considerations. Ideally spectra should be determined at more than one field strength in order to eliminate possible ambiguities.

## III. Applications

### 1) $A_2B_2$

The stereochemistry of the pigment carotenoid Bixin has been an outstanding problem for a long time.[59] N.M.R. spectroscopy has been used to solve the problem. The stereochemistry of bixin is shown in formula (I) and the N.M.R. proof of the cis-configuration of the 4,5-double bond is based on the observed deshielding of 6-proton by the 2,3-double bond. To confirm the existence of this shielding effect esters (II) and (III) have been studied. The olefinic protons of these compounds form an $A_2B_2$ system. The spectra (at 40 Mc/s) of (II) and (III) are reproduced together with the positions of the lines. It is seen that the A protons are interacting weakly with the methyl groups. However, the analysis can be carried out with B-band.

The coupling constants obtained for (II) and (III) were at 40 Mc/s in c/s:

| | $J_{34}$ | $J_{35}$ | $J_{36}$ | $J_{45}$ |
|---|---|---|---|---|
| 2 | 11.5 | -0.6 | $\pm$0.3 | 14.6 |
| 3 | 12.5 | -1.0 | $\pm$0.2 | 10.7 |

The spectrum of (II) was also measured at 56.4 Mc/s and lines 7 and 10 were observed where they had been theoretically predicted.

2) ABC.

The rotenone derivative, isorotenolone acetate has been shown[8] to possess either structure (IV) or (V ). Stereochemical considerations allow a decision between these two structures since the conformation about the $CH_CH_B$ - $CH_A$ bond differs considerably in the two structures. The conformational relation between the three protons can be established by measurement of the coupling constants $J_{AB}$ and $J_{AC}$, since it has been shown that these coupling constants are functionally related to the dihedral angles between the planes $H_ACC$ and $H_BCC$, and $H_ACC$ and $H_CCC$, respectively.

The absorption of the three protons is an ABC multiplet (figure ). The assignment in the figure permits the construction of the energy diagram ( page 4 ) which gives the elements of $\Lambda$ exp. Application of the iterative method yields the following values

$$J_{AB} = 2.5 \text{ c/s} \qquad J_{BC} = 11.5 \text{ c/s} \qquad J_{AC} = 6.8 \text{ c/s}$$

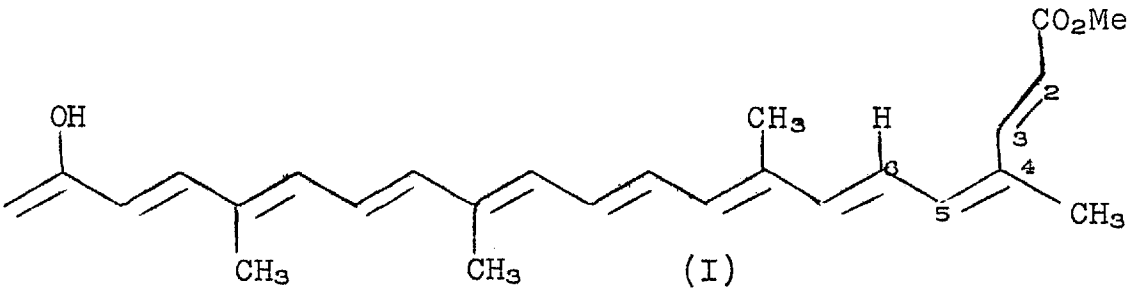
$$\delta_{AB} = 41 \text{ c/s} \qquad \delta_{BC} = 20 \text{ c/s}$$

after iteration. These parameters reproduce the observed spectrum within experimental error (and correspond to assignment 1 in Table 7 ). The values of $J_{AB}$ & $J_{AC}$ correspond to dihedral angles of $50^{\circ}$ and $70^{\circ}$, respectively, and are compatible with structure (IV).

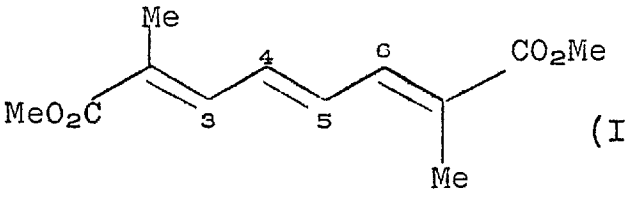
There are four reasonable assignments for the 12 lines of the observed spectrum. These assignments are given in table 7.

TABLE 7

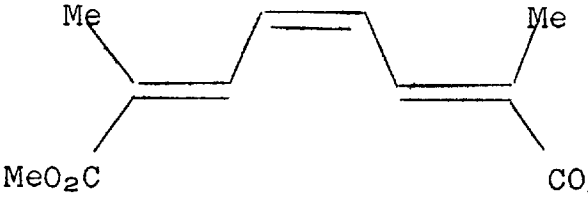
| OBSERVED LINES | TRANSITIONS (see TABLE 6) 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| 103.93 | 12 | 6 | 1 | 8 |
| 110.12 | 6 | 12 | 8 | 1 |
| 115.15 | 8 | 1 | 6 | 12 |
| 121.93 | 1 | 8 | 12 | 6 |
| 129.62 | 11 | 11 | 2 | 2 |
| 132.28 | 4 | 4 | 9 | 9 |
| 141.12 | 9 | 9 | 4 | 4 |
| 144.03 | 2 | 2 | 11 | 11 |
| 171.97 | 10 | 7 | 3 | 5 |
| 174.80 | 5 | 3 | 7 | 10 |
| 178.53 | 7 | 10 | 5 | 3 |
| 187.07 | 3 | 5 | 10 | 7 |


CO2Me
2
3
4
OH
CH3
H
6
5
CH3
CH3
CH3

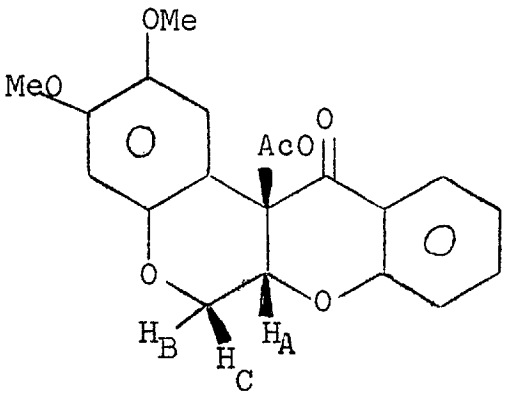
(I)


Me
4
6
CO2Me
MeO2C
3
5
Me

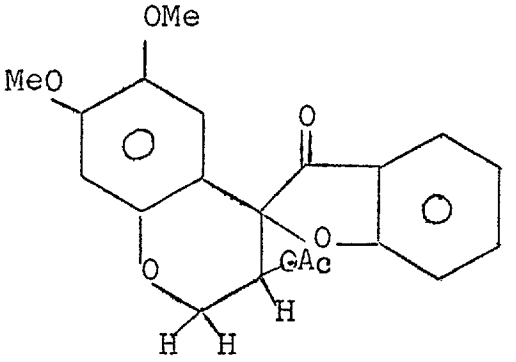
(II)


Me
Me
MeO2C
CO2Me

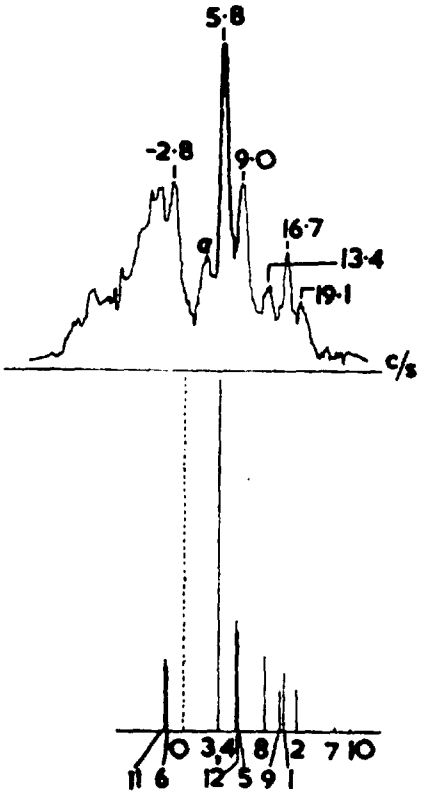
(III)


OMe
MeO
AcO
O
O
O
O
HB
HA
HC

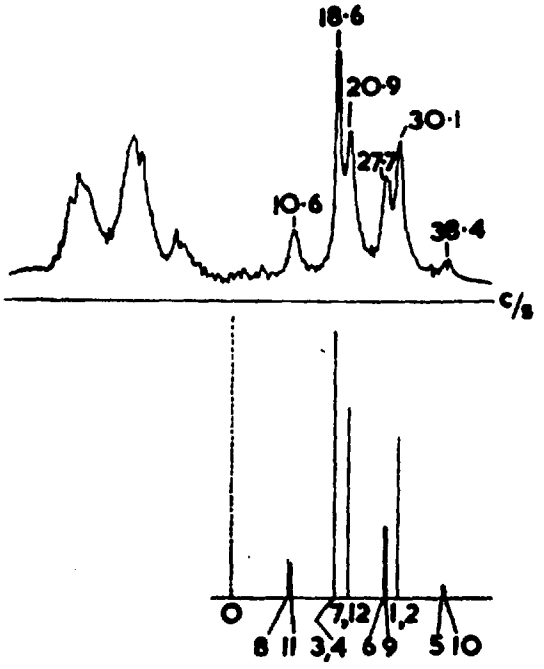
(IV)


OMe
MeO
O
O
O
GAc
H
H
H

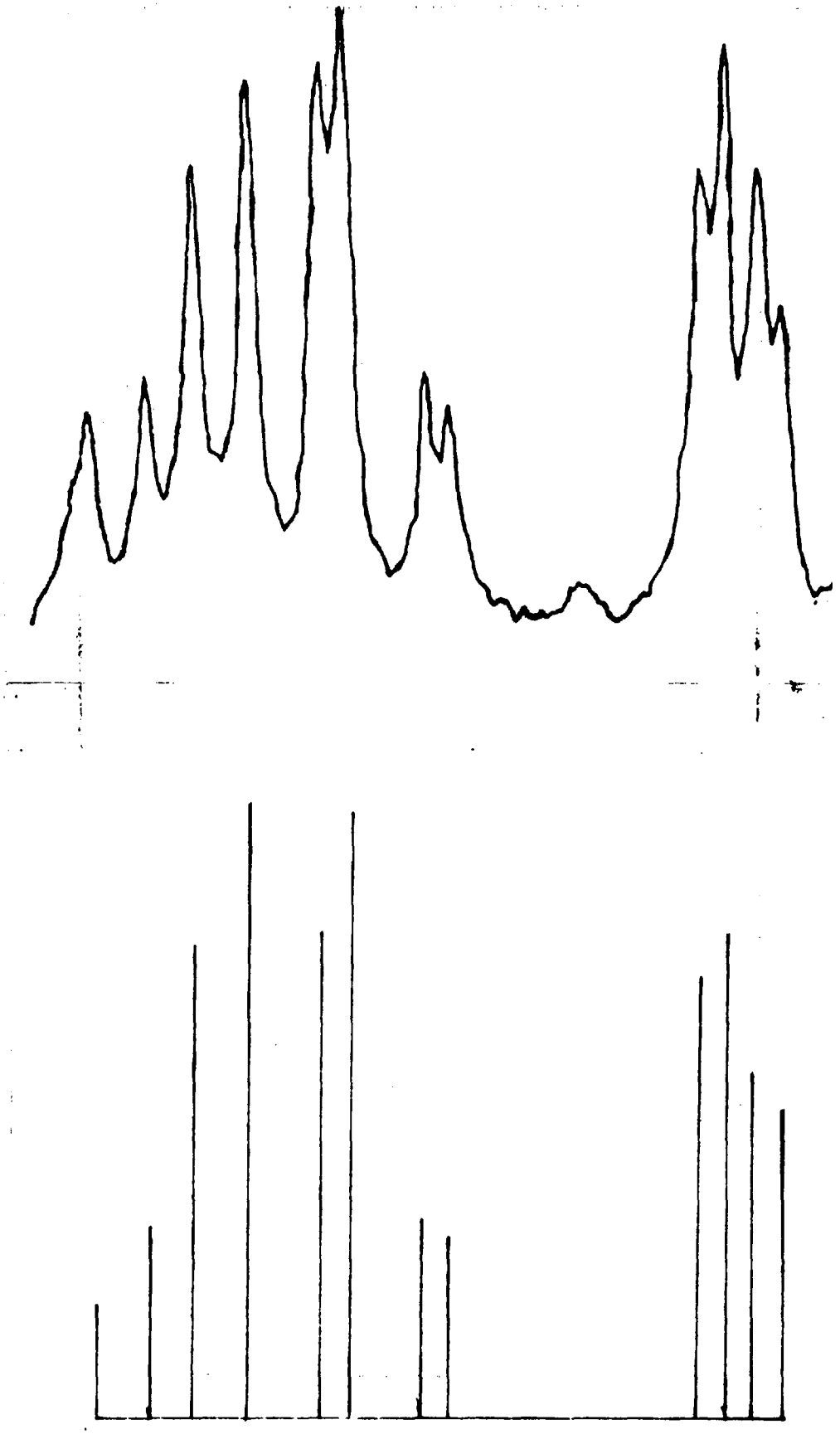
(V)




The observed and theoretical spectra at 40 Mc./sec. of methyl "all-trans" -2,7-dimethylocta-2,4,6-trienoate (II). Lines 6 and 11 of the B half-spectrum overlap the A half-spectrum. The band a arises from transitions of the A nuclei.




The observed and theoretical spectra at 40 Mc./sec. of methyl 2,7-dimethylocta-trans-2,cis-4,trans-6-trienoate (III).



The observed and theoretical spectra of isorotenolone C acetate at 56.445 Mc./sec.

## The Chemical Shift in Aromatic Compounds

### 1. Introduction

Protons attached directly to aromatic nuclei give rise to absorption in a characteristic region of the proton magnetic resonance spectrum. As this region corresponds to fields considerably weaker than observed for the resonances of olefinic protons it is clear that the peculiar $\pi$-electron configuration of aromatic molecules is associated with a specific shielding effect. Furthermore, it is known that the introduction of substituents or heteroatoms causes considerable variation in the chemical shifts of aromatic protons. Thus a study of the chemical shifts of aromatic protons should provide data, referring to the ground states of aromatic molecules, which might well be useful for investigating the various quantum mechanical methods currently employed in the study and description of aromatic $\pi$-electron systems. In particular, such data could form the basis of a new approach to the problem of evaluating parameters employed in semi-empirical quantum-mechanical treatments.

In the general case, the shielding of an aromatic proton can be separated into a number of terms, some

of which are more ameniable to theoretical consideration than others. These terms are listed and discussed in the next section. The remaining sections are principally concerned with the theoretical treatment of one of these terms, namely that associated with the induced circulations (ring currents) of $\pi$-electrons.

## 2.1 Origin of the Proton Chemical Shift.

The nuclear magnetic screening effect of the electrons for a hydrogen atom (neglecting electron spin) in a uniform magnetic field has been derived (Lamb[9]). The screening occurs because the applied magnetic field causes the whole electronic structure to rotate about the nucleus with the Larmor angular frequency $eH/2mc$. In a non-spherical environment, however, this free circulation is partly quenched. The shielding of a proton attached to a molecule arises from two types of magnetic fields. The larger contribution is by fields associated with induced circulations of the pair of electrons of the X-H bond which is derived in part from the 1s-orbital of the H atom in question. Pople[10] has classified shielding of this type as 'local diamagnetic shielding', since it is shown that the diamagnetic

current $j_{dia}$ arises approximately from 'localized' Larmor precession in each atom and corresponds to the usual source of diamagnetism.

$$\underline{j_{dia}} = \frac{e^2}{2mc} \sum_s \int \rho_s^{oo} \underline{\mathcal{L}(r-r_s)} \times \underline{H} \mathcal{J}$$

Strictly speaking there is also a paramagnetic term which in the case of hydrogen is believed to be small.[11]

The derivation of this formula involves the neglect of interatomic terms, and, as Pople points out, this is most serious when there is a possibility of diamagnetic current flowing in a closed path between two or more atoms. The magnitude of local diamagnetic shielding is influenced by electrostatic perturbations of the H atomic wave function, an effect which has been treated by Marshall and Pople[12]. Their analysis shows that an electric field reduces the magnetic screening by altering the paramagnetic term referred above. The reduction occurs for all directions of the electric field with respect to the magnetic field and is greatest when both are perpendicular. This lowering of the screening constant is only partly due to the paramagnetic term, for the diamagnetic Lamb

term is also reduced. This corresponds to the removal of electrons from the vicinity of the nucleus by the electric field. The weak diamagnetic shielding is influenced by an electrostatically induced variation in the ionic character of the X-H bond. Buckingham[13] has calculated the diamagnetic shielding due to the presence of neighbouring electric poles and dipoles. It is shown below that the electric field at a particular proton, which arises from polar groups in other parts of the molecule, can lead to chemical shifts proportional to the first power of the field strength

$$\Delta\sigma = -2 \times 10^{-12} E_z - 10^{-18} E^2$$

where $E_z$ is the component of E in the bond direction and is given in e.s.u. A field along the X-H bond and directed towards X draws the electrons in the enriched region between the nuclei away from the proton, thereby causing its resonance to occur at lower magnetic field strength. Conversely a field in the opposite direction leads to resonance at higher fields because this electronegativity governs the electron distributions between the atom and the proton. The shielding would be proportional to the population of the 1s orbital of the proton in the bond.

The local diamagnetic shielding will also depend on the effective electronegativity of the atom to which the proton is bonded.

McConnell[14] has studied the effect of the anisotropy of induced circulations of electrons about one or more neighbouring atomic centres. This is a long-range shielding effect and can be estimated using a point dipole approximation, provided the principal susceptibilities of the pertinent group of electrons are known. The formula found is

$$\sigma_N^G = \frac{\Delta\chi^G}{3R^3L_o} \langle 1-3\cos^2\gamma \rangle_{av.} \quad \text{(for axial symmetry)}$$

where $\Delta\chi^G$ is the anisotropy in the molar susceptibility of group G and $\gamma$ is the angle between R and the symmetry axis of the group G. The quantitative application of the formula is beset with two important difficulties. First, very few magnetic data for $\Delta\chi^G$ are available, and second, with decreasing R the shielding field becomes larger and more important, but the point dipole approximation becomes less and less accurate.

Variation of structure in aromatic systems influences the chemical shifts of aromatic protons, but its effect

on either or both the above shielding contributions in the manner now discussed.

## 2.2 Hybridisation of the carbon atom bearing the proton.

The polarity of the C-H bond is, in part, determined by the hybridisation of the carbon atom, since its effective electronegativity is influenced by the amount of s-character of the $p_x$ carbon atomic orbital involved in the C-H bond. In aromatic hydrocarbons, the major factor controlling the hybridisation of the carbon atoms is ring size. At present there is no definite information as to the magnitude of this effect. It is possible that it is significant and should be taken into account in treating azulene in which the sequence of proton resonances is incorrectly predicted if only ring currents and $\pi$-electron densities are considered[15] (see below).

## 2.3. The diamagnetic anisotropy of the $\pi$-electron system. (ring currents).

For alternant hydrocarbons the most important shielding term is that associated with the induced circulations of the $\pi$-electrons.[16,17] It is these

circulations or ring currents which are responsible for the exaltation of the diamagnetic susceptibility and the pronounced diamagnetic anisotropy of aromatic hydrocarbons, (18, and references mentioned therein). The theoretical methods for investigating the shielding associated with ring currents are discussed below.

## 2.4 The diamagnetic anisotropy of the $\sigma$-framework.

There is no reason to suppose[19] that the magnetic polarizabilities of carbon-carbon bonds constituting the framework of aromatic molecules will be isotropic, and thus the possibility exists that these bonds make a contribution, to the shielding of aromatic molecules. The magnitude of this effect, like that of the $\pi$-electron contribution, will depend on the geometric relation of the proton to the bonds concerned. No estimate of this contribution has been made but as the polarizabilities of $\sigma$-bonds will certainly be much less than that of the $\pi$-electron system, neglect of this term is possibly justified.

## 2.5 $\pi$-Electron charge densities

Partial localisation of $\pi$-electrons takes place in non-alternant and heterocyclic aromatic molecules

and can profoundly effect the chemical shifts of aromatic protons.

The simplest approximation[18,20,21,22] for the calculation of these shifts involves the assumption that only local diamagnetic shielding is affected and that the change in this is proportional to the $\pi$-electron charge density at the carbon atom to which the proton is attached. As yet this theory has not been adequately tested. A more rigorous treatment would take into account the partial charges at other atoms and the change in the paramagnetic term for each atom in the molecule.

## 2.6 Inductive and direct field effects of hetero-atoms.

The introduction of a heteroatom into an aromatic nucleus causes polarisation of the $\sigma$-bonds. The bond dipoles which result will give rise to an electric field at a proton, and, in general, there will also be a component acting along the bond attaching the proton to the nucleus. If a reliable estimate of the $\sigma$-bond dipoles can be made their effect on the local diamagnetic shielding can be calculated by Buckingham's theory. It is doubtless this effect which is responsible for

the abnormally low shielding of α-protons in pyridine and related nitrogen heterocycles.

Of these various terms which contribute to the shielding of aromatic protons that arising from the ring current is most easily handled by theoretical methods. Furthermore, an attempt has been made to separate the ring current contribution to the observed chemical shift in heterocyclic systems[12] so that comparison between theory and experiment is now possible.

## 3. Ring Current

### 3.1 Free electron model.

The model of a conjugated hydrocarbon in which the mobile electrons are treated as free electrons moving in a one-dimensional framework has been shown to be surprisingly good both as a qualitative explanation of the various properties of these molecules, and as a method of estimating their magnitudes.

Pauling[23] used this model to explain the large dimagnetic anisotropy of benzenoid aromatic molecules. He pointed out that an applied magnetic field would cause induced currents to flow around the various rings of the molecule, and that these currents would produce

a secondary magnetic field. Since all rings lie in one plane a large diamagnetic anisotropy results. His treatment begins with benzene, setting the Hamiltonian for an electron in a constant magnetic field of strength H, parallel to the z axis as

$$H = H^{o} + H' + H''$$

in which $H^{o}$ is the Hamiltonian for zero field strength and

$$H' = - \frac{He}{2\ mc} (xp_y - yp_x)$$

$$H'' = \frac{H^2e^2}{8\ mc^2} (x^2 + y^2)$$

where the origin of the co-ordinate system is at the centre of the hexagon. If the potential function in $H^{o}$ vanishes and the contribution to the susceptibility (per mol.) of the electron is given by the Pauli expression

$$\chi = - \frac{Ne^2}{4\ mc^2} \langle \rho^2 \rangle_{av.}$$

in which $\langle \rho^2 \rangle_{av.}$ is the mean square of the distance of the electron from the z axis. This expression is only valid for atoms and has to be corrected for the term in

$H'$ for molecules. But the $\pi$-electrons in benzene, occupying orbitals with antisymmetrical wave function with respect to the plane of the nuclei, have a probability distribution function large only in two ring-shaped regions, one above and one below the ring. Therefore the potential function is cylindrically symmetrical. Then, $\langle \rho^2 \rangle_{av.} = R^2$ , R being the radius of the hexagon; with these values $\Delta K = -49.2 \times 10^{-6}$ and the experimental value is $\Delta K = -54 \times 10^{-6}$.

In considering the condensed aromatic ring systems, the Maxwell's equations have to be solved, and a magnetic dipole of equivalent strength has to be calculated. The result is $\Delta K = -38.0 \times 10^{-6} \times \mu \sigma f$; where $\sigma$ is the electron density per C-C bond assumed uniform, and f a correction factor because the outermost lines have been replaced by circular arcs.

The effect of the induced magnetic field on the chemical shift of an attached proton was first pointed out by Pople.[16] He noted that, whereas the induced field opposes the external field in the region inside the ring, it augments it in the neighbourhood of the proton and so contributes to the chemical shift. The six electrons in benzene give a total current of

$\frac{3e^2H}{2\pi\ mc}$ which is equivalent to a magnetic dipole of $\frac{3e^2Ha^2}{2\ mc^2}$ at the centre of the hexagon, a being the radius of the circle. The secondary field due to the magnetic dipole at the proton position is then

$$H' = \frac{3e^2Ha^2}{2mc^2(a+b)^3}$$

where b is the C-H length. Averaging over all orientations of the molecule requires multiplication by a factor $\frac{1}{3}$ (This arises as $\langle \cos^2 \theta \rangle_{av.}$, where $\theta$ is the angle between the hexagonal axis and the field).

Bernstein et al.[25] extended this treatment to polycycles by placing point dipoles at the centres of all the rings and calculating the resulting field. They found the formula (in p.p.m.) for the chemical shift

$$\lambda = 10^6 \frac{H'}{H}$$

$$\lambda = 10^6 \frac{e^2a^2}{2\ mc^2} \sum_i R_i^{-3}$$

where $R_i$ is the distance to the centre of the ith hexagon.

Perhaps the most serious inadequacy of these treatments is the use of a point dipole instead of the ring current. A better approximation to the true field would be the use of a uniform magnetic shell. The calculations

for this modification have been performed by Waugh and Fessenden[26] and represent a considerable improvement. In particular, the way in which the field falls off with distance is more realistic. The averaged total current of the six electrons in benzene $I = \frac{e^2H}{4\pi mc}$ give rise to a magnetic field $H'$ whose z-component in cylindrical co-ordinates $(\rho, \phi, z)$ is

$$H'_z = \frac{Ik}{4\pi ca\rho^{\frac{1}{2}}} \left[K(k) + \frac{1-\rho^2-z^2}{(1-\rho)^2+z^2} E(k)\right]$$

where

$$k^2 = \frac{4\rho}{(1+\rho)^2+z^2}$$

and K(k) and E(k) are complete elliptical integrals. The expectation value of the induced field averaged over the motions of the molecule, in the direction $H_o$ is

$$H'_{eff} = \frac{1}{H_o} \iint H_o \cdot H' \, d\Omega$$

and eliminating $H'\rho$

$$H'_{eff} = \frac{ne^2H_o}{24\pi mc^2 a} B_o$$

where $B_o$ is

$$B_o = \frac{1}{2\pi\rho^{\frac{1}{2}}} \left[K(k) + \frac{1-\rho^2-z^2}{(1-\rho)^2+z^2} E(k)\right]$$

in which n is the number of $\pi$ electrons. The function $B_o$ is tabulated.

## 3.2. The l.c.a.o. theory.

The free electron model leads to estimates of the diamagnetic anisotropy which are surprisingly good, and yet are not accurate enough for a detailed understanding of the experimental results. A treatment which is to be preferred theoretically, is that of London[24], which is based on an expansion of the molecular orbitals as linear combinations of atomic orbitals, and this leads to an improved agreement with experiment[18]. The one-electron Hamiltonian in the presence of a magnetic field with vector potential $\underline{A}$ takes the form:

$$H = \frac{1}{2m}(\underline{p} + \frac{e}{c}\underline{A})^2 + V$$

where $V$ is the potential energy of one electron in the field produced by the rest of the molecule and $\underline{p}$ the momentum. For a uniform field $H_o$, $\underline{A}$ can take the form:

$$A = -\frac{1}{2}\underline{r} \times \underline{H_o}$$

where $\underline{r}$ is the position vector of the electron referred to any origin.

If $\phi_s$ are the $2p\pi$ carbon atomic orbitals in the absence of the field, the molecular orbitals $\psi_i$ in presence of the field can be expressed as linear combinations of the modified atomic orbitals:

$$\chi_s = \phi_s \, e^{-\frac{ie}{\hbar c} \underline{A_s} \cdot \underline{r}}$$

and

$$\psi_j = \sum_s c_{js} \chi_s$$

with these modified atomic orbitals $\chi_s$, London overcame the gauge difficulties because

$$(\underline{p} + \frac{e\underline{A}}{c})^2 \chi_s = e^{-\frac{ie}{\hbar c} \underline{A_s} \cdot \underline{r}} \left[\underline{p} + \frac{e}{c}(\underline{A} - \underline{A_s})\right]^2 \phi_s$$

The variational method leads to the secular equation for $c_{js}$ :

$$|H_{st} - E\Delta_{st}| = 0$$

where

$$H_{st} = \int \chi_s^* H \chi_t \, d\tau$$

$$\Delta_{st} = \int \chi_s^* \chi_t \, d\tau$$

and usually $\Delta_{st} = 0$ if $s \neq t$ and 1 if $s = t$.

So $H_{st}$ is :

$$H_{st} = \frac{1}{4m^2} \int e^{\frac{ie}{\hbar c}(\underline{A}_s - \underline{A}_t)\cdot \underline{r}} \phi_s^* \left\{ \left[ \underline{p} + \frac{e}{c}(\underline{A} - \underline{A}_t) \right]^2 + V \right\} \phi_t \, d\tau$$

The London method involves two further approximations 1) the term $\underline{A}-\underline{A}_t$ is omitted, because it measures the basic energy of the atomic orbital, as modified by the local diamagnetic circulation and 2) $\underline{r}$ is set equal to $\frac{1}{2}(\underline{R}_s + \underline{R}_t)$, $\underline{R}_s$ and $\underline{R}_t$ being the position vectors of the nuclei s and t. Then,

$$H_{st} = \beta_{st} \, e^{\frac{ie}{2\hbar c}(\underline{A}_s - \underline{A}_t)\cdot(\underline{R}_s + \underline{R}_t)}$$

where $$\beta_{st} = \int \phi_s^* \left[ \frac{1}{2m} \underline{p}^2 + V \right] \phi_t \, d\tau$$

Now, if $\underline{A}_s = -\frac{1}{2}\underline{R}_s \times \underline{H}$, the expression for the $H_{st}$ transforms into

$$H_{st} = \beta_{st} \, e^{\frac{ie}{\hbar c} S_{st} H}$$

where $S_{st}$ is the signed area of the triangle formed by the origin (at which A=o) and the bond $s \longrightarrow t$, counted positive if $s \longrightarrow t$ is right handed about $\underline{H}$ (if s=t, $H_{st} = \alpha$ in Hückel theory).

From this expression the total energy can be calculated as a power series in $\underline{H}$ and the diamagnetic anisotropy is found from the coefficient of $H^2$.

This theory can also be applied to calculate the chemical shifts due to ring current. A first attempt to do this was made by Pople.[17] Pople's treatment differs in that it does not involve an explicit form for $\underline{A}$ as in the London method putting $\underline{A} = -\frac{1}{2}\underline{r} \wedge \underline{H}_o$. The expansion of the secular equation

$$\left| H_{st} - x\beta\delta_{st} \right| = o$$

leads to a polynomial in x, the coefficients all being expressible in terms of closed cyclic products of the type

$$H_{ij}\, H_{jk}\, H_{kl} \;\ldots\; H_{pq}\, H_{qi} / \beta^n$$

n being the number of factors. These expressions will appear as products of a number of irreducible products, corresponding to the number of rings in the molecule. If for each irreducible circuit, the London's notation is used,

$$H_{ij}\, H_{jk} \ldots H_{qi} = \beta^n\, e^{2\pi i f}$$

where $f = \frac{e}{2hc} \sum' (\underline{A}_s - \underline{A}_t) \cdot (\underline{R}_s + \underline{R}_t)$

the sum $\sum'$ being over ordered pairs around the ring.

This sum can be approximated by using

$$\underline{A}_s - \underline{A}_t = \angle(\underline{R}_s - \underline{R}_t)\cdot\nabla\angle\ \underline{A}$$

and then

$$f = \frac{e}{hc} \oint R_\beta\ (\nabla\alpha\ A\beta)\ dR\alpha$$

where the greek suffixes refer to tensor notation. Then using Stokes' theorem

$$f = -\frac{e}{hc}\iint \underline{H}.d\underline{s}$$

If $\underline{H}$ is uniform and equal to $H_o$, Pople's treatment leads to the same formula as London. f is then proportional to the flux of the magnetic field through the ring. Pople then introduces a testing field $\underline{H}'$ the nature of which is not specified and replaces the quantities $f_i$'s by $f_i + f_i'$, where $f_i'$ is $-\frac{e}{hc}$ times the flux of the testing field through the ith circuit.

The first complete theory of the ring current contribution to the chemical shift was given by McWeeny.[27] He considers the molecule in the presence of an external uniform magnetic field and a point dipole field, origin of which is at the proton in question. Thus the whole problem is treated as a unity and not divided into a

separate problem of calculating a current and then a field.

If $\underline{m}$ is the proton dipole moment,

$$\underline{A} = -\tfrac{1}{2}\,\underline{r} \times \underline{H} \; - \frac{\underline{r} \times \underline{m}}{r^3}$$

and $H_{st}$ is now

$$H_{st} = \beta_{st}^{(o)}\, e^{\frac{ie}{\hbar c}\left\{ S_{st}\,(H + \frac{m}{R_s^3} + \frac{m}{R_t^3}\,)\right\}} = \beta_{st}^{(o)}\omega_{st}$$

The total energy is found in terms of the external field $\underline{H}$ and the dipole moment $\underline{m}$ and the coefficient of $\underline{Hm}$ in this energy leads to the shift required.

Using ordinary perturbation theory, McWeeny shows that the solution can be expressed in terms of the bond orders and what he calls imaginary polarizabilities, because there is no restriction to the <u>real</u> perturbations. These are similar to the Coulson and Longuet-Higgins polarizabilities:

$$\bar{\pi}(rs)(tu) = \pi_{rs,tu} - \pi_{rs,ut} + \pi_{sr,ut} - \pi_{sr,tu}$$

where $$\pi_{rs,tu} = 2 \sum_{J}^{occ} \sum_{K}^{unocc} \frac{C_{rJ}^{*}\, C_{sK}\, C_{tK}^{*}\, C_{uJ}}{E_J - E_K}$$

and the c's are coefficient of the unperturbed MO's.

If $K_{ij} = \frac{1}{R_i^3} + \frac{1}{R_j^3}$ the final formula is:

$$\delta E_{mag} = -2\beta \frac{e^2}{\hbar^2 c^2} (\sigma_1 + \sigma_2) Hm$$

where $\sigma_1 = \sum_{ij} P_{ij} S_{ij}^2 K_{ij}$

$$\sigma_2 = \sum_{ij} \sum_{kl} \beta \bar{\pi}_{(ij)(kl)} S_{ij} S_{kl} \frac{K_{ij} + K_{kl}}{2}$$

Because the evaluation of these sums would evidently be excessively tedious if the molecule under consideration was a large polycyclic, by a change of basis defined by

$$\bar{\varphi} = \varphi V$$

where the $\varphi$'s are the old functions and $V$ is a diagonal matrix

$$V = \text{dia}(1, \omega_{12}^*, \omega_{12}^* \omega_{23}^*, \omega_{12}^* \omega_{23}^* \omega_{34}^*, \ldots)$$

the problem may be reduced to one in which only the bond of each ring is perturbed. If $\varphi_{(\mu)} = \sum_{(\mu)} S_{ij}$ and $K_{(\mu)} = \sum_{(\mu)} S_{ij} K_{ij}$ are ordered sums around the $\mu$th circuit,

$$\sigma_1 = \sum_{(\mu)} P_{(\mu)} \mathcal{S}_{(\mu)} \mathcal{K}_{(\mu)}$$

$$\sigma_2 = \sum_{(\mu)} \sum_{(\nu)} \beta \bar{\pi}_{(\mu)(\nu)} \tfrac{1}{2} \left\{ \mathcal{S}_{(\mu)} \mathcal{K}_{(\nu)} + \mathcal{K}_{(\mu)} \mathcal{S}_{(\nu)} \right\}$$

It turns out that the induced field calculated in this theory is much larger than in the point dipole theory and comparable with that in the uniform magnetic shell theory.

The observable differences are not so large, however, since the ratio of the fields to that at the benzene proton are fairly close to those of the simpler model.

For modern calculations on conjugated molecules the Hückel theory, which underlies the London theory and its extensions, has been found inadequate. This is partly because it does not take the electron repulsion properly into account and partly because its basic assumptions are not clearly stated. In order to clarify the foundation of the theory and to give a formulation which includes all the minor corrections a more accurate and more mathematical theory is required.

## 4. Localized orbitals in a magnetic field

The molecular orbital theory of conjugated molecules is based on the use of a set of localized functions and their linear combinations to define the molecular orbitals of the mobile electrons. The simplest way of defining these functions, especially when their analytical form is unknown, is in terms of the standard excited state.[28,30] In this state all the mobile electrons are in singly-occupied orbitals but the internuclear distances are kept fixed at their ground state values in order to preserve the orbitals of the remaining electrons. This highly excited state is used merely to provide a definition of the localized orbitals.

In the absence of a field the localized orbitals are defined in terms of the singly-occupied orbitals. These orbitals can be transformed linearly among themselves and, if their orthonormality is preserved, the molecular wavefunction and the corresponding total energy are unchanged. On the other hand the total self-energy,

$$S = \sum_r \int |\chi_r(1)|^2 \, |\chi_r(2)|^2 \, 1/r_{12} \, d\tau_{12}, \quad (4.01)$$

will change depending on the concentration or localization of the orbitals. The orbitals $\chi_r$ for which S becomes a maximum, are defined as the localized orbitals. One advantage of this definition is that the orbitals become independent of the sets of basis functions used to describe them in a calculation from first principles. When the basis functions are atomic orbitals it is necessary to orthogonalize as well as to maximize S. The resulting $\chi_r$, as has been shown in a calculation on butadiene[29], are more localized than the original atomic orbitals and have a larger S. The localization would probably be even greater if several atomic orbitals were used at each atom so that the orthogonalization need not mix functions on different centres.

The equations which the localized orbitals satisfy are:

$$\left(-\tfrac{1}{2}\nabla^2-\sum_\alpha \frac{Z_\alpha}{r\alpha}+2\sum_\sigma \int \frac{\psi_\sigma^* \psi_\sigma}{r_{12}}\, d\tau_2 - \sum_\sigma \int \frac{\psi_\sigma^* P \psi_\sigma}{r_{12}}\, d\tau_2 + \sum_t \int \frac{\chi_t^* \chi_t}{r_{12}}\, d\tau_2 - \sum_t \int \frac{\chi_t^* P \chi_t}{r_{12}}\, d\tau_2\right)\chi_s = \sum_r \chi_r e_{rs} \qquad (4.02)$$

where $\psi_\sigma$ is an orbital of the framework and P an operator which permutes the variables in the two orbitals which follow it. The self-energy condition ensures that the remaining part of the exchange potential,

$$\left(\sum_{t\neq s}\int \frac{\chi_t^{*}P\chi_t d\tau_2}{r_{12}}\right)\chi_s \qquad (4.03)$$

is as small as possible. The omission of this term would reduce the equations to the same form as in the Hartree theory. This is known to give substantially the same results for atomic orbitals in atoms and should do also for these localized orbitals. Since the number of singly-occupied orbitals is equal to the number of electrons, each is fully occupied and all the atoms in the molecule are neutral as far as the mobile electrons are concerned. There are, therefore, no long range forces and the $e_{rs}$ decrease rapidly as $\chi_r$ and $\chi_s$ become further apart.

When a magnetic field is present, the momentum of an electron is changed from $\underline{p}$ to $\underline{p} + \alpha\underline{A}$, where $\underline{A}$ is the vector potential of the field in atomic units and $\alpha$ the fine structure constant. The kinetic energy operator changes correspondingly to

$$-\tfrac{1}{2}(\nabla + i\alpha\underline{A})^2 \qquad (4.04)$$

Now the vector potential for a uniform field $\underline{H}$ is

$$\underline{A} = \tfrac{1}{2}\underline{H}\wedge\underline{r} \qquad (4.05)$$

where the origin of the vector r can still be chosen arbitrarily, and this variation of $\underline{A}$ with position means that the kinetic energy operator depends on the choice of origin and is no longer the same around equivalent nuclei. This undesirable feature can be removed by introducing a phase factor into the orbitals. Thus if the localized orbitals in the presence of the field are $\omega_s$ and satisfy

$$\left(-\tfrac{1}{2}(\bar{\nabla}+i\alpha\underline{A})^2-\sum_\alpha \frac{Z_\alpha}{r_\alpha}+2\sum_\sigma\int\frac{\psi_\sigma^*\psi_\sigma}{r_{12}}d\tau_2-\sum_\sigma\int\frac{\psi_\sigma^* P\psi_\sigma}{r_{12}}d\tau_2+\right.$$
$$\left.+\sum_t\int\frac{\omega_t^*\omega_t}{r_{12}}d\tau_2-\sum_t\int\frac{\omega_t^* P\omega_t}{r_{12}}d\tau_2\right)\omega_s=\sum_r\omega_r\,\varepsilon_{rs}$$

then new functions $\bar{\chi}_s$ are introduced by the equation

$$\omega_s=\bar{\chi}_s\,e^{\,ig_s} \qquad (4.07)$$

where $g_s$ is a function of position. The effect of the kinetic energy operator is then

$$-\tfrac{1}{2}(\bar{\nabla}+i\alpha\underline{A})^2\omega_s=-\tfrac{1}{2}\,e^{ig_s}(\nabla+i\alpha\underline{A}+i\nabla g_s)^2\bar{\chi}_s \qquad (4.08)$$

and, when $g_s$ is fixed by

$$g_s=-\alpha\underline{A}_s\cdot\underline{r} \qquad (4.09)$$

with $\underline{A}_s$ the value of the vector potential at the sth nucleus, this becomes

$$-\tfrac{1}{2}\, e^{ig_s\left\{(\nabla + i\alpha\overline{A} - \underline{A}_s\overline{\jmath})^2 \chi_s\right\}} \qquad (4.10)$$

and so becomes the same around equivalent nuclei. Since

$$\int \frac{\omega_s^* \omega_s}{r_{12}}\, d\tau_2 = \int \frac{\chi_s^* \chi_s}{r_{12}}\, d\tau_2 \qquad (4.11)$$

the equation determining $\bar{\chi}_s$ becomes:

$$\left(-\tfrac{1}{2}(\nabla + i\alpha\overline{A} - \underline{A}_s\overline{\jmath})^2 - \sum_\alpha \frac{Z_\alpha}{r_\alpha} + 2\sum_\sigma \int \frac{\psi_\sigma^* \psi_\sigma}{r_{12}}\, d\tau_2 - \sum_\sigma \int \frac{\psi_\sigma^* P \psi_\sigma}{r_{12}}\, d\tau_2 + \right.$$

$$\left. + \sum_t \int \frac{\bar{\chi}_t^* \bar{\chi}_t}{r_{12}}\, d\tau_2 - \sum_t \int \frac{\bar{\chi}_t^* P \bar{\chi}_t}{r_{12}}\, d\tau_2 \right) \bar{\chi}_s = \sum_r \bar{\chi}_r\, e^{i\alpha(\underline{A}_s - \underline{A}_r)\cdot \underline{r}}\, \varepsilon_{rs} \qquad (4.12)$$

where the small term in (4.03) is treated approximately. It is possible to solve this equation by perturbing the field-free equation (4.02) since the vector potential terms vanish at the nucleus. The zero-order solution is just $\chi_s$. Now, for a uniform magnetic field $\underline{H}$,

$$(\underline{A} - \underline{A}_s)\cdot\nabla = \tfrac{1}{2}\underline{H} \wedge (\underline{r} - \underline{r}_s)\cdot\nabla = \tfrac{1}{2}\underline{H}\cdot(\underline{r} - \underline{r}_s)\wedge\nabla = \frac{i}{2}\, \underline{H}\cdot\underline{L} \qquad (4.13)$$

where $\underline{L}$ is the angular momentum around the nucleus s; and if $\chi_s$ is $p_z$-like,

$$L_z \chi_s = 0 \qquad (4.14)$$

so that, for a field in the z direction,

$$-\tfrac{1}{2}(\nabla + i\alpha|\underline{A}-\underline{A}_s|)^2 \chi_s = -\tfrac{1}{2}\nabla^2 \chi_s + \frac{\alpha^2}{2}|\underline{A}-\underline{A}_s|^2 \chi_s \qquad (4.15)$$

(Equation 4.14 can be satisfied, when $\chi_s$ is constructed from atomic orbitals, if the orthogonalization is performed by mixing $2p_z$-like and $3p_z$-like orbitals on one centre instead of using functions on other centres). Thus the choice of phase in (4.09) not only ensures that the effective Hamiltonian in (4.12) is equivalent around equivalent nuclei but also that the terms of first order in the field have no effect. The first correction to the orbital is then quadratic in the field i.e.

$$\bar{\chi}_s = \chi_s + O(H^2) \qquad (4.16)$$

The values of the matrix elements $\xi_{rs}$ are found by multiplying (4.12) by $\chi_u^*$ and integrating to give

$$e_{us} + \frac{\alpha^2}{2}\int \chi_u^* |A-A_s|^2 \chi_s \, d\tau = \sum_r \xi_{rs} \int \chi_u^* e^{i\alpha(\underline{A}_s-\underline{A}_r)\cdot\underline{r}} \chi_r \, d\tau$$

(4.17)

The final integral can be expanded as

$$\int \chi_u^* \chi_r (1+i\alpha(\underline{A}_s-\underline{A}_r)\cdot\underline{r} - \frac{\alpha^2}{2}[(\underline{A}_s-\underline{A}_r)\cdot r]^2 + )\, d\tau =$$

$$= \delta_{ur} + i\alpha(\underline{A}_s-\underline{A}_r)\cdot\int \chi_u^* \underline{r} \chi_r \, d\tau - \frac{\alpha^2}{2}\int \chi_u^* [(\underline{A}_s-\underline{A}_r)\cdot\underline{r}]^2 \chi_r \, d\tau + \ldots\ldots$$

(4.18)

and, if $\chi_u$ and $\chi_r$ are sufficiently localized for the transition integral to be negligable, this becomes

$$\delta_{ur}\left(e^{i\alpha(\underline{A}_s-\underline{A}_r)\cdot\underline{r}_r} - \frac{\alpha^2}{2}\int \chi_r^* [(\underline{A}_s-\underline{A}_r)\cdot(\underline{r}-\underline{r}_r)]^2 \chi_r \, d\tau\right) \quad (4.19)$$

and $\underline{r}_r$ is the position of the rth nucleus. Thus the result becomes

$$\mathcal{E}_{us} = [e]_{us} + \frac{\alpha^2}{2}\delta_{us}\int \chi_s^* |\underline{A}-\underline{A}_s|^2 \chi_s \, d\tau] \, e^{i\alpha(\underline{A}_u-\underline{A}_s)\cdot\underline{r}_u} +$$

$$+ \frac{\alpha^2}{2} e_{us}\int \chi_s^* [(\underline{A}_s-\underline{A}_s)\cdot\underline{r}-\underline{r}_s)]^2 \chi_s \, d\tau \quad (4.20)$$

at least as far as the terms linear and quatratic in $\underline{H}$ are concerned. The exponential is often put into the more symmetric form

$$e^{\frac{1}{2}i\alpha(\underline{A}_u-\underline{A}_s)\cdot(\underline{r}_u+\underline{r}_s)} \qquad (4.21)$$

which has the same value when $\underline{H}$ is uniform.

## 5. The molecular ground state in a magnetic field

The purpose of the discussion of the standard excited state is to provide a definition of the localized orbitals which takes account of their molecular environment but avoids the problems of delocalization, movement of charge and ring current which complicate the ground state. Once these orbitals are obtained they are used to describe the ground state without further reference to the excited state. The ground state molecular orbitals are

$$\psi_n = \sum_s \omega_s \, a_{sn} \qquad (5.01)$$

and the bond order matrix is

$$p_{st} = 2 \sum_n^{occ} a_{sn} \, a^*_{tn} \qquad (5.02)$$

where the sum includes only the occupied molecular orbitals.

The equation determining the molecular orbitals, in the presence of the field, is

$$\left[-\tfrac{1}{2}(\nabla + i\alpha\underline{A})^2 - \sum_\alpha \frac{Z_\alpha}{r_\alpha} + 2\sum_\sigma \int \frac{\psi_\sigma^* \psi_\sigma}{r_{12}}\, d\tau_2 - \sum_\sigma \int \frac{\psi_\sigma^* P \psi_\sigma}{r_{12}}\, d\tau_2 + \right.$$
$$\left. + 2 \sum_n^{occ} \int \frac{\psi_n^* \psi_n}{r_{12}}\, d\tau_2 - \sum_n^{occ} \int \frac{\psi_n^* P \psi_n}{r_{12}}\, d\tau_2 \right] \psi_s = E_s \psi_s \qquad (5.03)$$

and, on substituting (5.01), multiplying by $\omega_r^*$ and integrating, the matrix form of (5.03) is obtained as

$$(F_{rs} - E_n \delta_{rs})\, a_{sn} = 0 \qquad (5.04)$$

where

$$F_{rs} = \mathcal{E}_{rs} + \sum_{ut} p_{ut}(tu|rs) - \sum_u (uu|rs) - \tfrac{1}{2}\sum_{ut} p_{ut}(ts|ru) + \sum_u (us|ru) \qquad (5.05)$$

$$(ab|cd) = \int \omega_a^*(1)\, \omega_b(1) \frac{1}{r_{12}}\, \omega_c^*(2)\, \omega_d(2)\, d\tau_{12} \qquad (5.06)$$

When the orbitals are orthogonal and as localized as these the Pariser-Parr approximation,

$$(ab|cd) = \delta_{ab}\delta_{cd}\int \omega_a^*(1)\,\omega_a(1)\,\frac{1}{r_{12}}\,\omega_c^*(2)\,\omega_c(2)\,d\tau_{12}$$

$$= \delta_{ab}\delta_{cd}\int \chi_a^*(1)\,\chi_a(1)\,\frac{1}{r_{12}}\,\chi_c^*(2)\,\chi_c(2)\,d\tau_{12}$$

$$= \delta_{ab}\delta_{cd}\gamma_{ac} \qquad (5.07)$$

has been shown[29] to be a close approximation and (5.05) simplifies to

$$F_{rs} = \varepsilon_{rs} - \tfrac{1}{2}P_{rs}\gamma_{rs} + \delta_{rs}\left(\sum_t P_{tt}\gamma_{tr} - \sum_{t\neq r}\gamma_{tr}\right) \qquad (5.08)$$

The total electronic energy of the molecule in its ground state can be written as

$$W = \sum_n^{occ}(E_n + H_n) + \sum_\tau (E_\tau + H_\tau) \qquad (5.09)$$

where

$$H_n = \int \psi_n^*\left[-\tfrac{1}{2}(\nabla + i\alpha\underline{A})^2 - \sum_\alpha \frac{Z_\alpha}{r_\alpha}\right]\psi_n\, d\tau \qquad (5.10)$$

and $E_n$ can be defined as in (5.04), or as

$$E_n=H_n+2\sum_{\sigma}\int\psi_n^*(1)\psi_n(1)\frac{1}{r_{12}}\psi_\sigma^*(2)\psi_\sigma(2)d\tau_{12}-$$
$$-\sum_{\sigma}\int\psi_n^*(1)\psi_\sigma(1)\frac{1}{r_{12}}\psi_\sigma^*(2)\psi_n(2)d\tau_{12}+$$
$$+\sum_{rs}p_{rs}\int\omega_s^*(1)\omega_r(1)\frac{1}{r_{12}}\psi_n^*(2)\psi_n(2)d\tau_{12}-$$
$$-\tfrac{1}{2}\sum_{rs}p_{rs}\int\omega_s^*(1)\psi_n(1)\frac{1}{r_{12}}\psi_n^*(2)\omega_r(2)d\tau_{12} \qquad (5.11)$$

Thus, for the mobile electrons alone, the contribution to the total energy is

$$\sum_{n}^{occ}(E_n+H_n)=\tfrac{1}{2}\sum_{rs}p_{rs}(\mathcal{F}_{sr}+h_{sr}) \qquad (5.12)$$

where

$$h_{sr}=\int\omega_s^*\left[-\tfrac{1}{2}(\nabla+i\alpha\underline{A})^2-\sum_{\alpha}\frac{Z_\alpha}{r_\alpha}\right]\omega_r d\tau \qquad (5.1\ )$$

The core electrons must also be considered because of their interaction with the mobile electrons so that the total electronic energy becomes

$$W=\sum_{\tau}\left\{2H_\tau+2\sum_{\sigma}\int\psi_\sigma^*(1)\psi_\sigma(1)\frac{1}{r_{12}}\psi_\tau^*(2)\psi_\tau(2)d\tau_{12}-\right.$$
$$\left.-\sum_{\sigma}\int\psi_\sigma^*(1)\psi_\tau(1)\frac{1}{r_{12}}\psi_\tau^*(2)\psi_\sigma(1)d\tau_{12}\right\}+$$
$$+\sum_{rs}p_{rs}\sum_{\tau}\int\omega_s^*(1)\omega_r(1)\frac{1}{r_{12}}\psi_\tau^*(2)\psi_\tau(2)d\tau_{12}-$$
$$-\tfrac{1}{2}\sum_{rs}p_{rs}\sum_{\tau}\int\omega_s^*(1)\psi_\tau(1)\frac{1}{r_{12}}\psi_\tau^*(2)\omega_r(2)d\tau_{12}+ \qquad (5.14)$$
$$+\tfrac{1}{2}\sum_{rs}p_{rs}(\mathcal{F}_{sr}+h_{sr})$$

but

$$h_{sr}+2\sum_{\tau}\int\omega_s^*(1)\omega_r(1)\frac{1}{r_{12}}\psi_\tau^*(2)\psi_\tau(2)d\tau_{12}-$$
$$-\sum_{\tau}\int\omega_s^*(1)\psi_\tau(1)\frac{1}{r_{12}}\psi_\tau^*(2)\omega_r(2)d\tau_{12}=$$
$$=\mathcal{E}_{sr}-\sum_t(tt|sr)+\sum_t(tr|st) \qquad (5.15)$$

so that

$$W=W_\sigma+\tfrac{1}{2}\sum_{rs}p_{rs}\left\{\mathcal{F}_{sr}+\mathcal{E}_{sr}-\sum_t(tt|sr)+\sum_t(tr|st)\right\} \qquad (5.16)$$

and using (5.07) this becomes

$$W=W_\sigma+\tfrac{1}{2}\sum_{rs}p_{rs}\left\{\mathcal{F}_{sr}+\mathcal{E}_{sr}-\sum_{t\neq r}\gamma_{tr}\delta_{sr}\right\} \qquad (5.17)$$

where $W_\sigma$ is quite independent of the mobile electrons.

## 6. The shielding of a magnetic dipole

In order to calculate the shielding effect of the ring current on an attached proton the molecule is subject to two perturbations. The first of these is the uniform magnetic field H, which is imposed on the molecule, and the second is the field due to the magnetic dipole of moment m, located at the proton and

directed perpendicular to the ring. These two fields combine to give a vector potential which has the form

$$\underline{A} = \tfrac{1}{2}\underline{H} \wedge \underline{r} + m \frac{\underline{n} \wedge \underline{r}}{r^3} \qquad (6.01)$$

where the proton is chosen as the origin of $\underline{r}$ and $\underline{n}$ is the normal to the molecular plane.[27] The total energy, is, then, a function of both H and m and the ring current contribution to the diamagnetic anisotropy is derived from the coefficient of $H^2$ in its power series expansion while the ring current contribution to the chemical shift is the coefficient of -Hm. These coefficients can be calculated by perturbation theory carried to second order.

Since the ring current contributions are to be isolated from the contributions localized in the separate orbitals the matrix elements $\mathcal{E}_{us}$ are taken as

$$\mathcal{E}_{us} = e_{us}\, e^{\frac{i\alpha}{2}(\underline{A}_u - \underline{A}_s)\cdot(\underline{r}_r + \underline{r}_s)}$$

$$= e_{us}\left\{1 + \frac{i\alpha}{2}(\underline{A}_u - \underline{A}_s)\cdot(\underline{r}_u + \underline{r}_s) - \frac{\alpha}{8}^2\left[(\underline{A}_u - \underline{A}_s)\cdot(\underline{r}_u + \underline{r}_s)\right]^2 + \right.$$

$$\left. + \ldots\ldots\right\} \qquad (6.02)$$

If $S_{us}$ is the signed area of the triangle formed by the proton and the nuclei u and s, i.e.

$$S_{is} = \tfrac{1}{2}(\underline{r}_u \wedge \underline{r}_s) \qquad (6.03)$$

and $K_{us}$ is the geometrical factor

$$K_{us} = \underline{r}_u^{-3} + r_s^{-3} \qquad (6.04)$$

then for a field normal to the molecular plane and a dipole in the same direction

$$\tfrac{1}{2}(\underline{A}_u - \underline{A}_s)\cdot(\underline{r}_u + \underline{r}_s) = H\, S_{us} + mS_{us}K_{us} \qquad (6.05)$$

Thus the expansion becomes

$$\mathcal{E}_{us} = e_{us}\left\{1 + i\alpha S_{us}(H+mK_{us}) - \frac{\alpha^2}{2} S_{us}^2(H^2+2HmK_{us}+m^2K_{us}^2)+\ldots\right\} \qquad (6.06)$$

It is to be noted that $\mathcal{E}_{us}$ remains Hermitean since $S_{us}$ is a skew matrix. The first order perturbations are, then, purely imaginary.

## 7. The perturbation theory

Although the formulae required to apply perturbation theory to the self-consistent equations are well-known for simpler forms of perturbation they require

some extensions before they can be applied here.

The molecular orbital coefficients, $a_{sn}$, are expanded as power series in iH and im in order to keep the remaining factors real. This gives

$$a_{sn} = a^{o}_{sn} + iHa'_{sn} + im'a_{sn} - H^2a''_{sn} - Hm\,'a'_{sn} \cdots\cdots \tag{7.01}$$

and, hence, the bond order matrix has a similar expansion

$$p_{rs}=p^{o}_{rs} + iHp'_{rs} + im\,'p_{rs} - H^2\,p''_{rs} - H_m\,'p'_{rs} - \cdots\cdots \tag{7.02}$$

where

$$p^{o}_{rs} = 2\sum_{n}^{occ} a_{rn}a_{sn} \tag{7.03}$$

$$p'_{rs} = 2\sum_{n}^{occ} (a'_{rn}\,a^{o}_{sn} - a^{o}_{rn}\,a'_{sn}) \tag{7.04}$$

$$'p_{rs} = 2\sum_{n}^{occ} ('a_{rn}a^{o}_{sn} - a^{o}_{rn}\,'a_{sn}) \tag{7.05}$$

$$p''_{rs} = 2\sum_{n}^{occ} (a''_{rn}\,a^{o}_{sn} - a'_{rn}\,a'_{sn} + a^{o}_{rn}\,a''_{sn}) \text{ etc.} \tag{7.06}$$

It follows from these equations that the first order changes in the charges vanish. In a similar way the formal expansion of $\mathcal{F}_{rs}$ is

$$\mathcal{F}_{sr} = F_{sr} + iHF'_{sr} + im'F_{sr} - H^2 F''_{sr} - H_m {}'F'_{sr} - \ldots \tag{7.07}$$

and, from (6.06) and (5.02), $F_{rs}$ is the usual field-free matrix,

$$F'_{sr} = \alpha S_{sr} e_{sr} - \tfrac{1}{2} p'_{sr} \gamma_{sr} \tag{7.08}$$

$$'F_{sr} = \alpha S_{sr} K_{sr} e_{sr} - \tfrac{1}{2} {}'p_{sr} \gamma_{sr} \tag{7.09}$$

$$F''_{sr} = \frac{\alpha^2}{2} S^2_{sr} e_{sr} - \tfrac{1}{2} p''_{sr} \gamma_{sr} + \delta_{sr} \sum_t p''_{tt} \gamma_{tr} \tag{7.10}$$

$$'F'_{sr} = \alpha^2 S^2_{sr} K_{sr} e_{sr} - \tfrac{1}{2} {}'p'_{sr} \gamma_{sr} + \delta_{sr} \sum_t {}'p'_{tt} \gamma_{tr} \tag{7.11}$$

The self-consistent equations become to zero order

$$\sum_r (F_{sr} - \delta_{sr} E^o_n) a^o_{rn} = o \tag{7.12}$$

to first order

$$\sum_r (F_{sr} - \delta_{sr} E_n^\circ) a'_{rn} = \sum_r (E'_n \delta_{sr} - F'_{sr}) a^\circ_{rn} \qquad (7.13)$$

$$\sum_r (F_{sr} - \delta_{sr} E_n^\circ) {}'a_{rn} = \sum_r ({}'E_n \delta_{sr} - {}'F_{sr}) a^\circ_{rn} \qquad (7.14)$$

and to second order

$$\sum_r (F_{sr} - \delta_{sr} E_n^\circ) a''_{rn} = \sum_r (E'_n \delta_{sr} - F'_{sr}) a'_{rn} + \sum_r (E''_n \delta_{sr} - F''_{sr}) a^\circ_{rn} \qquad (7.15)$$

$$\sum_r (F_{sr} - \delta_{sr} E_n^\circ) {}'a'_{rn} = \sum (E'_n \delta_{sr} - F'_{sr}) {}'a_{rn} + \sum_r ({}'E_n \delta_{sr} - {}'F_{sr}) a'_{rn} + + \sum_r ({}'E'_n \delta_{sr} - {}'F'_{sr}) a^\circ_{rn} \qquad (7.16)$$

where the eigenvalue $E_n$ has been similarly expanded. Since $E_n^\circ$ is an eigenvalue of $F_{sr}$, the equations (7.13) can be solved only if

$$\sum_{rs} a^\circ_{sn} (E'_n \delta_{sr} - F'_{sr}) a^\circ_{rn} = o \qquad (7.17)$$

but since $F'_{sr}$ is skew this implies

$$E'_n = o \qquad (7.18)$$

and similarly, from (7.14),

$${}'E_n = o \qquad (7.19)$$

the corresponding relation for (7.15) is

$$E_n'' = \sum_{sr} F''_{sr}\, a^{o}_{rn}\, a^{o}_{sn} + \sum_{sr} F'_{sr}\, a'_{rn}\, a^{o}_{sn} \tag{7.20}$$

so that

$$\sum_{n}^{occ} E_n'' = \tfrac{1}{2} \sum_{sr} F''_{sr}\, p^{o}_{rs} + \tfrac{1}{4} \sum_{sr} F'_{sr}\, p'_{rs} \tag{7.21}$$

and for (7.16)

$$'E_n' = \sum_{sr} {}'F'_{sr}\, a^{o}_{rn} a^{o}_{sn} + \sum_{sr} {}'F_{sr}\, a'_{rn}\, a^{o}_{sn} + \sum_{sr} F'_{sr}\, {}'a_{rn}\, a^{o}_{sn} \tag{7.22}$$

$$\sum_{n}^{occ} {}'E_n' = \tfrac{1}{2} \sum_{sr} {}'F'_{sr}\, p^{o}_{rs} + \tfrac{1}{4} \sum_{sr} {}'F_{sr}\, p'_{rs} + \tfrac{1}{4} \sum_{sr} F'_{sr}\, {}'p_{rs} \tag{7.23}$$

On the other hand, from (5.12),

$$\sum_{n}^{occ} E_n'' = \tfrac{1}{2} \sum_{sr} F''_{sr}\, p^{o}_{rs} + \tfrac{1}{2} \sum_{sr} F'_{sr}\, p'_{rs} + \tfrac{1}{2} \sum_{sr} F^{o}_{sr}\, p''_{rs} \tag{7.24}$$

and, therefore,

$$\sum_{sr} F'_{sr}\, p'_{rs} = -2 \sum_{sr} F^{o}_{sr}\, p''_{rs} \tag{7.25}$$

and, similarly,

$$\sum_{sr} {}'F_{sr}\, p'_{rs} + \sum_{sr} F'_{sr}\, {}'p_{rs} = -2 \sum_{sr} F_{sr}\, {}'p'_{rs} \qquad (7.26)$$

The changes in the total energy are most conveniently obtained by using a modified form of (5.17) viz.

$$W = W_0 + \sum_{n}^{occ} E_n + \tfrac{1}{2} \sum_{rs} (\varepsilon_{sr} - \sum_{t\neq r} \gamma_{tr}\, \delta_{sr})\, p_{rs} \qquad (7.27)$$

so that

$$W'' = \sum_{n}^{occ} E''_n + \tfrac{1}{2} \sum_{rs} \Big\{ (e_{sr} - \sum_{t\neq r} \gamma_{tr}\, \delta_{sr}) p''_{rs} + S_{sr} e_{sr} p'_{rs} + \tfrac{1}{2} S^2_{sr}\, e_{sr}\, p^o_{rs} \Big\} \qquad (7.28)$$

$$'W' = \sum_{n}^{occ} {}'E'_n + \tfrac{1}{2} \sum_{rs} \Big\{ (e_{sr} - \sum_{t\neq r} \gamma_{tr}\delta_{sr})'p'_{rs} + S_{sr} e_{sr}\, {}'p_{rs} + S_{sr} K_{sr} e_{sr} p'_{rs} + S^2_{sr} K_{sr} e_{sr} p^o_{rs} \Big\} \qquad (7.29)$$

These equations can be simplified using (7.21), (7.23), (7.25), (7.26) to give

$$W'' = \frac{\alpha^2}{2} \sum_{rs} S^2_{sr} e_{sr} p^o_{rs} + \frac{\alpha^2}{2} \sum_{rs} S_{sr} e_{sr} p'_{rs} \qquad (7.30)$$

$$'W' = \alpha^2 \sum_{rs} S^2_{sr} K_{sr} e_{sr} p^o_{rs} + \frac{\alpha^2}{2} \sum_{rs} S_{sr} e_{sr}\, {}'p_{rs} + \frac{\alpha^2}{2} \sum_{rs} S_{sr} K_{sr} e_{sr} p'_{rs} \qquad (7.31)$$

It can be easily deduced from (7.13) and (7.14) that the last two terms in (7.31) are equal so that

$$'W' = \alpha^2 \sum_{rs} S_{sr}^2 K_{sr} e_{sr} p_{rs}^o + \alpha^2 \sum_{rs} S_{sr} K_{sr} e_{sr} p_{rs}' \qquad (7.32)$$

Thus the final expressions for the two coefficients of interest involve only the unperturbed bond orders $p_{rs}^o$ and their first order change in the presence of the uniform field $p_{rs}$. The calculation of this second matrix is more difficult since the basic equation (7.13) involves the matrices $F_{sr}$ and $F_{sr}^1$.

## 8. Numerical Procedure

The first step in the numerical calculation of the coefficients is to solve the field-free equations and so obtain $F_{sr}$ and $p_{rs}^o$. The second step is to solve the perturbation equation (7.13). If the matrix $F_{sr}^1$ is assumed known, the equations can be solved for the various $a_{rn}^1$ using either the method of expanding in terms of the unperturbed eigenvectors as in ordinary perturbation theory or by solving the linear equations with the additional condition, which can be imposed

without loss of generality, that the perturbed eigenvector is orthogonal to the unperturbed one i.e.

$$\sum_r a'_{rn}\, a_{rn} = o \qquad (8.01)$$

These $a'_{rn}$ are then used to produce a new $F'_{sr}$ and the process is repeated until this matrix is consistent. Unfortunately this procedure converges slowly but it can be accelerated by using an extrapolation formula such as

$$(F'_{sr})_{ext} = \frac{(F'_{sr})_1(F'_{sr})_3 - (F'_{sr})_2(F'_{sr})_2}{(F'_{sr})_1 - 2(F'_{sr})_2 + (F'_{sr})_3}$$

which implies that the matrix elements in successive iterations are in geometric progressions. Once $F'_{sr}$ has been found, the evaluation of the coefficients from (7.30) and (7.32) is immediate.

This entire calculation has been programmed for the English Electric computer 'Deuce'. The solution of the field-free equations is continued until the elements of $p^o_{rs}$ are consistent to within 0.0002. Similarly, the iteration of the perturbation equations continues until the elements of $p'_{rs}$ are consistent to within 0.0002.

## 9. Results

For purposes of calculation, the unit of energy was chosen to be

$$\beta = -4.79 \text{ eV}$$

so that $\beta_{cc}$ and $\beta_{cN}$ for nearest neighbour elements are $0.5\beta$ and $0.538\beta$ respectively.[31,32] For the electrostatic integrals $\gamma_{rs}$ the values of McWeeny and Peacock[31,32] in units of $\beta$ have been chosen, and when necessary, have been calculated by the Pariser and Parr[34] formula

$$ar + br^2 = \tfrac{1}{2}\left[(pp|pp) + (qq|qq)\right] - (pp|qq)$$

for r, distance between centres, $\leq 2.80$ A. a and b were fixed by the McWeeny and Peacock values. When $r > 2.80$ A, interpolation in the Pariser table[35] was used.

The unit of length was chosen to be 1.40 Å, the C-C internuclear distance in benzene. Both $S_{sr}$ and $K_{sr}$ were calculated in terms of this unit. All C-C and C-N bond distances were assumed to have this value and the rings are assumed to be regular polygones. The C-H bond distance was taken to be 1.09 Å.

The zero order S.C.F. Hamiltonian was calculated using McWeeny steepest descent method,[33] which has the advantage of not requiring diagonalization of $\mathcal{H}$ in each iteration.

For each heteromolecule, three different values of $\delta_N$ and $\delta_O$ were chosen, where

$$\delta_X = \frac{\alpha_X - \alpha_C}{\beta}$$

The reason for doing this is that there is no certainty concerning these values and chemical shift data might ultimately lead to correct empirical evaluation of $\delta_X$. In Hückel treatment, the values $\delta_{\dot{N}} \simeq 0.5$* and $\delta_{\dot{O}} \simeq 1$ reproduce experimental dipole moments.[36-44] If the electron-density distribution given by S.C.F. calculations are sought, the values of $\delta_{\dot{N}} = 0.1\text{-}0.35$, $\delta_{\ddot{N}} = 2$ and $\delta_{\dot{O}} = 0.15$ are found.[31,32,45-47] So, the values of $\delta_{\dot{N}} = 0.2, 0.5, 0.8$, $\delta_{\ddot{N}} = 1, 1.5, 2$ $\delta_{\dot{O}} = 0.19, 0.49, 0.79$ in the Hückel treatment have been chosen. The corresponding values for S.C.F. treatment are found by using the approximative formula[31]

$$\delta_{\text{Hückel}} = \delta_{\text{SCF}} + \tfrac{1}{2}\,(Z_r\,\gamma_{rr} - \gamma_C^{(o)})$$

* The dots over the N and O refer to the number of $\pi$ electrons.[52]

The corresponding values are: $\delta'_N = 0.35, 0.65, 0.95$; $\delta''_N = 2.50, 3.00, 3.50$; $\delta'_O = 0.40, 0.70, 1.00$. In the presence of the field the total energy of the molecule is

$$W = W_o - H^2 W'' - Hm\,'W' \ldots\ldots$$

since the terms in H and m vanish for a normal molecule with doubly-occupied orbitals. The diamagnetic susceptibility is

$$-\frac{\partial^2 W}{\partial H^2} = 2\,W''$$

and the chemical shift

$$-\frac{\partial^2 W}{\partial H \partial m} = {}'W'$$

It is necessary to emphasize that the calculations include only the ring current contribution to both magnitudes and are based on a field which is normal to the molecular plane, since a field in the molecular plane produces no ring current. In practice, the chemical shift is averaged over all orientations and reduces to $\frac{1}{3}\,'W'$.

The results of these calculations are shown together with the corresponding results in the Hückel-London theory.

This theory can be derived formally from the self--consistent theory by putting $\gamma_{rs} = o$.

It is important to consider the accuracy of the experimental measurements with which the calculated results are to be compared. Chemical shift measurements, by means of nuclear magnetic resonance are considered first. The compound under investigation is dissolved in a suitable solvent and another substance is added as internal reference. The chemical shift is then determined relative to the internal reference. This procedure is necessary because it is not feasible to measure absolute resonance frequencies. There are a number of possible sources of error in this technique, the most important being the solvent effect.[53] This effect is composed of six major parts: a) Bulk susceptibility, b) anisotropy in the susceptibility of the solvent, c) solvent-solute complexing, d) Van der Waals forces, e) Polar effect and f) self-complexing of solute. Comparison of experiment with theory ideally should be made with experimental results at infinite dilution in a suitable solvent or better in gazeous state. A suitable solvent should be magnetically isotropic, chemically inert and non-polar so that when employed with

an internal reference, the factors a), b), and c) will be negligible. By extrapolating to infinite dilution it is then possible to reduce the importance of factors e) and f). It is then necessary to assume that effect of non-bonding interaction d) on the chemical shift are negligible or are constant for a series of compounds under investigation. This latter assumption could introduce errors of as much as 5 cps. in extreme cases,[53] but is likely to be unimportant for a series of closely related compounds.

Elvidge and Jackman[48] have an experimental technique for the estimation of the aromatic character, defined by ability to sustain an induced ring current, of the 2--pyridone ring system, by comparing the chemical shifts of methyl groups attached to this ring with those derived from non-aromatic model compounds. A second approach used by these authors was to subtract the estimated contribution of the ring current (assumed to be the same as in benzene), from the shifts of methyl groups and protons attached to the ring in pyridine and pyridinium salts models and then compare these values with those observed in the 2-pyridones. It was found that the pyridine model overestimated the ring current contribution whereas the pyridinium model underestimated it.

The authors therefore suggested that a linear combination of the form

$$\tau_{cal} = \tau_A - x\,(\tau_A - \tau_B) + (1 - x)\,r$$

where $\tau_A$ and $\tau_B$ are the shifts observed in pyridine and pyridinium models respectively, r is the estimated ring current contribution and x the functional aromaticity, should give a more accurate result. By comparing the observed shifts with those calculated from this equation a value for x was obtained.

The methods gave 0.36 and 0.31 based on methyl protons and ring protons, respectively as the fractional aromaticity of the 2-pyridone ring compared with benzene.

In the case of the diamagnetic anisotropy, the measurements are made on single crystals in a torsion balance and this, clearly, involves a big difficulty in comparing with theoretical results. Once again, it is important to draw attention to the fact that this theory calculates the London diamagnetic anisotropy and that this only accounts for $\frac{2}{3}$ of the total diamagnetic anisotropy of benzene.[18,56,57,58] The rest is made up from the $2p\pi$ atomic orbitals and the $\sigma$ framework. This $\sigma$ contribution is known to be very small.

Table 1 contains the results for naphthalene and azulene. For naphthalene, no significant difference between the two methods is found. This is expected as naphthalene is an alternant hydrocarbon and has unit $\pi$-electron charge densities at each carbon atom. In the case of azulene, a non-alternant hydrocarbon in which some degree of non-uniformity of the $\pi$-electron distribution develops, the S.C.F. model predicts significantly lower shielding of the protons attached to the five membered ring. This results in an improved agreement with experiment since the 3- and 2-protons are known to be less shielded than the 5- and 6-protons, respectively, even though the $\pi$-electron charge densities (table 1) at positions 3 and 2 are respectively higher than at 5 and 6. Even better agreement might result if a correction for the different hybridisation of the carbon atoms of five and seven membered rings (see however reference 20) could be made in addition to corrections for ring current and charge densities. The two methods predict almost the same value for the diamagnetic susceptibility of azulene.

Table 1

Calculated chemical shifts and diamagnetic anisotropies (relative to benzene) in naphthalene and azulene.

Naphthalene

| | Chemical Shifts | | | Diamagnetic anisotropy | |
|---|---|---|---|---|---|
| Position | "Huckel | S.C.F. | obs.[b] | "Huckel | S.C.F. |
| 1 | 1.31 | 1.28 | 1.34[c] | 2.18 | 2.14 |
| 2 | 1.17 | 1.15 | 1.12 | - | - |

Azulene

| | Chemical Shifts | | | | Diamagnetic anisotropy | |
|---|---|---|---|---|---|---|
| Position | "Huckel | S.C.F | obs.[d] | a | "Huckel | S.C.F. |
| 1,3 | 1.27 | 1.37 | 1.04 | +0.113 | 2.26 | 2.28 |
| 2 | 1.14 | 1.23 | 1.37 | -0.011 | | |
| 4,8 | 1.34 | 1.32 | 1.61 | -0.128 | | |
| 5,7 | 1.22 | 1.18 | 0.82 | +0.040 | | |
| 6 | 1.20 | 1.16 | 1.11 | -0.082 | | |

[a] Nett $\pi$-electron charges

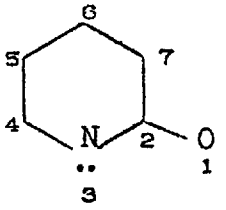
[b] Based on an experimental estimate of 1.55 p.p.m. for the ring current shift in benzene.[22]

[c] Ref. 49

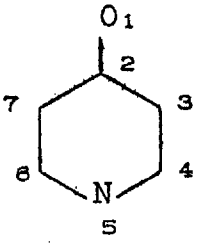
[d] Ref. 20.

The real value of the S.C.F. method becomes apparent in the treatment of molecules such as 1-methyl-2--pyridone (I) in which considerable π-charge separation occurs.

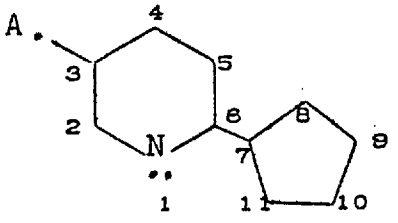
Table 2



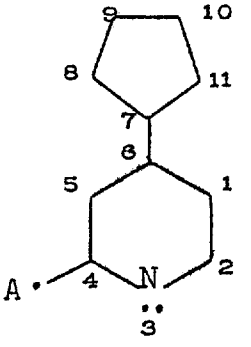
(I)



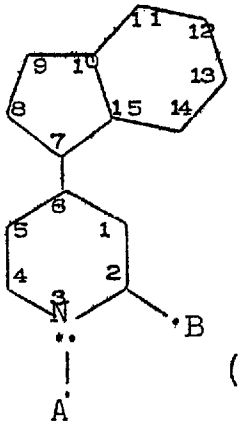
(II)



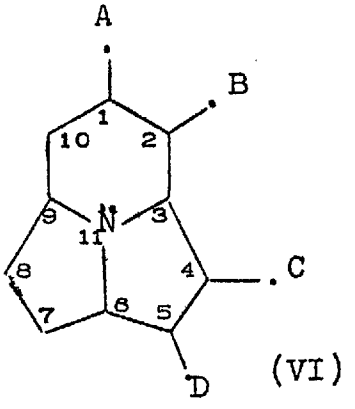
(III)



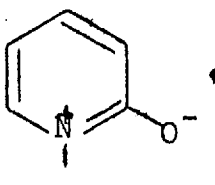
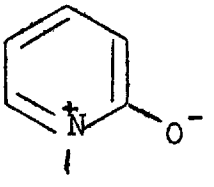
(IV)



(V)



(VI)

(VII)  (VIII) 

Tables 3 and 4 give the results of calculations of the ring current contribution to the chemical shift of the ring protons in 1-methyl-2-pyridone (I), 1-methyl-4--pyridone (II), 1-methyl-2-cyclopentadienyl-1, 2-dihydropyridine (III), 1-methyl-4-cyclopentadienyl-1, 4-dihydropyridine (IV) and 4-(1-Indenylidene)-1-methyl-1,4-dihydropyridine (V). It is seen that the Hückel method substantially overestimates the ring current since it allows for a greater contribution by the zwitter-ionic structures of the types (VII) and (VIII) to the ground states of these molecules. Furthermore, the Hückel method predicts similar magnitudes in the 2- and 4-series whereas the results of the S.C.F. method suggest that the ring current in the 4-compounds is significantly less than in 2-compounds, in accordance with the smaller separation between oxygen and nitrogen in the latter compounds.

Although a detailed study of the chemical shifts associated with ring currents has been made only for 1-methyl-2-pyridone, some data are available for (II), (III), and (IV). The shifts of protons $\alpha$ to nitrogen and of the protons of the 1-methyl groups are particularly sensitive to the charge on nitrogen. Thus, for these protons, large ring currents will be associated with

Table 3

Calculated chemical shifts and diamagnetic anisotropies (relative to benzene) in the heterocycles I and II.

| | | (I) | | (II) | |
|---|---|---|---|---|---|
| $\delta_{N}^{::}$ | $\delta_{O}^{:}$ | "Hückel | S.C.F. | "Hückel | S.C.F. |
| 1.02 | 0.19 | 0.52 | 0.33 | 0.53 | 0.18 |
| 1.02 | 0.49 | 0.64 | 0.49 | 0.65 | 0.37 |
| 1.02 | 0.79 | 0.71 | 0.62 | 0.73 | 0.52 |
| 1.52 | 0.19 | 0.42 | 0.23 | 0.44 | 0.14 |
| 1.52 | 0.49 | 0.55 | 0.37 | 0.56 | 0.29 |
| 1.52 | 0.79 | 0.63 | 0.48 | 0.64 | 0.41 |
| 2.02 | 0.19 | 0.34 | 0.16 | 0.36 | 0.11 |
| 2.02 | 0.49 | 0.47 | 0.28 | 0.48 | 0.23 |
| 2.02 | 0.79 | 0.55 | 0.38 | 0.56 | 0.33 |

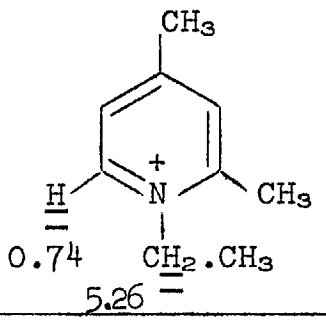
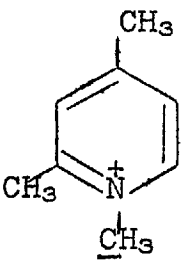
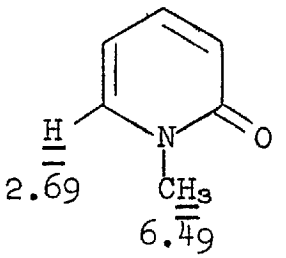
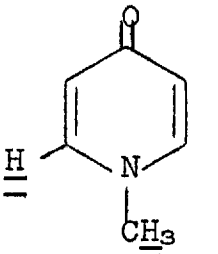
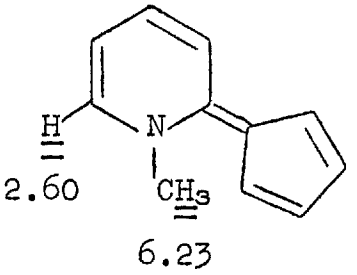
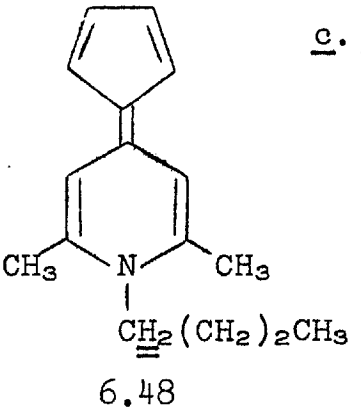
Table 4

Calculated chemical shifts (relative to benzene) in the heterocycles III, IV and V.

| | | (III) | | (IV) | | (V) | |
|---|---|---|---|---|---|---|---|
| $\delta_{\ddot{N}}$ | Position | "Hückel | S.C.F. | "Hückel | S.C.F. | "Hückel | S.C.F. |
| 1.02 | A | 0.82 | 0.56 | 0.83 | 0.44 | 0.79 | 0.36 |
| | B | | | | | 0.81 | 0.38 |
| 1.52 | A | 0.74 | 0.42 | 0.75 | 0.34 | 0.70 | 0.27 |
| | B | | | | | 0.72 | 0.29 |
| 2.02 | A | 0.65 | 0.31 | 0.67 | 0.26 | 0.61 | 0.21 |
| | B | | | | | 0.64 | 0.22 |

Table 5

Chemical Shifts ($\tau$-values) of protons of some heterocycles

| | |
|---|---|
| a.   | a.   |
| a.   | b.   |
| c.   | c.   |

a) reference 48 b) reference 50 c) reference 51.

shifts to lower fields, not only because of the shielding arising from the ring current, but also because large ring currents are provided by contributions of the zwitter-ionic structures in which the nitrogen carries a positive charge. Table 5 lists $\tau$-values (low values correspond to low shielding) for molecules of the types (I) - (IV). These data suggest the following orders for the ring currents in the four types

$$(I) > (II)$$
$$(III) > (IV)$$
$$(III) \sim (I)$$

The first two inequalities are clearly in accord with the S.C.F. calculations, irrespective of the values of the parameters employed. The Hückel treatment does not predict these results. The third relation is consistent with the S.C.F. predictions for the most likely values of the parameters for oxygen and nitrogen. In the present calculations the value of $\delta_O$ should presumably be kept small in order to compensate for the assumption that $\beta$ for the partial double bond between carbon and oxygen is equal to that for benzene.

It is interesting to note that the experimental estimate of $0.35 \pm 0.05$ for the ring current in

1-methyl-2-pyridone[48] is reproduced by the S.C.F. treatment using reasonable values for the oxygen and nitrogen parameters.

The ring current in (III) has been shown to be very close to that in 1-Me-2-pyridone (I).[51]

For the heterocycle (V) experimental shifts suggest virtually no ring current.[51] This is not in agreement with the calculated chemical shift and is probably due to steric deformation caused by the proximity of protons attached to carbons 1 and 14 (see table 2), which would require a smaller β value for the bond between the two rings 6-7.

For the pyridones (I), (II) the calculated Magnetic Susceptibilities expressed as ratios to benzene are identical with chemical shift ratios. Table 6 gives calculated values of the diamagnetic anisotropy in compounds (III), (IV) and (V). The difference in the results of two treatments is even more pronounced

Table 6

Calculated diamagnetic anisotropies (relative to benzene) in the heterocycles III, IV and V.

| $\delta_{N}$ | (III) | | (IV) | | (V) | |
|---|---|---|---|---|---|---|
| | "Hückel | S.C.F. | "Hückel | S.C.F. | "Hückel | S.C.F. |
| 1.02 | 1.24 | 0.79 | 1.25 | 0.59 | 2.28 | 1.49 |
| 1.52 | 1.15 | 0.58 | 1.15 | 0.42 | 2.15 | 1.33 |
| 2.02 | 1.05 | 0.41 | 1.06 | 0.28 | 2.04 | 1.20 |

Table 7

Calculated chemical shifts (relative to benzene) in the heterocycle VI.

| $\delta_{\ddot{N}}$ | Position | "Huckel" | S.C.F. |
|---|---|---|---|
| 1.02 | A | 1.41 | 1.44 |
| | B | 1.51 | 1.54 |
| | C | 1.20 | 1.22 |
| | D | 1.08 | 1.09 |
| 1.52 | A | 1.44 | 1.47 |
| | B | 1.55 | 1.59 |
| | C | 1.31 | 1.36 |
| | D | 1.19 | 1.24 |
| 2.02 | A | 1.46 | 1.48 |
| | B | 1.58 | 1.61 |
| | C | 1.39 | 1.45 |
| | D | 1.27 | 1.33 |

than for the chemical shifts. Table 7 gives the calculated chemical shifts in cyclazine (VI). It is seen to produce an increase in the value of chemical shift with increase in $\delta_{N}^{..}$. This can be explained by the fact that the bigger is $\delta_{N}^{..}$, the more the molecule approaches the Hückel type of $4n + 2$, where n is the number of $\pi$-electrons, because with $\delta_{N}^{..}$ increasing the electrons are localized in the nitrogen. This can be confirmed by calculations in the hypothetical molecule formed by the perimeter of (VI), which conforms to the Hückel rule of $4n + 2$ (in this case 10) $\pi$-electrons. The results are 1.5-1.6 for the chemical shift, higher than those for cyclazine. Table 8 gives the diamagnetic anisotropy

Table 8

Calculated diamagnetic anisotropies (relative to benzene) in the heterocycle VI.

| $\delta_{N}^{..}$ | Hückel | S.C.F. |
|---|---|---|
| 1.02 | 2.53 | 2.58 |
| 1.52 | 2.69 | 2.78 |
| 2.02 | 2.80 | 2.89 |

for this molecule, and the same reasons apply to the diam. aniso. (the value for the hypothetical molecule is 3.09).

Table 9 gives the calculated chemical shifts and diamagnetic anisotropies for pyridine, pyrimidine and S-triazine. There are two main features in this

Table 9

Calculated chemical shifts and diamagnetic anisotropies (relative to benzene) in Pyridine, Pyrimidine and S-Triazine.

| | Pyridine | | Pyrimidine | | S-Triazine | |
|---|---|---|---|---|---|---|
| $\delta_N$ | Hückel | S.C.F. | Hückel | S.C.F. | Hückel | S.C.F. |
| 0.20 | 1.00 | 1.02 | 0.99 | 1.03 | 0.98 | 1.04 |
| 0.50 | 0.98 | 0.99 | 0.95 | 0.96 | 0.90 | 0.89 |
| 0.80 | 0.96 | 0.95 | 0.87 | 0.83 | 0.76 | 0.67 |

table. First, there is no appreciable change in the results for pyridine as $\delta_N$ increases. Mason[55] thinks that this could be explained by the small localization of the $\pi$-electron charge in small size molecules, for

there is now some experimental evidence that from acridine to 1,2-5,6-dibenzoacridine the localization of the charge doubles from 0.1 electrons to 0.2 electrons. The second feature is that the S.C.F. value for pyridine with $\delta' = 0.2$ gives a value greater than for the Hückel value and the value for benzene. This can be explained by the influence of the value of $\beta_{CN} = 0.538$. If the pyridine molecule is calculated with $\delta'_N = 0.2$ and $\beta_{CN} = 0.5$, the S.C.F. result is 0.99, lower than the Hückel value and the value for benzene.

The experimental value of the diamag. anisotropy for S-triazine is unknown; only the value for trichloro-S-triazine is available,[56] and comparison is not possible because of the presence of the three chlorine atoms in the molecule.

Table 10 gives the chemical shifts and diamagnetic

Table 10

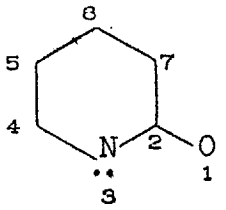
Calculated chemical shifts and diamagnetic anisotropies (relative to benzene) in Cyclopentadienyl, Tropilium.

| | | Hückel | S.C.F. |
|---|---|---|---|
| Cyclopentadienyl | Chem. Shift | 0.69 | 0.69 |
| | diamag. anisot. | 0.51 | 0.51 |
| Tropilium | Chem. Shift | 1.26 | 1.26 |
| | diamag. anisot. | 1.61 | 1.61 |

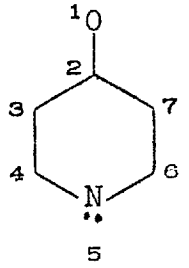
anisotropies in cyclopentadienyl, tropilium. These are only of pure theoretical interest since comparison with experiment is difficult because of the magnitude of solvation and ion-pairing effects.[21]

The values of the diagonal elements of the density matrix in S.C.F. treatment are set out in subsequent tables. These values will be of importance when more experimental values become available, and a detailed comparison of calculated and observed chemical shifts can be attempted.

# S.C.F. Diagonal Elements of the Density Matrix.

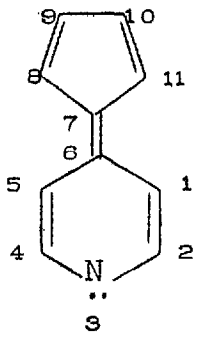


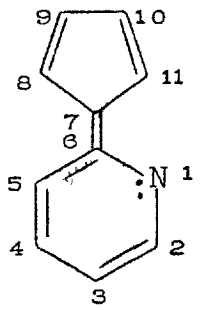

| | | $\delta_O = 0.19$ | $\delta_O = 0.49$ | $\delta_O = 0.79$ |
|---|---|---|---|---|
| $\delta_N = 1.02$ | 1 | .6602 | .7333 | .7969 |
| | 2 | .4842 | .4436 | .4103 |
| | 3 | .8046 | .7871 | .7712 |
| | 4 | .4955 | .4983 | .4995 |
| | 5 | .5519 | .5461 | .5402 |
| | 6 | .4868 | .4819 | .4784 |
| | 7 | .5147 | .5097 | .5035 |
| $\delta_N = 1.52$ | 1 | .6340 | .7079 | .7739 |
| | 2 | .4711 | .4258 | .3871 |
| | 3 | .8780 | .8645 | .8517 |
| | 4 | .4807 | .4785 | .4765 |
| | 5 | .5410 | .15383 | .5354 |
| | 6 | .4866 | .4789 | .4726 |
| | 7 | .5085 | .5061 | .5028 |
| $\delta_N = 2.02$ | 1 | .6147 | .6891 | .7565 |
| | 2 | .4637 | .4151 | .3726 |
| | 3 | .9217 | .9121 | .9028 |
| | 4 | .4741 | .4693 | .4649 |
| | 5 | .5329 | .5321 | .5309 |
| | 6 | .4869 | .4774 | .4690 |
| | 7 | .5059 | .5050 | .5033 |

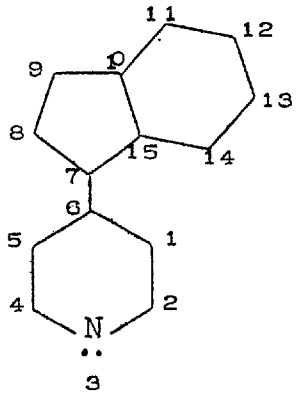



| | | $\delta_{\dot{O}}$= 0.19 | $\delta_{\dot{O}}$=0.49 | $\delta_{\dot{O}}$=0.79 |
|---|---|---|---|---|
| $\delta_{\ddot{N}}$=1.02 | 1 | .6176 | .6937 | .7630 |
| | 2 | .4784 | .4341 | .3961 |
| | 3,7 | .5257 | .5188 | .5112 |
| | 4,6 | .5179 | .5145 | .5118 |
| | 5 | .8168 | .8057 | .7948 |
| $\delta_{\ddot{N}}$=1.52 | 1 | .6006 | .6772 | .7479 |
| | 2 | .4745 | .4281 | .3874 |
| | 3,7 | .5218 | .5163 | .5102 |
| | 4,6 | .4992 | .4936 | .4887 |
| | 5 | .8829 | .8750 | .8670 |
| $\delta_{\ddot{N}}$=2.02 | 1 | .5888 | .6657 | .7371 |
| | 2 | .4721 | .4242 | .3817 |
| | 3,7 | .5180 | .5134 | .5083 |
| | 4,6 | .4897 | .4825 | .4760 |
| | 5 | .9236 | .9182 | .9127 |

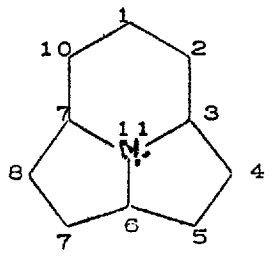
| $\delta_N^{..}$ | 1.02 | 1.52 | 2.02 | 1.02 | 1.52 | 2.02 |
|---|---|---|---|---|---|---|
| 1 | 0.5083 | 0.5102 | 0.5100 | 0.7672 | 0.8521 | 0.9052 |
| 2 | 0.5105 | 0.4873 | 0.4751 | 0.4983 | 0.4760 | 0.4659 |
| 3 | 0.7855 | 0.8626 | 0.9110 | 0.5278 | 0.5254 | 0.5222 |
| 4 | 0.5105 | 0.4873 | 0.4751 | 0.4765 | 0.4718 | 0.4699 |
| 5 | 0.5083 | 0.5102 | 0.5100 | 0.5012 | 0.5021 | 0.5030 |
| 6 | 0.4459 | 0.4416 | 0.4395 | 0.4558 | 0.4376 | 0.4281 |
| 7 | 0.5489 | 0.5391 | 0.5314 | 0.5858 | 0.5685 | 0.5545 |
| 8 | 0.5612 | 0.5549 | 0.5509 | 0.5439 | 0.5434 | 0.5429 |
| 9 | 0.5298 | 0.5260 | 0.5231 | 0.5394 | 0.5331 | 0.5282 |
| 10 | 0.5298 | 0.5260 | 0.5231 | 0.5280 | 0.5250 | 0.5224 |
| 11 | 0.5612 | 0.5549 | 0.5509 | 0.5760 | 0.5649 | 0.5576 |



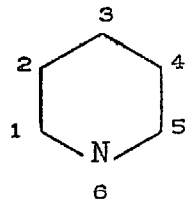






| | $\delta_{\ddot{N}}$=1.02 | $\delta_{\ddot{N}}$=1.52 | $\delta_{\ddot{N}}$=2.02 |
|---|---|---|---|
| 1 | .5126 | .5137 | .5130 |
| 2 | .5095 | .4889 | .4786 |
| 3 | .7960 | .8701 | .9160 |
| 4 | .5103 | .4897 | .4794 |
| 5 | .5145 | .5148 | .5136 |
| 6 | .4631 | .4609 | .4602 |
| 7 | .5593 | .5459 | .5362 |
| 8 | .5276 | .5269 | .5265 |
| 9 | .5366 | .5293 | .5240 |
| 10 | .5085 | .5079 | .5077 |
| 11 | .5003 | .4991 | .4982 |
| 12 | .5177 | .5145 | .5122 |
| 13 | .5156 | .5125 | .5103 |
| 14 | .5143 | .5115 | .5094 |
| 15 | .5141 | .5144 | .5147 |



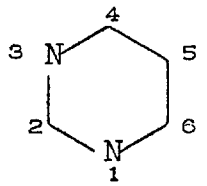

| | $\delta_{\ddot{N}}=1.02$ | $\delta_{\ddot{N}}=1.52$ | $\delta_{\ddot{N}}=2.02$ |
|---|---|---|---|
| 1 | .5136 | .5078 | .5042 |
| 2,10 | .4966 | .4998 | .5016 |
| 3,9 | .5281 | .5119 | .5018 |
| 4,8 | .5583 | .5480 | .5395 |
| 5,7 | .5041 | .5040 | .5036 |
| 6 | .5759 | .5512 | .5340 |
| 11 | .7360 | .8137 | .8689 |




Pyridine

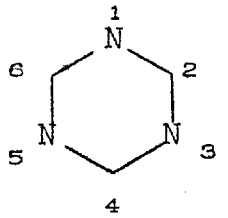
| | $\delta_{N}$=0.2 | $\delta_{N}$=0.5 | $\delta_{N}$=0.8 |
|---|---|---|---|
| 1,5 | .4757 | .4405 | .4078 |
| 2,4 | .5053 | .5130 | .5201 |
| 3 | .4891 | .4732 | .4582 |
| 6 | .5488 | .6199 | .6860 |

Pyrimidine




| | $\delta_{N}$=0.2 | $\delta_{N}$=0.5 | $\delta_{N}$=0.8 |
|---|---|---|---|
| 1,3 | .5534 | .6304 | .7002 |
| 2 | .4525 | .3836 | .3201 |
| 4,6 | .4651 | .4150 | .3708 |
| 5 | .5106 | .5254 | .5379 |

S-Triazine




| | $\delta_{\dot{N}=0.2}$ | $\delta_{\dot{N}=0.5}$ | $\delta_{\dot{N}=0.8}$ |
|---|---|---|---|
| 1,3,5 | .5580 | .6401 | .7113 |
| 2,4,6 | .4420 | .3599 | .2887 |

## 10. A General Theory

The form of perturbation theory developed in Chapter 7 has been adapted to suit conjugated molecules since it assumes a separation into $\sigma$ and $\pi$ electrons, and is formulated in matrix terms. For more general applications it is convenient to have a form of the theory which is written in differential equation form and has no further restrictions. This is needed, in particular, in order to discuss small molecules. Since the argument is almost the same as before, it is presented more briefly.

Consider doubly occupied m.o. with Hamiltonian of the form:

$$h = \sum_i f_i(H) + \sum_{i<j} g_{ij}$$

where H is the external field, $f_i$ the Hamiltonian operator for the ith electron moving in the field of the muclei and $g_{ij}$ the Hamiltonian operator corresponding to interaction between electrons.

The orbitals satisfy,

$$h_{eff.}\, \phi_n = E_n\, \phi_n \qquad (10.1)$$

with $\phi_n = \phi_n(H)$

$E_n = E_n(H)$

$$h_{eff} = f(H) + \sum_n \int \bar{\phi}_n(2)\ g(1,2)\ (2-P_{12})\ \phi_n(2)\ dV_2$$

where $P_{12}$ is the permutation operator which interchanges variables in the two orbitals following it. Expanding in powers of H it is found that:

$$f = f^o + Hf' + m\,'f + H^2 f'' + Hm\,'f' + \ldots..$$

$$h_{eff} = h^o_{eff} + H\,h'_{eff} + m\,'h_{eff} + H^2 h''_{eff} + Hm\,'h'_{eff}$$

$$\phi_n = \phi^o_n + H\,\phi'_n + m\,'\phi_n + H^2\,\phi''_n + Hm\,'\phi'_n$$

$$E_n = E^o_n + HE'_n + m\,'E_n + H^2\,E''_n + Hm\,'E'_n$$

Because the problem deals with a non-degenerate singlet state and the magnetic field does not perturb such a state in first order, $E'_n = o$, $'E_n = o$ and the last equation becomes:

$$E_n = E^o_n + H^2\,E''_n + Hm\,'E'_n.$$

substituting in (10.1) and dropping the subscript eff,

$$h^{\circ}\,\phi_n^{\circ} = E_n^{\circ}\,\phi_n^{\circ}$$

$$(h^{\circ}-E_n^{\circ})\phi_n^{'} = -h^{'}\,\phi_n^{\circ} \tag{10.2a}$$

$$(h^{\circ}-E_n^{\circ})^{'}\phi_n = -{}^{'}h\,\phi_n^{\circ} \tag{10.2b}$$

$$(h^{\circ}-E_n^{\circ})\phi_n^{''} = -h^{'}\phi_n^{'} + (E_n^{''}-h^{''})\phi_n^{\circ} \tag{10.3a}$$

$$(h^{\circ}-E_n^{\circ})^{'}\phi_n^{'} = -h^{'}\,{}^{'}\phi_n - {}^{'}h\,\phi_n^{'} + ({}^{'}E_n^{'} - {}^{'}h^{'})\,\phi_n^{\circ} \tag{10.3b}$$

From (10.2a) and (10.2b):

$$(\phi_n^{'},\ (h^{\circ}-E_n^{\circ})\phi_n^{'}) = -(\phi_n^{'},\ h^{'}\,\phi_n^{\circ}) \tag{10.4a}$$

$$({}^{'}\phi_n,\ (h^{\circ}-E_n^{\circ})^{'}\phi_n) = -({}^{'}\phi,\ {}^{'}h\,\phi_n^{\circ}) \tag{10.4b}$$

From (10.3a):

$$E_n^{''} = (\phi_n^{\circ},\ h^{''}\,\phi_n^{\circ}) + (\phi_n^{\circ},\ h^{'}\,\phi_n^{'}) \tag{10.5a}$$

From (10.3b):

$${}^{'}E_n^{'} = (\phi_n^{\circ},\ h^{'}\,{}^{'}\phi_n) + (\phi_n^{\circ},\ {}^{'}h\,\phi_n^{'}) + (\phi_n^{\circ},\ {}^{'}h^{'}\,\phi_n^{\circ}) \tag{10.5b}$$

The normalization condition $(\phi_n,\ \phi_n) = 1$, gives

$$(\phi_n^\circ,\ \phi_n') + (\phi_n',\ \phi_n^\circ) = 0$$

$$(\phi_n^\circ,\ {}'\phi_n) + ({}'\phi_n,\ \phi_n^\circ) = 0 \qquad (10.6)$$

$$(\phi_n^\circ,\ \phi_n'') + (\phi_n',\ \phi_n') + (\phi_n'',\ \phi_n^\circ) = 0$$

$$(\phi_n^\circ,\ {}'\phi_n') + (\phi_n',\ {}'\phi_n) + ({}'\phi_n,\ \phi_n') + ({}'\phi_n',\ \phi_n^\circ) = 0$$

By expansion of $\phi_n$,

$$h' = f' + \sum_n (\phi_n^\circ,\ g(2-P)\phi_n') + \sum_n (\phi_n',\ g(2-P)\phi_n^\circ) \qquad (10.6a)$$

$${}'h = {}'f + \sum_n (\phi_n^\circ,\ g(2-P){}'\phi_n) + \sum_n ({}'\phi_n,\ g(2-P)\phi_n^\circ) \qquad (10.6b)$$

$$h'' = f'' + \sum_n (\phi_n^\circ,\ g(2-P)\phi_n'') + \sum_n (\phi_n',\ g(2-P)\phi_n') + \sum_n (\phi_n'',\ g(2-P)\phi_n^\circ)$$

$${}'h' = {}'f' + \sum_n (\phi_n^\circ,\ g(2-P){}'\phi_n') + \sum_n (\phi_n',\ g(2-P){}'\phi_n) + \sum_n ({}'\phi_n,\ g(2-P)\phi_n') + \sum_n ({}'\phi_n',\ g(2-P)\phi_n^\circ)$$

The total energy can be written as:

$$W(H) = \sum_n (\phi_n,\ (h+f)\phi_n) = \sum_n E_n + \sum_n (\phi_n,\ f\phi_n)$$
$$= W^\circ + HW' + m\,{}'W + H^2 W'' + Hm\,{}'W' + \ldots\ldots$$

$$W^{\circ} = \sum_n E_n^{\circ} + \sum_n (\phi_n^{\circ},\ f^{\circ}\ \phi_n^{\circ})$$

$$W' = \sum_n (\phi_n^{\circ},\ f'\ \phi_n^{\circ}) + \sum_n (\phi_n^{\circ},\ f^{\circ}\ \phi_n') + \sum_n (\phi_n',\ f^{\circ}\ \phi_n^{\circ})$$

$$'W = \sum_n (\phi_n^{\circ},\ 'f\ \phi_n^{\circ}) + \sum_n (\phi_n^{\circ},\ f^{\circ}\ '\phi_n) + \sum_n ('\phi_n,\ f^{\circ}\ \phi_n^{\circ})$$

$$W'' = \sum_n E_n'' + \sum_n (\phi_n^{\circ},\ f''\phi_n^{\circ}) + \sum_n (\phi_n^{\circ},\ f'\ \phi_n') + \sum_n (\phi_n^{\circ}, f^{\circ}\ \phi_n'')$$
$$+ \sum_n (\phi_n',\ f^{\circ}\ \phi_n') + \sum_n (\phi_n',\ f'\ \phi_n^{\circ}) + \sum_n (\phi_n'',\ f^{\circ}\phi_n^{\circ})$$

(10.7a)

$$'W' = \sum_n 'E_n' + \sum_n (\phi_n^{\circ},\ 'f'\ \phi_n^{\circ}) + \sum_n (\phi_n^{\circ},\ f'\ '\phi_n) + \sum_n (\phi_n^{\circ},\ 'f\phi_n')$$
$$+ \sum_n (\phi_n',\ f^{\circ}\ '\phi_n) + \sum_n (\phi_n',\ 'f\phi_n^{\circ}) + \sum_n ('\phi_n, f^{\circ}\ \phi_n')$$
$$+ \sum_n ('\phi_n,\ f'\ \phi_n^{\circ}) + \sum_n ('\phi_n',\ f^{\circ}\ \phi_n^{\circ}) +$$
$$+ \sum_n (\phi_n^{\circ},\ f^{\circ}\ '\phi_n')$$

(10.7b)

Using the expression for $h''$ in (10.5a):

$$\sum_n (\phi_n^{\circ},\ h''\ \phi_n^{\circ}) = \sum_n (\phi_n^{\circ},\ f''\ \phi_n^{\circ}) +$$
$$+ \sum_{nl} (\phi_n^{\circ}\ \phi_l^{\circ},\ g(2-P)\ \phi_l''\ \phi_n^{\circ}) +$$
$$+ \sum_{nl} (\phi_n^{\circ}\ \phi_l',\ g(2-P)\ \phi_l'\ \phi_n^{\circ}) +$$
$$+ \sum_{nl} (\phi_n^{\circ}\ \phi_l'',\ g(2-P)\ \phi_l^{\circ}\ \phi_n^{\circ})$$

$$\sum_n (\phi_n^o,\ h''\phi_n^o) = \sum_n (\phi_n^o,\ f''\phi_n^o) +$$

$$+ \sum_l (\phi_l^o,\ (h^o-f^o)\phi_l'') + \sum_l (\phi_l',\ (h^o-f^o)\phi_l') +$$

$$+ \sum_l (\phi_l'',\ (h^o-f^o)\phi_l^o)$$

From (10.2a)

$$\bar{\phi}_n'\ (h^o-E_n^o) = -\ \bar{\phi}^o\ h' \qquad (10.8)$$

$$(\phi_n^o,\ h'\ \phi_n') = E_n^o\ (\phi_n',\ \phi_n') - (\phi_n',\ h^o\ \phi_n')$$

so,

$$\sum_n E_n'' = \sum_n (\phi_n^o,\ f''\phi_n^o) + \sum_n (\phi_n^o,\ (h^o-f^o)\phi_n'') + \sum_n (\phi_n',h^o-f^o)\phi_n')$$

$$+ \sum_n (\phi_n'',\ (h^o-f^o)\phi_n^o) - \sum_n (\phi_n',\ h^o\ \phi_n') + \sum_n E_n^o\ (\phi_n',\ \phi_n')$$

and the expression for the energy (10.7a) becomes:

$$W'' = 2\sum_n (\phi_n^o,\ f''\phi_n^o) + \sum_n (\phi_n^o,\ f'\phi_n') + \sum_n (\phi_n',\ f'\phi_n^o) +$$

$$+ \left\{ \sum_n (\phi_n^o,\ h^o\phi_n'') + \sum_n (\phi_n'',\ h^o\phi_n^o) + \sum_n E_n^o\ (\phi_n',\ \phi_n') \right\}$$

The sum in brackets can be written:

$$\sum_n E_n^o \left\{ (\phi_n^o,\ \phi_n'') + (\phi_n'',\ \phi_n^o) + (\phi_n',\ \phi_n') \right\}$$

This sum is zero by the third relation (10.6). So:

$$W'' = 2 \sum_n (\phi_n^o, f'' \phi_n^o) + \sum_n (\phi_n^o, f' \phi_n') + \sum_n (\phi_n', f' \phi_n^o) \quad (10.9)$$

In the same way, the expression for $'W'$ is found. Using the expression for $'h'$:

$$\sum_n (\phi_n^o, 'h' \phi_n^o) = \sum_n (\phi_n^o, 'f' \phi_n^o) +$$

$$+ \sum_{n1} (\phi_n^o \phi_1^o, g(2-P) '\phi_1' \phi_n^o) + \sum_{n1} (\phi_n^o \phi_1', g(2-P) '\phi_1 \phi_n^o) +$$

$$+ \sum_{n1} (\phi_n^o '\phi_1, g(2-P) \phi_1' o_n^o) + \sum_{n1} (\phi_n^o '\phi_1', g(2-P) \phi_1^o \phi_n^o )$$

$$= \sum_n (\phi_n^o, 'f' \phi_n^o) +$$

$$+ \sum_n (\phi_n^o, (h^o - f^o) '\phi_n') + \sum_n (\phi', (h^o - f^o) '\phi_n) + \sum_n ('\phi_n, (h^o - f^o) \phi_n')$$

$$+ \sum_n ('\phi_n', (h^o - f^o) \phi_n^o)$$

From (10.2b)

$$'\phi_n (h^o - E_n^o) = -\phi_n^o 'h$$

$$(\phi_n^o, 'h \phi_n') = E_n^o ('\phi_n, \phi_n') - ('\phi_n, h^o \phi_n')$$

and from (10.8):

$$(\phi_n^o, h' '\phi_n) = E_n^o (\phi_n', '\phi_n) - (\phi_n', h^o '\phi_n)$$

So,

$$\sum_n {}'E_n' = \sum_n (\phi_n^\circ,\ {}'f'\ \phi_n^\circ) + \sum_n (\phi_n^\circ,\ (h^\circ - f^\circ)\ {}'\phi_n') +$$

$$+ \sum_n (\phi_n',\ (h^\circ - f^\circ)\ {}'\phi_n,\ (h^\circ - f^\circ)\ {}'\phi_n) +$$

$$+ \sum_n ({}'\phi_n,\ (h^\circ - f^\circ)\phi_n') + \sum_n ({}'\phi_n',\ (h^\circ - f^\circ)\ \phi_n^\circ) +$$

$$\sum_n E_n^\circ\ ({}'\phi_n,\ \phi_n') + (\phi_n'\ {}'\phi_n)\ - \sum_n ({}'\phi_n,\ h^\circ\ \phi_n') -$$

$$- \sum_n (\phi_n',\ h^\circ\ {}'\phi_n)$$

And the expression for the energy (10.7b):

$${}'W' = 2\sum_n (\phi_n^\circ,\ {}'f'\ \phi_n^\circ) + \sum_n (\phi_n^\circ,\ f'\ {}'\phi_n) + \sum_n (\phi_n^\circ,\ {}'f\ \phi_n') +$$

$$+ \sum_n (\phi_n',\ {}'f\ \phi_n^\circ) + \sum_n ({}'\phi_n,\ f'\ \phi_n^\circ) +$$

$$+\Big( \sum_n E_n^\circ\ ({}'\phi_n,\ \phi_n') + \sum_n E_n^\circ\ (\phi_n',\ {}'\phi_n) + \sum_n (\phi_n^\circ,\ h^\circ\ {}'\phi_n') +$$

$$+ \sum_n ({}'\phi_n',\ h^\circ\ \phi_n^\circ)\Big)$$

and the sum in brackets can be written:

$$\sum_n E_n^\circ \Big\{ (\phi_n^\circ,\ {}'\phi_n') + ({}'\phi_n',\ \phi_n^\circ) + ({}'\phi_n,\ \phi_n') + (\phi_n',\ {}'\phi_n) \Big\}$$

which is zero by the fourth relation (10.6).

So:

$$'W' = 2\sum_n (\phi_n^\circ, {}'f'\,\phi_n^\circ) + \sum_n (\phi_n^\circ, f'\,{}'\phi_n) + \sum_n (\phi_n^\circ, {}'f\,\phi_n') + \\ + \sum_n (\phi_n', {}'f\,\phi_n^\circ) + \sum_n ({}'\phi_n, f'\,\phi_n^\circ) \qquad (10.10)$$

If in (10.9), the Hamiltonian character of the f's gives:

$$(\phi_n', f'\,\phi_n^\circ) = (f'\,\phi_n', \phi_n^\circ)^* = (\phi_n^\circ, f'\,\phi_n')$$

and so:

$$W'' = 2\sum_n (\phi_n^\circ, f''\,\phi_n^\circ) + 2\sum_n (\phi_n^\circ, f'\,\phi_n')$$

And in (10.10), similarly:

$$(\phi_n', {}'f\,\phi_n^\circ) = ({}'f\,\phi_n', \phi_n^\circ)^* = (\phi_n^\circ, {}'f\,\phi_n')$$

$$({}'\phi_n, f'\,\phi_n^\circ) = (f'\,{}'\phi_n, \phi_n^\circ)^* = (\phi_n^\circ, f'\,{}'\phi_n)$$

and (10.10) becomes:

$$'W' = 2\sum_n (\phi_n^\circ, {}'f'\,\phi_n^\circ) + 2\sum_n (\phi_n^\circ, f'\,{}'\phi_n) + 2\sum_n (\phi_n^\circ, {}'f\,\phi_n')$$

As for the terms $(\phi_n^\circ,\ f'\ {}'\phi_n)$ and $(\phi_n^\circ,\ {}'f\ \phi_n')$, from (10.2a) and (10.2b), :

$$({}'\phi_n,\ (h^\circ - E_n^\circ)\ \phi_n') = -({}'\phi_n,\ h'\ \phi_n^\circ)$$

$$(\phi_n',\ (h^\circ - E_n^\circ)\ {}'\phi_n) = -(\phi_n',\ {}'h\ \phi_n^\circ)$$

$$\sum_n (\phi_n^\circ,\ h'\ {}'\phi_n) = \sum_n (\phi_n^\circ,\ {}'h\ \phi_n')$$

and substituting for $h'$ and ${}'h$, the expressions from (10.6a) and (10.6b), it is seen after simplifying:

$$\sum_n (\phi_n^\circ,\ f'\ {}'\phi_n) = \sum_n (\phi_n^\circ,\ {}'f\ \phi_n')$$

and

$${}'W' = 2\sum_n (\phi_n^\circ,\ {}'f'\ \phi_n^\circ) + 4\sum_n (\phi_n^\circ,\ {}'f\ \phi_n')$$

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