

CONFIGURATION INTERACTION  
AND THE CALCULATION OF  
E.S.R. AND N.M.R. COUPLING CONSTANTS

A thesis presented for the degree of  
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by

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## Section One

Introduction

The objective of this work was to develop a computer program using the Configuration Interaction (CI) method to investigate various molecular properties. It was intended that the program should be constructed so as to be as adaptable as possible, particularly with respect to the choice of configurations which could be included in the CI. To give this flexibility a list of configurations was to be kept, which would allow any arbitrary set of configurations up to the complete set of all the configurations it is possible to construct to be used in a calculation. It was essential, in implementing this, to find an efficient means of storing and handling these configurations.

These requirements were met by utilising the computer's binary notation, which is ideal for the representation of configurations. They are represented in a single word of computer memory by taking advantage of its internal bit structure: a bit set to 1 indicates an occupied orbital while a bit set to 0 indicates an unoccupied orbital. Stored in this form, the computer's assembler language can be used to manipulate the configurations and extract information from them.

One of the great problems associated with the CI method is the sheer quantity of configurations which it is possible to construct. This usually means that it is impossible to carry out anywhere near complete CI calculations except with small basis sets and that the set of configurations must be cut down in some way. Unfortunately, it is very difficult to find a workable criteria for excluding configurations; though the individual contributions of configurations may be small, because of their number, it is difficult to be certain of their effect overall. However, the usual method of establishing a truncated set of configurations is to include only those that can be formed by up to a

given number of excitations from the ground state configuration. This approach has been followed in our scheme, allowing any excitation limit to be imposed up to that which gives a complete CI calculation. Using this system it was found to be convenient to keep lists of the configurations of the alpha and beta spins separately, which gives a saving in the storage required. These alpha and beta spin configurations can be combined as and when required to give the full configurations, which can be easily tested to reject any that are unwanted. This is something of a departure from the original intention, but still retains a good deal of flexibility.

The program is dealt with in detail in the next section and succeeding sections describe its application to the calculation of ESR and NMR hyperfine coupling constants.

## Section Two

The Configuration Interaction Program

## Introduction

Following a brief discussion of the background theory of the CI method, the remainder of this section is devoted to the way this method was implemented in the present program and the scope for development in the light of recent advances in the field.

The whole basis of the program is the use of the computer's binary notation for the representation of configurations. This makes it necessary to give some details of the workings of a computer. Although it is to be understood that some of what is said will only be applicable to Control Data Cyber 70 and 170 models of computer, most of the developments can be readily and efficiently implemented on other computer models (with the possible exception of the population count instruction which adds up the number of bits set in a word). The Control Data assembler language is called Compass; a description of the most important of its instructions for our purposes is given in an appendix at the end of this thesis.

## Theory

The starting point for these CI calculations is a single determinant wavefunction over molecular orbitals provided by an earlier Restricted Hartree-Fock (RHF) calculation. In the single determinant approximation there is no correlation between the positions of electrons of opposite spin. An electron is only affected by the average field of the other electrons, which does not allow for the fact that at any instant electrons of opposite spin would be expected to keep apart so as to minimise the repulsion between them. It is to overcome this defect and include electron correlation that the CI method is used.

The ground state CI wavefunction consists of a linear combination of Slater determinants corresponding to the RHF ground and excited states:

$$\Psi = \sum_{\mathbf{K}} C_{\mathbf{K}} \Phi_{\mathbf{K}} \quad (2.1)$$

The normalised determinants are of the form

$$\begin{aligned} \Phi &= (N!)^{-\frac{1}{2}} \det |\psi_1(1) \cdot \psi_2(2) \cdot \psi_3(3) \cdot \psi_4(4) \dots \psi_N(N)| \\ &= (N!)^{-\frac{1}{2}} \det |a_1(1) \cdot b_1(2) \cdot a_2(3) \cdot b_2(4) \dots \dots \dots | \end{aligned}$$

with spin-orbitals

$$\psi_1 = a_1 = \phi_1\alpha, \quad \psi_2 = b_1 = \phi_1\beta, \quad \psi_3 = a_2 = \phi_2\alpha, \text{ etc.}$$

so that, for example, the symbol  $\psi_1(1)$  signifies that electron 1 is of alpha spin and occupies molecular orbital  $\phi_1$  and so on.

Now Schrödinger's equation takes the form

$$H_{op} \Psi = E \Psi, \quad (2.2)$$

where  $H_{op}$  is the Hamiltonian operator

$$H_{op} = \sum_i h(i) + \sum_{j>i} g(i,j) \quad (2.3)$$

Here

$$h(i) = -\frac{1}{2}\nabla^2(i) - \sum_v z_v/r_{iv}$$

is the one-electron part of the Hamiltonian operator, describing both the kinetic energy and the potential energy in the field of nuclei of charge  $z_v$ , of electron  $i$  and

$$g(i,j) = 1/r_{ij}$$

is the two-electron part, describing the interelectronic repulsion between electrons  $i$  and  $j$ . It is the electronic energy,  $E$ , that appears here; the internuclear repulsion energy

$$V = \sum_{\mu>\nu} z_\mu z_\nu/R_{\mu\nu}$$

may be evaluated separately from the electronic terms.

The use of orthogonal molecular orbitals will be assumed throughout this treatment, and in this case the matrix representation of equation (2.2) is

$$Hc = Ec \quad (2.4)$$

where the vector  $c$  has elements  $c_k$  as in equation (2.1) and the Hamiltonian matrix  $H$  has elements

$$H_{ij} = \langle \Phi_i | H_{op} | \Phi_j \rangle$$

These latter can be readily expressed in terms of integrals over the molecular orbitals by, for example, using Slater's rules [1], of which a summary is given below.

Should the determinants  $\Phi_i$  and  $\Phi_j$  be identical then the interaction between them is

$$\sum_I \langle \psi_I | h | \psi_I \rangle + \sum_{I>J} [\langle \psi_I \psi_J | g | \psi_I \psi_J \rangle - \langle \psi_I \psi_J | g | \psi_J \psi_I \rangle]$$

(The numerical value of the interaction is given here, so that the labelling as to the electrons involved has been dispensed with.) For the off-diagonal matrix elements, there are non-vanishing results in only two cases. If there is just one difference between the determinants (say  $\psi_I \neq \psi_K$ ), then the interaction is

$$\langle \psi_I | h | \psi_K \rangle + \sum_J [\langle \psi_I \psi_J | g | \psi_K \psi_J \rangle - \langle \psi_I \psi_J | g | \psi_J \psi_K \rangle]$$

And if there are two differences, say  $\psi_I \neq \psi_K$  and  $\psi_J \neq \psi_L$ , the interaction is

$$\langle \psi_I \psi_J | g | \psi_K \psi_L \rangle - \langle \psi_I \psi_J | g | \psi_L \psi_K \rangle$$

Interactions between determinants with more than two differences between them are zero. The first term in the two-electron integral contributions is known as the coulomb integral and the second as the exchange integral. There is only an exchange integral if the spin-orbitals involved are of the same spin.

There remains the question of the parity, that is the positive or negative sign, of the interactions between determinants. The way this arises is best shown by taking a specific example:

$$\begin{aligned} \Phi_1 &= (6!)^{-\frac{1}{2}} \det | \psi_A(1) \cdot \psi_B(2) \cdot \psi_C(3) \cdot \psi_D(4) \cdot \psi_E(5) \cdot \psi_H(6) | \\ \text{and } \Phi_2 &= (6!)^{-\frac{1}{2}} \det | \psi_A(1) \cdot \psi_C(2) \cdot \psi_D(3) \cdot \psi_E(4) \cdot \psi_G(5) \cdot \psi_H(6) | \\ &= -(6!)^{-\frac{1}{2}} \det | \psi_A(1) \cdot \psi_C(2) \cdot \psi_E(3) \cdot \psi_D(4) \cdot \psi_G(5) \cdot \psi_H(6) | \\ &= (6!)^{-\frac{1}{2}} \det | \psi_A(1) \cdot \psi_E(2) \cdot \psi_C(3) \cdot \psi_D(4) \cdot \psi_G(5) \cdot \psi_H(6) | \end{aligned}$$

$$= -(6!)^{-\frac{1}{2}} \det |\psi_A(1) \cdot \psi_E(2) \cdot \psi_C(3) \cdot \psi_D(4) \cdot \psi_G(5) \cdot \psi_H(6) |$$

$$\Phi_1 = (6!)^{-\frac{1}{2}} \det |\psi_A(1) \cdot \psi_B(2) \cdot \psi_C(3) \cdot \psi_D(4) \cdot \psi_F(5) \cdot \psi_G(6) |$$

So that the interaction between  $\Phi_1$  and  $\Phi_2$  is

$$\langle \Phi_1 | H_{op} | \Phi_2 \rangle = -\langle \psi_A | \psi_A \rangle \langle \psi_C | \psi_C \rangle \langle \psi_D | \psi_D \rangle \langle \psi_G | \psi_G \rangle \langle \psi_B \psi_F | g | \psi_E \psi_H \rangle$$

$$= -\langle \psi_B \psi_F | g | \psi_E \psi_H \rangle$$

the parity being negative.

The eigenvalue problem as expressed in equation (2.4) is solved by diagonalisation of the H matrix. This has been done using the iterative method of Nesbet [2] to obtain the lowest eigenvalue E and the corresponding eigenvector c. Starting with an initial guess for c (e.g. 1 for the dominant component of c and 0 for all the rest), an estimate is made for E:

$$E = \frac{\sum_{i,j} c_i H_{ij} c_j}{\sum_i c_i^2} \quad (2.5)$$

This estimate is a minimum at the vector corresponding to the lowest eigenvalue. If one component of the vector c, say  $c_i$  is varied by an amount  $\Delta c_i$ , holding all other components constant, the optimum choice for  $\Delta c_i$  is when

$$\frac{\partial E}{\partial c_i'} = 0, \quad c_i' = c_i + \Delta c_i.$$

So differentiating equation (2.5)

$$\frac{dE}{dc_i} = \frac{2 \sum_{j \neq i} H_{ij} c_j + H_{ii} c_i}{\sum c_j^2} - \frac{\sum c_i H_{ij} c_j 2c_i}{\left\{ \sum c_j^2 \right\}^2} = 0$$

giving

$$\sum_{j \neq i} H_{ij} c_j + H_{ii} c_i - E c_i = 0 .$$

Therefore

$$c_i' = \frac{\sum_{j \neq i} H_{ij} c_j}{(E - H_{ii})}$$

or 
$$\Delta c_i = \frac{q_i}{(E - H_{ii})} \tag{2.6}$$

where 
$$q_i = \sum_j H_{ij} c_j - E c_i .$$

Here E should be evaluated for  $c_i'$ , but is approximated by that for the original  $c_i$ . Now if

$$D = \sum_j c_j^2$$

then 
$$\Delta E = \frac{\Delta c_i \cdot q_i}{D + \Delta D} \tag{2.7}$$

where 
$$\Delta D = (2c_i + \Delta c_i) \Delta c_i \tag{2.8}$$

A complete iteration consists of the adjustment of  $c_i$ , D, and E according to equations (2.6), (2.7), and (2.8) for all the components of the vector c successively. This is continued until the largest value of  $|\Delta c_i|$  in one complete iteration is less than a specified criterion.

A modification of the basic Nesbet procedure has been put forward by Shavitt [3]. This allows the use of just the lower triangular part of the Hamiltonian matrix.

## The Configuration Interaction Program

The basic program structure can best be summarised under the following headings.

- [1] Generation of the spin-configurations. All the spin-configurations which can be formed by up to a given number of excitations from the ground state configurations are generated. There will be both alpha and beta lists for an open shell system, but there need only be the one list for a closed shell system.
- [2] Transformation of the one and two electron integrals. A Restricted Hartree Fock (RHF) calculation resulting in a set of molecular orbitals will already have been carried out. The integrals will have been evaluated for this calculation, so that they now need only be transformed from over the original atomic orbitals to the RHF molecular orbitals.
- [3] Formation of the Hamiltonian matrix. This is done by application of Slater's rules. In the hope of cutting down the processing time, the terms between the alpha and between the beta spin-configurations are worked out beforehand. These are required repeatedly during the construction of the full CI matrix. The configurations are tested at this stage to see if they meet the various criteria which can be imposed, if they do not they are discarded.
- [4] Diagonalisation of the Hamiltonian matrix. Nesbet's routine is used to diagonalise the Hamiltonian matrix and obtain the lowest eigenvalue and eigenvector [2]. The matrix is often sizeable;

but it is also sparse, so that the non-zero elements with their labelling as to row and column are held on backing store and read through once for each iteration.

Here we will principally be concerned with the third heading, that is, with the formation of the Hamiltonian matrix. It is at this stage that Compass routines are of such importance for the processing of the configurations.

Prior to embarking on the construction of the Hamiltonian matrix itself, the terms between the alpha and between the beta spin-configurations are assembled. This gives two 'spin-CI' matrices of order of the number of alpha and beta spin-configurations respectively. Using these matrices Slater's rules can be rewritten, distinguishing between the alpha spin orbitals  $a_i$  and the beta spin-orbitals  $b_i$ . Now the interaction between two identical configurations is

$$A + B + \sum_{ij} \langle a_i b_j | g | a_i b_j \rangle$$

where A is an element of the alpha spin matrix such that

$$A = \sum_i \langle a_i | h | a_i \rangle + \sum_{i>j} [\langle a_i a_j | g | a_i a_j \rangle - \langle a_i a_j | g | a_j a_i \rangle]$$

and B is a corresponding element of the beta spin matrix. If there is a single difference between the interacting configurations, this must mean that the alpha spin-configurations differ and the betas are the same or vice versa. For a difference between the alphas ( $a_i \neq a_j$ ) the interaction is

$$A' + \sum_k \langle a_i b_k | g | a_j b_k \rangle$$

where the element of the alpha spin matrix

$$A' = \langle a_i | h | a_j \rangle + \sum_k [\langle a_i a_k | g | a_j a_k \rangle - \langle a_i a_k | g | a_k a_j \rangle]$$

Two differences may appear with both in the alphas, both in the betas, or one in each. In the first two cases the interaction comes directly from the spin-CI matrices, as only spin-orbitals of one type are involved. For the alpha case the element would be

$$\langle a_i a_j | g | a_k a_1 \rangle - \langle a_i a_j | g | a_1 a_k \rangle$$

However, the interaction involving both spins,

$$\langle a_i b_j | g | a_k b_1 \rangle$$

is found separately.

When the Hamiltonian matrix is constructed, the lists of spin-configurations are read through, and each alpha spin-configuration  $\phi^\alpha$  is combined with any of the beta spin-configurations  $\phi^\beta$  which produce an acceptable total configuration. This means that the elements of both the spin-CI matrices are accessed sequentially and are conveniently buffered in from auxiliary storage as needed. The elements are usually required for a number of interactions, for instance, the element  $A_{ij}$  will contribute to all the interactions of the form  $\langle \phi_i^\alpha \phi_k^\beta | H_{op} | \phi_j^\alpha \phi_k^\beta \rangle$  involving any acceptable beta spin-configuration  $\phi_k^\beta$ , so that a substantial time saving may be expected from the use of these spin-CI matrices. In addition, the remaining terms are generally simpler than those collected in the matrices, all the one-electron and exchange integrals for the two-electron parts of the interactions having already been evaluated.

It must be apparent how important it is to be able to establish the number of differences there are between spin-configurations. Once

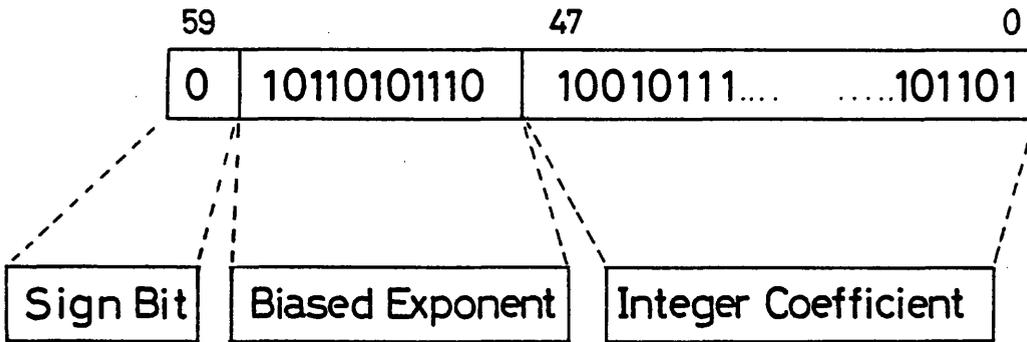
this is done the necessary integrals which comprise an interaction have to be accessed. In our program these functions are carried out by Compass routines acting upon the spin-configurations stored as binary patterns. To understand the merits of this method we must also take a look at the way a computer functions.

Operands needed by the computer to implement arithmetical and logical machine instructions are transferred from central memory to its registers, from where the specialised functional units of the computational section can access them. This allows much more rapid operation than would be possible if values were accessed directly from central memory. The registers are of three types: the eight X-registers, X0 to X7, hold 60-bit words (each bit of which may be set to 0 or 1) and are the principal data handling registers for computation; the eight A-registers, A0 to A7, are operand address registers and allow transfers of information to and from the X-registers and central memory; the eight B-registers, B0 to B7, are primarily indexing registers for controlling counts. The way in which a floating point number is stored within a 60-bit word, whether in central memory or in a X-register, is shown in Figure 1. It can be seen that the binary representation is well suited to the storage of spin-configurations. These are set up from the 46th. bit downwards, so as to take up the position normally used for the integer coefficient. This allows the use of the important normalise instruction. More than 47 molecular orbitals can be used e.g. up to 94 if two words are used.

The Compass assembler language allows transfers to be made to and from the registers, and operands stored there to be used with the full range of individual arithmetical and logical machine instructions. The logical instructions are not generally available in higher level

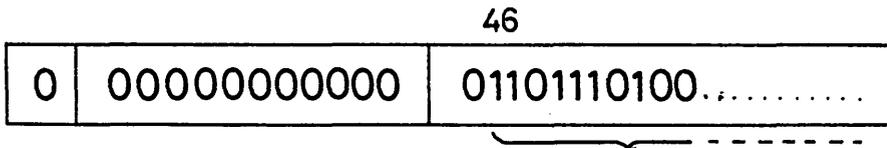
FIGURE 1.

The Structure of a 60-bit word as used to store a floating point number:



Configuration  $\Phi$  can be stored as a bit pattern:

$$\Phi = \Psi_1 \cdot \Psi_2 \cdot \Psi_4 \cdot \Psi_5 \cdot \Psi_6 \cdot \Psi_8$$



Configuration displayed between bit 46 and bit 0 of a 60-bit word.

languages, but are invaluable for extracting information from and making comparisons between configurations stored as a bit pattern. A selection of the most important of these instructions for our purposes is described in detail in the Appendix. It is necessary that the normalise instruction in particular should be understood for the discussion which follows so its operation is illustrated in Figure 2 [4,5].

Examples of the way in which Compass routines were written to deal with the construction of the Hamiltonian matrix are shown in flow diagram form in Figures 3, 4 and 5, which are based on some of the coding needed to form the spin-CI matrices, but the principles involved are quite general. Firstly it is necessary to establish how many differences there are between a pair of configurations (Figure 3). A logical difference instruction establishes which bits in the two configurations do not correspond, and these can be counted up by the population count instruction. For example, the determinants in Figure 3,

$$\Psi_1 = \det \begin{vmatrix} \psi_1 & \psi_2 & \psi_4 & \psi_6 & \psi_8 \end{vmatrix}$$

and

$$\Psi_2 = \det \begin{vmatrix} \psi_1 & \psi_4 & \psi_5 & \psi_6 & \psi_8 \end{vmatrix}$$

are displayed as binary patterns (written here from bit 47 downwards)

$$\begin{array}{r} \Psi_1 = \quad 0 \ 1 \ 1 \ 0 \ 1 \ 0 \ 1 \ 0 \ 1 \ \text{-----} \\ \Psi_2 = \quad 0 \ 1 \ 0 \ 0 \ 1 \ 1 \ 1 \ 0 \ 1 \ \text{-----} \\ \hline \text{Logical difference} = \quad 0 \ 0 \ 1 \ 0 \ 0 \ 1 \ 0 \ 0 \ 0 \ \text{-----} \end{array}$$

The count is two i.e. there is one difference between the determinants corresponding to  $\psi_2 \neq \psi_5$ .

Once the number of differences is known a specialised piece of



FIGURE 3.

FLOW DIAGRAM TO ESTABLISH HOW MANY DIFFERENCES THERE ARE BETWEEN TWO CONFIGURATIONS

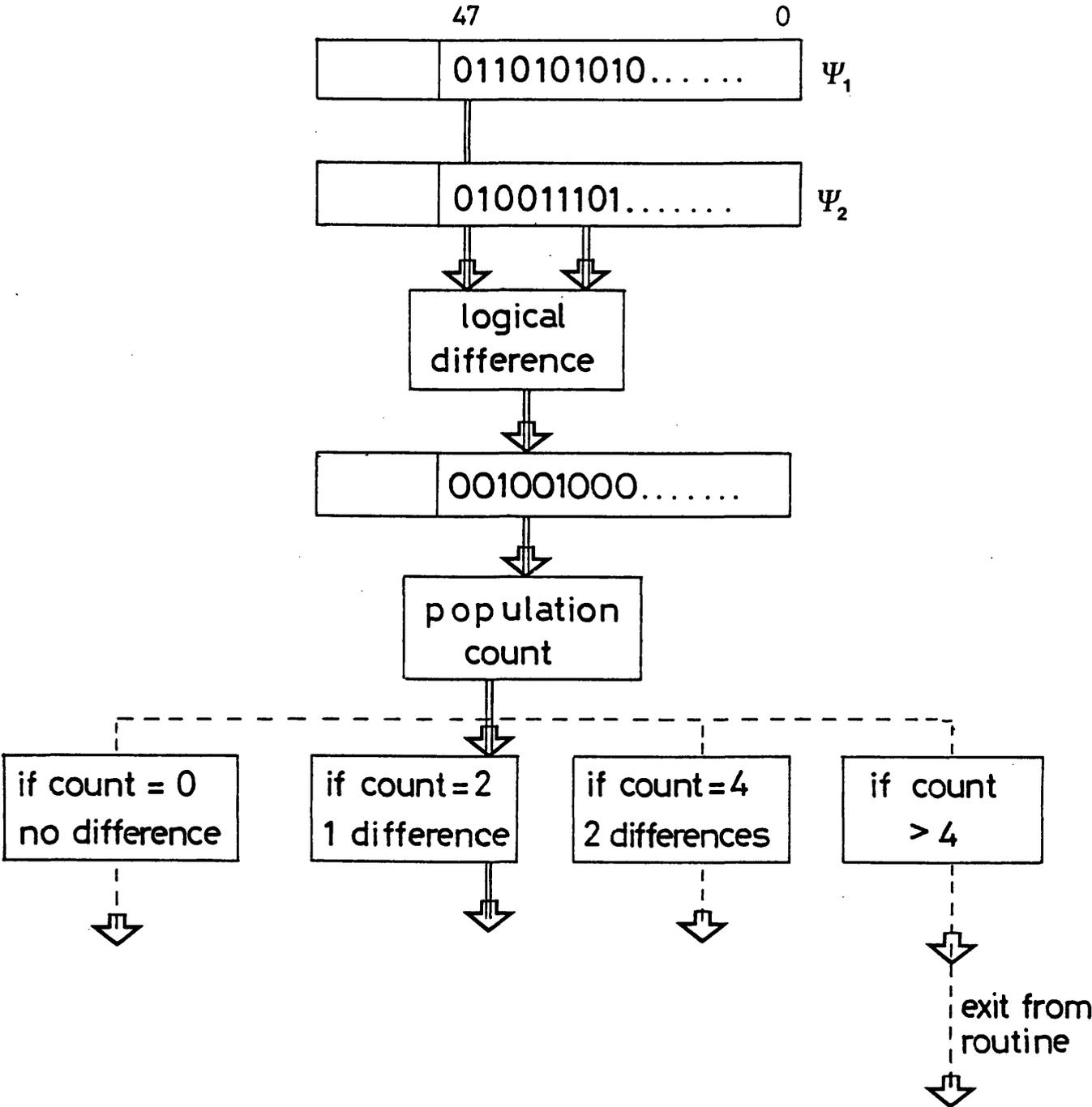


FIGURE 4.

FLOW DIAGRAM TO EVALUATE THE INTERACTION FOR CONFIGURATIONS  
WITH ONE DIFFERENCE BETWEEN THEM

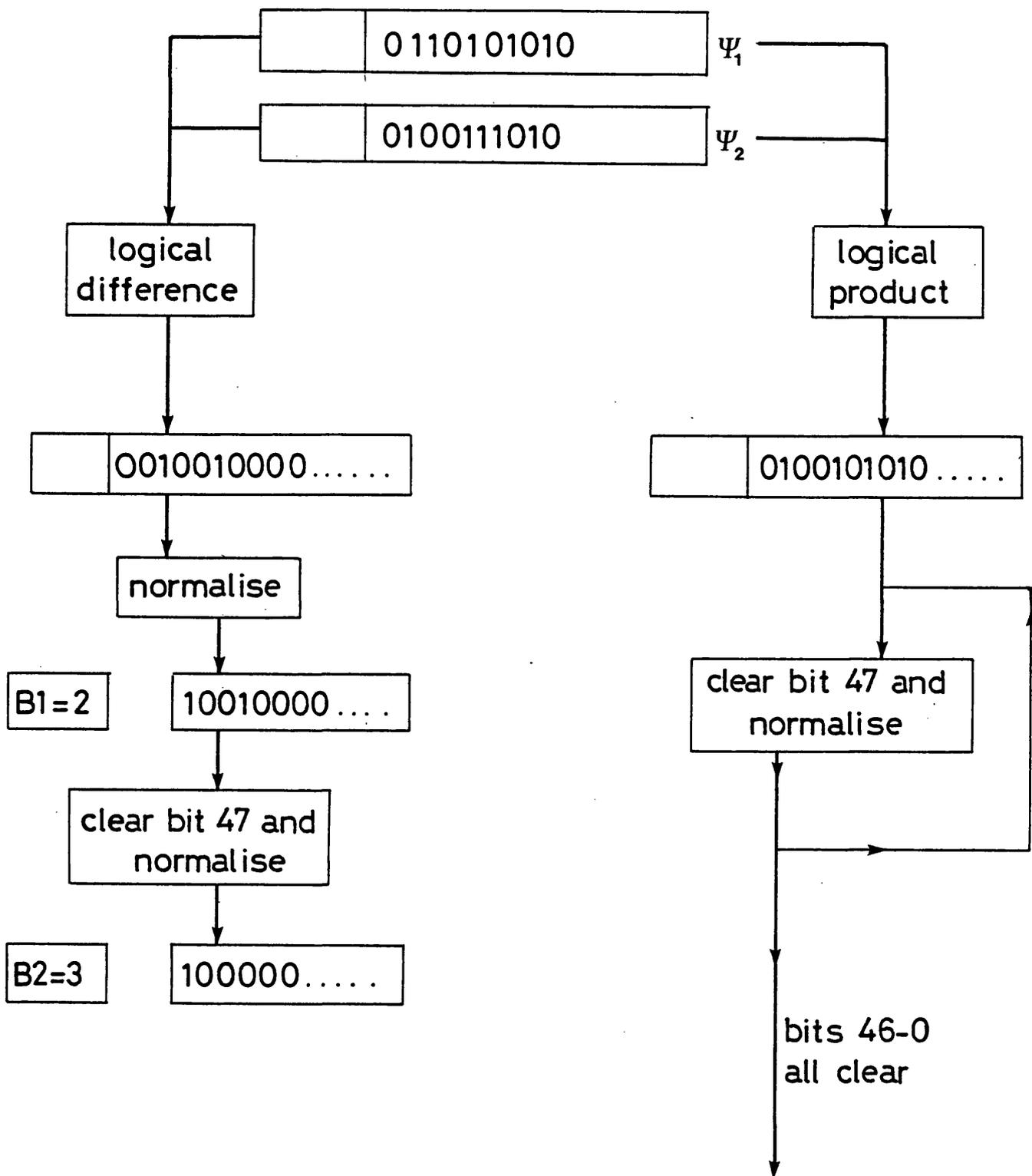
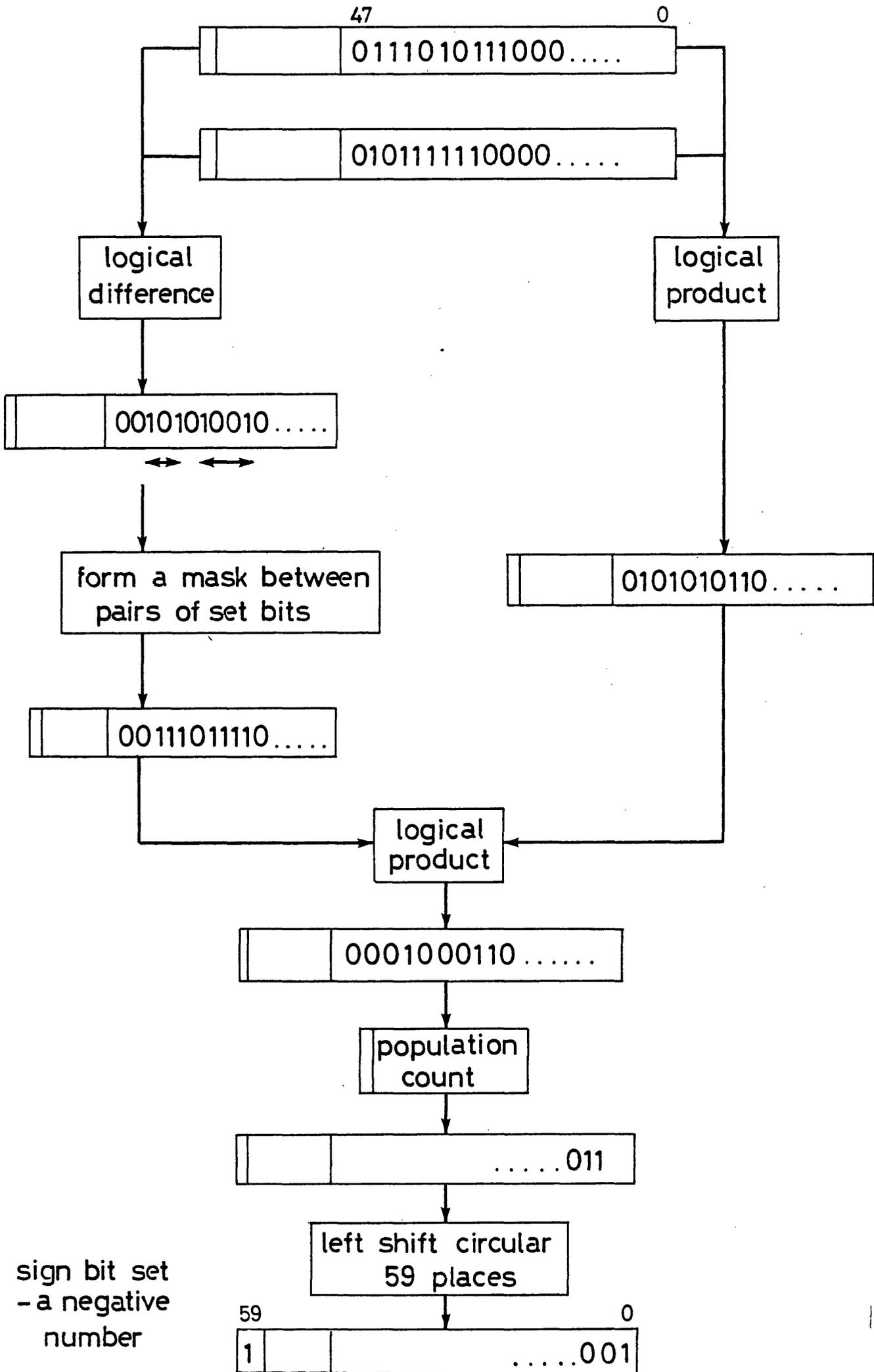


FIGURE 5 - FLOW DIAGRAM TO FIND THE PARITY OF AN INTERACTION



coding to deal with each situation - there being either two, one, or no differences - is brought into play. If there are more than two differences, of course, the interaction is zero, so that the procedure begins again with a fresh pair of configurations. Figure 4 shows a flow diagram illustrating the coding which will evaluate the interaction between configurations with just one difference between them. The logical difference instruction finds the bits that do not correspond and the logical product finds those that do correspond in the pair of patterns. Next the positions of the set bits in each case, and so the orbitals they represent, have to be located; it is for this purpose that the normalise instruction is used. Continuing with our example we have:

```

Logical difference = 0 0 1 0 0 1 0 0 0 -----
                    ←←←
                    1 0 0 1 0 0 0 0 0 -----

```

The normalise instruction shifts the pattern two positions to the left so that bit 47 is different from the sign bit and automatically places the number two in a B-register (B1 say). Now bits 47 and above are cleared and the process repeated:

```

0 0 0 1 0 0 0 -----
←←←←
1 0 0 0 0 0 0 -----

```

This time there is a left shift of three positions, which number is placed in a second B-register (B2 say). The first set bit was shifted two positions (B1) and therefore represents  $\psi_2$ ; the second set bit was shifted a total of five positions (B1 + B2) and represents  $\psi_5$ . With this information the one-electron integral  $\langle \psi_2 | h | \psi_5 \rangle$  can be accessed.

Looking now to the logical product of the two configurations:

$$\Psi_1 = 0 1 1 0 1 0 1 0 1 \text{ -----}$$

$$\Psi_2 = 0 1 0 0 1 1 1 0 1 \text{ -----}$$

---


$$\text{Logical product} = 0 1 0 0 1 0 1 0 1 \text{ -----}$$

The normalise instruction is used in a loop to give the positions of the set bits, which correspond to the orbitals  $\psi_1$ ,  $\psi_4$ ,  $\psi_6$ , and  $\psi_8$ .

This allows the two-electron integrals to be accessed in turn:

$$\langle \psi_2 \psi_5 | g | \psi_1 \psi_1 \rangle - \langle \psi_2 \psi_1 | g | \psi_5 \psi_1 \rangle$$

$$\langle \psi_2 \psi_5 | g | \psi_4 \psi_4 \rangle - \langle \psi_2 \psi_4 | g | \psi_5 \psi_4 \rangle$$

etc.

The interaction having been calculated, its parity must be found. The routine which was used to determine the parity is shown in flow diagram form in Figure 5. It is necessary to find the number of permutations needed to align the two configurations, and this is done by counting the number of bits which correspond in the two configurations and are between the bits indicating differences. The count is shifted to set up the sign bit as a flag to indicate whether a change of sign is to be made. In the example given in Figure 5 we have the determinants

$$\Phi_1 = \det | \psi_1(1) . \psi_2(2) . \psi_3(3) . \psi_5(4) . \psi_7(5) . \psi_8(6) . \psi_9(7) |$$

$$\text{and } \Phi_2 = \det | \psi_1(1) . \psi_3(2) . \psi_4(3) . \psi_5(4) . \psi_6(5) . \psi_7(6) . \psi_8(7) |$$

There are two differences between these determinants,  $\psi_2 \neq \psi_4$  and  $\psi_9 \neq \psi_6$ . The orbitals  $\psi_3$ ,  $\psi_7$ , and  $\psi_8$  are present in both determinants and are situated between the differences, therefore three permutations of the orbitals are necessary to align the determinants and the parity is nega-

tive. The routine in this way reproduces the effect of rewriting the determinants as:

$$\begin{aligned}\Phi_1 &= \det |\psi_1(1) \cdot \psi_2(2) \cdot \psi_3(3) \cdot \psi_5(4) \cdot \psi_7(5) \cdot \psi_8(6) \cdot \psi_9(7)| \\ \text{and } \Phi_2 &= -\det |\psi_1(1) \cdot \psi_4(2) \cdot \psi_3(3) \cdot \psi_5(4) \cdot \psi_7(5) \cdot \psi_8(6) \cdot \psi_6(7)|\end{aligned}$$

It has already been mentioned that it is the separate configurations of alpha and beta spin electrons that are kept so as to enable a saving in storage to be made. The full configurations are formed by running through the spin-configuration lists as and when necessary. There are a number of points to be considered in deciding which of the configurations it is possible to form should be included in a calculation.

The number of possible configurations is often vast, increasing rapidly as the number of basis orbitals is increased, as shown in Table I, for a system of ten electrons. It is necessary, therefore, to be able to limit them in some way. The usual method is to include only those configurations which can be obtained from the ground state configuration by up to a specified number of excitations. In our scheme this limit is applied to the spin-configurations at the time of their generation, but if two excitations are permitted, for example, this would still allow some three and four excitation total configurations to be formed. It would perhaps be convenient to have these included in the calculation, but unfortunately such a set of configurations will not yield a wavefunction which is an eigenfunction of the  $s^2$  operator. For a singlet system these three and four excitation configurations have to be ignored entirely, but for a doublet system some of the three excitation configurations must be picked out and included to complete spin states otherwise only involving two excitation configurations. Since our program has been applied mainly to doublet systems, it is

TABLE 1

Number of configurations for a system of ten electrons

<u>Number of orbitals</u>	<u>Complete C.I.</u>	<u>Single and double excitations only</u>
10	63,504	345
15	9,018,009	3,501
20	240,374,016	7,876
25	2,822,796,900	14,001

perhaps worthwhile considering in some detail the special problems associated with arriving at a wavefunction which is a spin eigenfunction with these systems.

The total spin operator

$$S^2 = S_x^2 + S_y^2 + S_z^2 \quad (2.9)$$

where

$$S_\gamma = \sum_{i=1}^N S_\gamma(i) \quad (\gamma = x, y, z)$$

which have the properties

$$\begin{aligned} S_x \alpha &= \frac{\hbar}{2} \beta & S_x \beta &= \frac{\hbar}{2} \alpha \\ S_y \alpha &= -\frac{i\hbar}{2} \beta & S_y \beta &= \frac{i\hbar}{2} \alpha \\ S_z \alpha &= \frac{\hbar}{2} \alpha & S_z \beta &= -\frac{\hbar}{2} \beta \end{aligned}$$

Expanding equation (2.9)

$$S^2 = \sum_{i=1}^N \sum_{j=1}^N S_x(i) S_x(j) + S_y(i) S_y(j) + S_z(i) S_z(j) \quad (2.10)$$

It is convenient to introduce the operators

$$\begin{aligned} S_+ &= S_x + i S_y \\ \text{and } S_- &= S_x - i S_y, \end{aligned}$$

which for a one-electron system gives the results

$$\begin{aligned} S_+ \alpha &= 0, & S_+ \beta &= \hbar \alpha, \\ S_- \alpha &= \hbar \beta, & S_- \beta &= 0. \end{aligned}$$

Now

$$\begin{aligned} S_+ S_- &= (S_x + i S_y)(S_x - i S_y) \\ &= S_x S_x + S_y S_y - i(S_x S_y - S_y S_x) \end{aligned}$$

which because of the commutation relation

$$S_x S_y - S_y S_x = i\hbar S_z$$

gives  $S_x S_y + S_y S_x = S_+ S_- - \hbar S_z$  .

So that, considering only the terms in  $S_x$  and  $S_y$  when  $i=j$  in equation (2.10), we get

$$\sum_i S_x(i) S_x(i) + S_y(i) S_y(i) = \sum_i S_+(i) S_-(i) - \hbar S_z(i).$$

and because

$$S_+(i) S_-(j) = S_x(i) S_x(j) + S_y(i) S_y(j) - i[S_x(i) S_y(j) - S_y(i) S_x(j)]$$

and  $S_-(i) S_+(j) = S_x(i) S_x(j) + S_y(i) S_y(j) + i[S_x(i) S_y(j) - S_y(i) S_x(j)]$

the same terms when  $i=j$  are equal to

$$\sum_i \sum_{j(\neq i)} \frac{1}{2} [S_+(i) S_-(j) + S_-(i) S_+(j)]$$

Substituting these expressions into equation (2.10), we have

$$S^2 = \sum_i S_+(i) S_-(i) - \hbar S_z(i) + \sum_i \sum_j S_z(i) S_z(j) + \sum_i \sum_j \frac{1}{2} [S_+(i) S_-(j) + S_-(i) S_+(j)] \quad (2.11)$$

Having regard for the properties of these operators, we find for a system of  $p$  alpha and  $q$  beta electrons the equation

$$S^2 = \frac{\hbar}{2} (p+q) + \frac{\hbar^2}{4} (p-q)^2 + \hbar \sum_{i=1}^p \sum_{j=1}^q P_{ij} \quad (2.12)$$

where  $P_{ij}$  effects the permutation  $\alpha(i)$  goes to  $\beta(i)$  and  $\beta(j)$  to  $\alpha(j)$ .

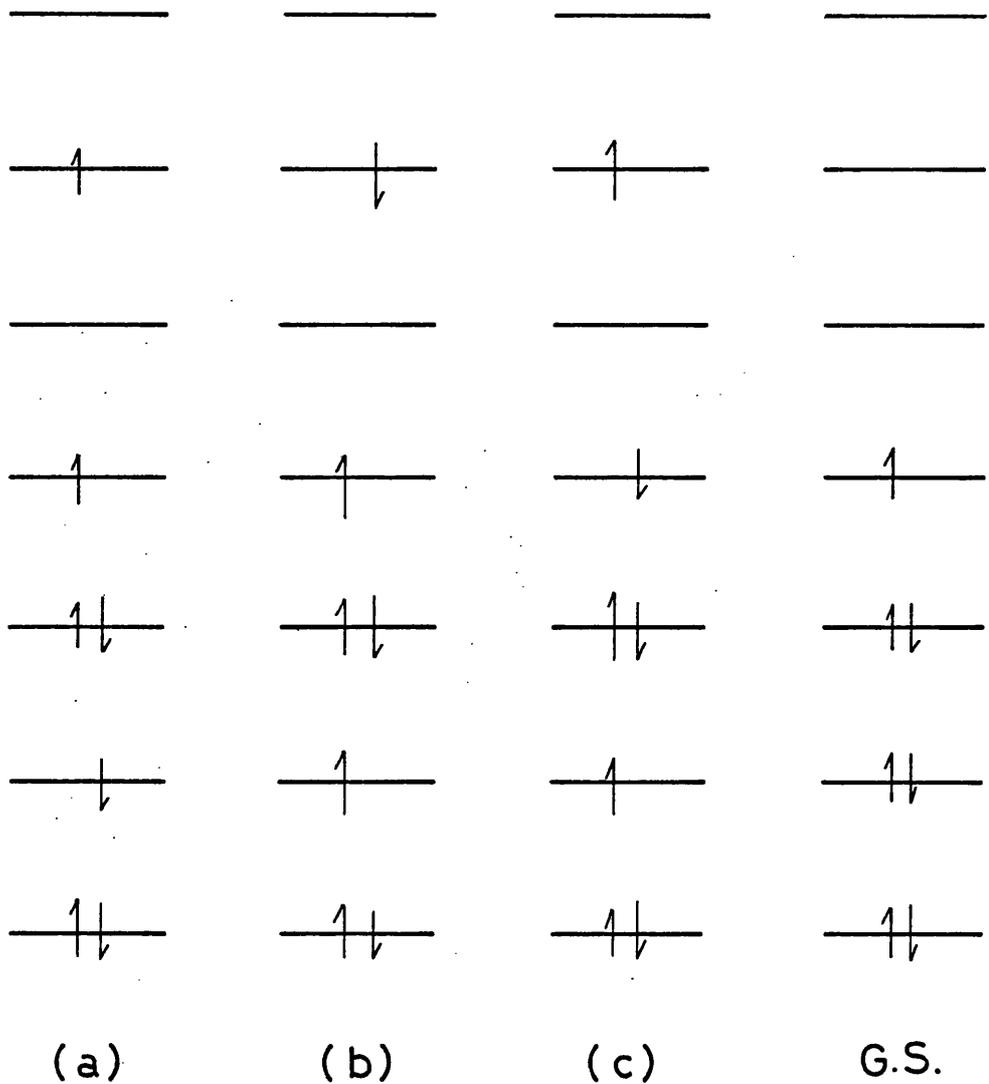
It is the permutation operator  $P_{ij}$  which has to be considered when trying to construct a wavefunction which is a eigenfunction of the  $s^2$

operator. Only those determinants with but one unpaired spin, for the doublet systems being considered, have a  $\langle s^2 \rangle$  value of 0.75 and in general it is a sum involving a number of determinants which have the desired  $\langle s^2 \rangle$  value. Configurations representing an example of such a set of determinants are illustrated in Figure 6. It can be seen that while configurations (a) and (b) need only one excitation from the ground state to construct, configuration (c) requires two. Because of this a configuration list limited by allowing only a certain number of excitations is unacceptable, some configurations which require one over the allowed number are always necessary to complete the set for a spin eigenfunction. This is easily coped with in our program, in which it is lists of spin-configurations which are kept. If both the alpha and beta spin-configurations are limited to a single excitation from the ground state then, apart from the one excitation full configurations that can be produced, there are also some two excitations and it is from amongst these latter that configurations such as (c) can be found. This is done by examining the singly occupied level of the ground state, if it is occupied by a beta but not by an alpha electron then the configuration should be included.

Another approach would have been to have used states rather than single determinants in the configuration interaction. This would have removed the need to find the extra configurations representing single determinants to complete the eigen states of  $s^2$  and would lead to a saving in numbers of configurations. Determinants with only the one unpaired spin are an eigen state in any case and give no saving. But the permutation of three unpaired spins can be combined to give a quartet and two doublets, the latter being of the form

$$2 \psi_1 - \psi_2 - \psi_3$$

FIGURE 6 - EXAMPLE OF A SET OF CONFIGURATIONS COMPRISING AN EIGENSTATE



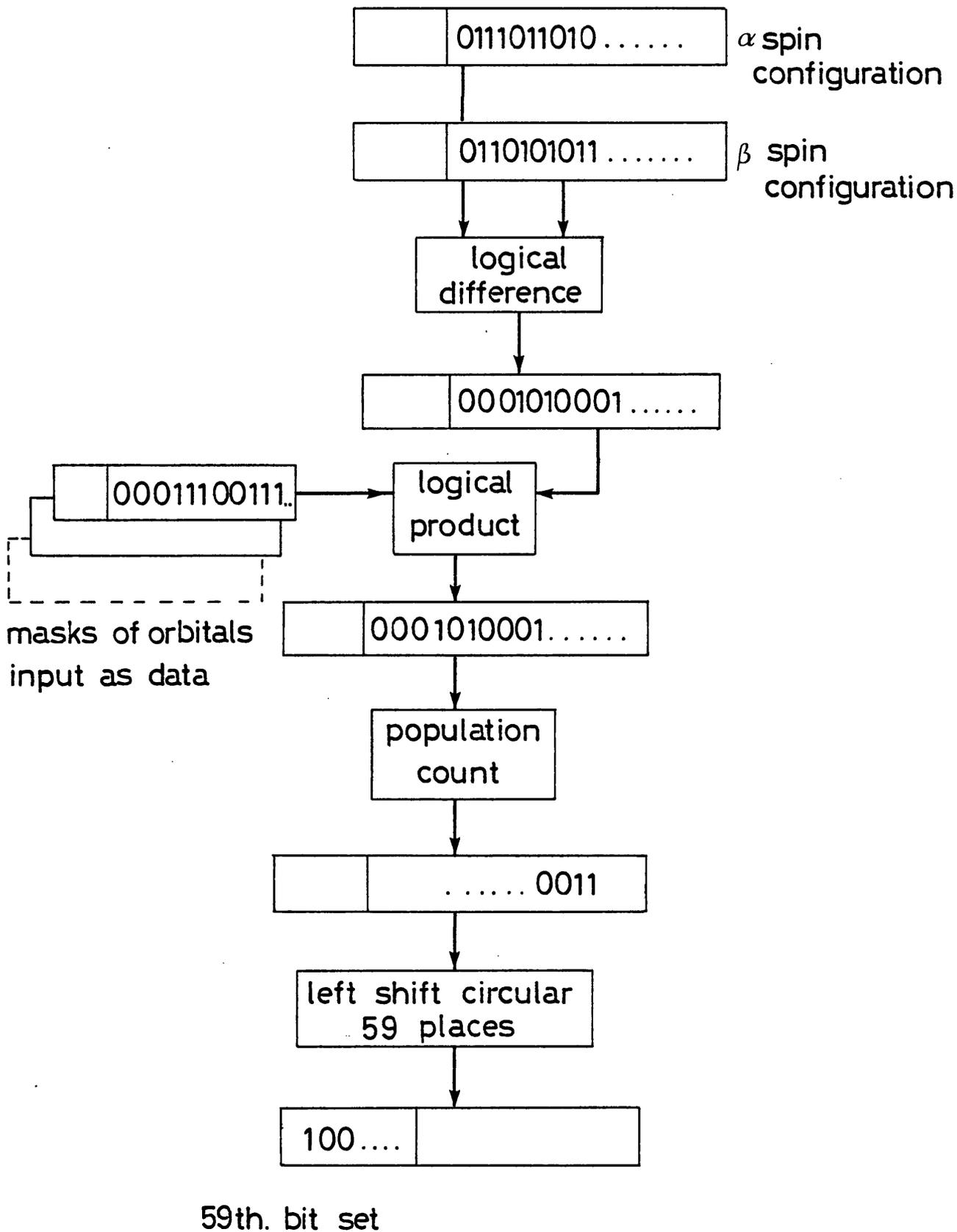
and  $\psi_2 - \psi_3$  .

The use of states then would reduce the number of configurations with three unpaired spins to two-thirds of the original. For the case of five unpaired spins, there are ten possible permutations which can be combined to give five doublet states, thus giving a reduction to half of the original number of this type of configuration by the use of states. If a limit of two excitations from the ground state is imposed upon the configurations then five unpaired electrons would be the maximum that would be obtained.

There is no doubt that something approaching a halving of the number of configurations would be advantageous in certain instances, however such is the rapid manner in which the number of configurations increases with the increase in number of orbitals and so on, that the value of such a reduction is limited. Moreover the work which must be carried out in forming and using states as opposed to single determinants would be quite extensive, and since the coding of this would have to be specifically related to the number of determinants over which linear combinations were being constructed it would be out of keeping with the intended generality of the present program.

It is often the case that certain configurations will not contribute to the wavefunction for reasons of symmetry. These may be ignored in the calculation to obtain a saving in time and storage requirements. This was done in our program by inputting as data a number of masks positioned in a word in the same way as the configurations themselves. The masks have bits set to 1's to indicate all the molecular orbitals of a certain symmetry, the configurations of this symmetry being the ones that are to be removed. Figure 7 shows how these are used to determine whether a configuration should be included in a calculation.

FIGURE 7 - FLOW DIAGRAM FOR THE MASKING OUT OF UNWANTED CONFIGURATIONS



A logical difference instruction finds the unpaired electrons in the configuration; if an odd number of these should correspond to the orbitals designated by a mask, then a X-register is set negative as a flag to indicate that the configuration should be discarded.

Ideally one would wish to have the number of basis orbitals and the number of configurations used in calculations as large as possible, but inevitably these quantities are restricted in practice. The number of basis orbitals (N) determines the size of arrays needed for the one and two electron integrals. It is the two electron integrals, of which there are  $N^4$ , which require the most storage. However, the requirement at the transformation stage can be readily reduced to  $N^3$  or  $N^2$  by the use of backing store. It is unfortunate that the method of constructing the Hamiltonian matrix used in our program requires the random access of the two electron integrals, and this means that they are best kept in core at this stage, if at all possible, rather than use backing store which would doubtless result in a large increase in processing time. The number of integrals to be stored are reduced to approximately  $N^4/8$  by removing those which are duplicated. This is done by imposing as an integral  $\langle IJ|KL \rangle$  the conditions that

$$I \geq J$$

$$I \geq K$$

$$J \geq L$$

if  $I = K$ , then  $J \geq K$ .

This last condition is not imposed in our program. The integrals are stored linearly and are accessed by the use of formulae.

The Hamiltonian matrix is constructed and accessed during diagonalisation element by element and row by row, so that backing store is very easily employed, with only buffer areas needed in central memory. Even

so, since the matrix's size is dependent upon the square of the number of configurations included in the calculation, there comes a point when the matrix will exhaust the readily available backing store. However, these problems are common to all conventional CI programs and a great deal of research has gone into trying to make the most effective use of available computer resources.

## Conclusion

Having stated some of the limitations of the present program it may be useful to describe the possible scope for development in the light of recent advances in the implementation of the CI method. One line of approach has been to work with existing computational techniques, but to try and improve the quality of the truncated CI wavefunction in other ways. This has been done by defining a new set of orbitals, as in the Natural Orbital method [6]. Natural orbitals may be found by diagonalising the charge density matrix constructed from a CI wavefunction. They then can be used as the basis of a second CI calculation and so on, giving an iterative sequence that can be repeated until energy convergence occurs. Also the configurations included in a calculation may be subjected to a selection procedure in an endeavour to find those of most significance. Buenker and Peyerimhoff [7] have used such a method with the refinement of an extrapolation technique to account for those configurations which are discarded. The configuration selection approach was one with which one scheme was intended to be compatible and could readily be implemented.

Computationally, the major impediment to progress in this field has been the calculation, manipulation, and diagonalisation of large Hamiltonian matrices. Roos [8] has presented a method which is capable of calculating CI eigenvalues and eigenvectors directly from the one- and two-electron integrals, without the need to form the Hamiltonian matrix at all. This allows many more configurations to be included in a calculation (Roos estimates 40,000 configurations if 100K words of store are available, which may be compared to something of the order of 10000 if a Hamiltonian matrix is formed and has to be stored on disc).

Hausman, Bloom, and Bender [9], with their Vector method, have given a useful formulism for this approach. They define their wavefunction in terms of Slater determinants, written as a product of N single particle creation operators

$$\Phi = \sum_{\alpha\beta\cdots\omega} \Gamma_{\alpha\beta\cdots\omega} a_{\alpha}^{\dagger} a_{\beta}^{\dagger} \cdots a_{\omega}^{\dagger} | 0 \rangle , \quad (2.13)$$

where  $\Gamma_{\alpha\beta\cdots\omega}$  is the coefficient for the corresponding Slater determinant.

The Hamiltonian operator can then be expressed as

$$H_{Op} = \sum_{\alpha\beta} \langle \alpha | H_1 | \beta \rangle a_{\alpha}^{\dagger} a_{\beta} + \frac{1}{2} \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta | H_2 | \gamma\delta \rangle a_{\alpha}^{\dagger} a_{\beta}^{\dagger} a_{\delta} a_{\gamma}. \quad (2.14)$$

Here  $H_1$  and  $H_2$  are the one and two-electron parts of the Hamiltonian operator respectively. But, since it is inconvenient to have to bother with these parts separately, they give a more useful form of the operator

$$H_{Op} = \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta | H | \gamma\delta \rangle a_{\alpha}^{\dagger} a_{\beta}^{\dagger} a_{\delta} a_{\gamma} \quad (2.15)$$

where

$$\langle \alpha\beta | H | \gamma\delta \rangle = \frac{1}{N+1} \langle \alpha | H_1 | \gamma \rangle \langle \beta | \delta \rangle + \frac{1}{2} \langle \alpha\beta | H_2 | \gamma\delta \rangle \quad (2.16)$$

With this method then, the term in  $H_{Op}$  corresponding to the integral  $\langle \alpha\beta | H | \gamma\delta \rangle$  will operate on all configurations with the orbitals  $\gamma$  and  $\delta$  occupied and the orbitals  $\alpha$  and  $\beta$  unoccupied to give a second configuration, with which the first will interact, where the reverse is true.

This method is very compatible with our scheme: the function of annihilation and creation operators can be readily undertaken by logical instructions, acting on configurations stored as a binary pattern, using masks to designate the affected orbitals. However, the vector method

presentation tends to obscure the computational processes involved.

With the direct CI method the vector  $v$ , with components

$$v_i = \sum_j H_{ij} c_j ,$$

is built up from the vector  $c$  and the integral list. Efficiency dictates that the integral list should be held on backing store and that it be read through consecutively once in an iteration, while the vectors  $v$  and  $c$  should be stored in core, so that they can be randomly accessed. For each integral, the indices  $i$  and  $j$  must be found for the pairs of configurations to whose interaction it contributes. For a truly general program, it would seem that this can only be done by some degree of searching, with a consequent lack of efficiency. The alternative is to classify and sort both the integrals and the configurations, so that formulae can be used to direct the integrals to the appropriate components of the vectors. This gives greater efficiency, but has the disadvantage that the program becomes very code dependent and is only applicable to a specific situation; the classifications to be used differ between singlet and doublet systems and for whatever level of excitation is to be allowed. It seems likely that this latter alternative would have to be adopted so as to give reasonable processing times, making it unlikely that our present scheme could be used.

It remains to look at the demands made by the direct CI method upon the diagonalisation algorithm, with which it must be integrated. The Nesbet routine has been described elsewhere, and it will be remembered that the components  $c_i$  of the trial vector are normally adjusted sequentially by

$$\Delta c_i = \frac{\sum_j H_{ij} c_j - E c_i}{(E - H_{ii})} , \quad (2.17)$$

which is a stable method for finding the lowest eigenvalue. If simultaneous change of all the components of the trial vector is used, this usually does not lead to convergence. Now with the direct CI method simultaneous adjustment is required, since the vector  $Hc$  is built up as a whole from a single reading of the integrals every iteration, so that a new algorithm will be necessary in adopting this method. A number of different procedures have been employed, but that of Davidson [10], based on the use of equation (2.17), but adapted to the Lanczos method [11], seems particularly attractive and has been used with the direct CI method by Dacre [12]. It has the added advantage of being able to generate higher eigenvalues.

## Section Three

The Calculation of Electron Spin Resonance  
Hyperfine Coupling Constants

## Introduction

This section deals with the application of the RHF + CI method to the evaluation of Electron Spin Resonance (ESR) hyperfine coupling constants. This method has already been used by Platt [13] to look at a number of radicals using mainly minimal basis sets, obtaining quite good results for  $\sigma$ -radicals, but far from satisfactory results for  $\pi$ -radicals. In the case of the  $\sigma$ -radicals, the direct contribution predominates and it would seem that a minimal basis is often able to describe this term with fair accuracy. Here a range of more extensive basis sets have been used to study the  $\pi$ -radicals  $\text{NH}_2$ ,  $\text{BH}_3^-$ ,  $\text{CH}_3$ , and  $\text{NH}_3^+$  and the  $\sigma$ -radicals  $\text{BeOH}$  and  $\text{BeH}$ .

Advantage was taken of the program's flexibility to undertake complete and various truncated CI calculations. It will be seen that, while it is perfectly possible to perform a complete CI when using small basis sets, as the number of orbitals rises it becomes necessary to limit the excitations included in the calculations. Therefore a major aim of this work was to find a balance, within the limits of the computing resources available, between the size of the basis set and the proportion of the configurations taken into account, so as to obtain reliable values of ESR hyperfine coupling constants.

The isotropic hyperfine coupling constant of a nucleus A is given as  $a(A)$  and arises from the Fermi contact interaction described in equation (4.1). Similarly the anisotropic coupling constant along the principal axes is given as  $B(A)$  and arises from the dipole interaction described in equation (4.2).

## The NH<sub>2</sub> Radical

CI calculations of isotropic hyperfine coupling constants for the NH<sub>2</sub> radical and other  $\pi$ -radicals using minimal basis sets have given poor results, the calculated couplings being close to twice the observed values [13]. In an attempt to obtain improved results, calculations were carried out for the NH<sub>2</sub> radical as a test case using a range of basis sets. The geometry and the scaling factor for the hydrogen atomic orbital exponent in each case were the optimum for a minimal basis set calculation, namely  $R(\text{N-H}) = 2.0$  a.u,  $\theta(\text{H-N-H}) = 105^\circ$ , and  $\xi(\text{H}) = 1.35$ .

The minimal basis set calculations presented in Table I used the gaussian expansions of Huzinaga [15], 9s-type and 5p-type for nitrogen and 6s-type for hydrogen. The greater than minimal sets of Table II were created by breaking up these expansions to form new orbitals, in which the coefficients retained the same proportions to one another as in the original Huzinaga 1s and 2p orbitals where appropriate. For example, the (4sp/3s) basis was constructed by splitting the nine gaussian functions of the Huzinaga 1s atomic orbital on nitrogen into four new s-orbitals and the six functions of the hydrogen 1s into three new s-orbitals. The details of these splittings are given in Table III. For each basis calculations employing the Unrestricted Hartree Fock method with annihilation of the contaminating quartet spin state and the RHF + CI method have been performed.

The results of this series of calculations show a convergence of both the UHF and the CI values for the isotropic hyperfine coupling constants of NH<sub>2</sub> as more flexibility is introduced by extending the basis set. Comparison should be made with the experimentally observed values, which have been reported as

$$\begin{aligned}
 a(\text{N}) &= 10.3 \text{ G} & \text{and} & & a(\text{N}) &= 13.3 \text{ G} \\
 a(\text{H}) &= -23.9 \text{ G [16]} & & & a(\text{H}) &= -27.3 \text{ G [17]}
 \end{aligned}$$

The UHF method has been found to give quite reasonable values for isotropic coupling constants using minimal basis sets, however, in this case extending the basis leads to much poorer results. In contrast, the CI couplings have approached the experimentally determined ones. For example, the (9sp/3s) basis gave

$$\begin{aligned}
 a(\text{N}) &= 8.98 \text{ G} \\
 a(\text{H}) &= -25.00 \text{ G} .
 \end{aligned}$$

This calculation included all single and the necessary double excitations, a total of 174 configurations, and took some 230 seconds to execute on the University of Leicester's Control Data Cyber 72.

Comparison of the results for the different basis sets shows that the isotropic coupling constants are very significantly affected by uncontracting the s-orbital expansions, but hardly at all by splitting the nitrogen p-expansion. The influence of the s-orbital contractions appear largely confined to the coupling of the nucleus on which they are centred, so that changes in the nitrogen contraction has little effect upon the hydrogen coupling and vice versa.

It is difficult to be certain about the effects produced by imposing various limits on the configurations included in a calculation, as it was only possible to use a range of limits for the smaller basis sets. However, it is noticeable that calculations including all single and necessary double excitations (CI1) do not give values for the isotropic hyperfine coupling constants so very far from those obtained by including all single, double, and necessary triple excitations (CI2) or from the complete CI, even though many more configurations have been included in these latter calculations. If we look at the minimal basis,

the values of the  $a(N)$  coupling are very close: 20.5, 20.7, and 21.3 for CI1, CI2, and complete CI respectively. A greater difference is evident in the case of the  $a(H)$  couplings, with values of -38.6, -44.9, and -46.8. But it must be remembered that the number of  $\pi$ -symmetry configurations (and only these will interact with the ground state) has risen from 13 for the CI1 calculation to 69 for the CI2 calculation and 169 for the complete CI. Turning to the energies, it can be seen that such CI2 calculations as it was found possible to carry out have given significantly lower values than the corresponding CI1 calculations.

These results seem to show that, in trying to obtain reliable isotropic coupling constants, the emphasis should be placed on improving the basis set rather than trying to include the maximum number of configurations in a calculation. It is impossible to do both because of the explosion in the number of configurations as the number of basis orbitals increases. The (9s p/3s) basis is a total of 18 orbitals occupied by nine electrons, which would give a complete CI involving over 26 million configurations. Even a CI2 calculation would have over 7,000 configurations, though this figure could be reduced by perhaps a half by retaining only the configurations of  $\pi$ -symmetry and, unfortunately, time restrictions prevented such a calculation being performed.

A second series of basis orbitals were constructed by atomic RHF calculations upon nitrogen and hydrogen with all the s-type gaussian functions separated, but keeping the nitrogen p-expansion contracted. A scaling factor was not used for the hydrogen orbital exponents as it was thought that the flexibility introduced in the larger basis sets would remove the need for it. This provided a new set of nine s-orbital gaussian expansions for nitrogen and six for hydrogen for calculations on the  $NH_2$  radical. The results of Tables IV and V were obtained with

various bases, starting with (2s p/1s) and adding on successive s-orbitals of lowest energy, and by including all single and necessary double excitations in the CI. The comparatively good  $a(\text{H})$  value for the minimal basis is fortuitous and arises from ignoring the optimum scaling factor for the hydrogen orbital exponent. Fairly good results for both isotropic coupling constants were achieved by using at least the (5s p/4s) basis, but the method offers little improvement in economy or accuracy over the first series of calculations. The best calculation of the second series, that is the one employing the (9s p/6s) basis corresponding to complete extension of the s-type expansions, involved 252 configurations and gave the isotropic coupling constants as

$$\begin{aligned} a(\text{N}) &= 9.38 \text{ G} \\ a(\text{H}) &= -25.83 \text{ G.} \end{aligned}$$

TABLE I

CI calculations for the NH<sub>2</sub> radical using a minimal basis set  
 [Energies in Hartree, couplings in Gauss]

<u>CALCULATION</u>	<u>ENERGY</u>	<u>a(N)</u>	<u>a(H)</u>	<u>NO. OF CONFIGURATIONS</u>
UHF	-55.5259118	8.45	-21.10	
CI1	-55.5267156	20.55	-38.63	13*, 31
CI2	-55.569696	20.70	-44.91	69*
Full CI	-55.570366	21.29	-46.84	169*, 735
Full CI (Huckel orbitals)	-55.570366	21.29	-46.84	169*, 735

In Tables I and II the total number of configurations of whatever symmetry is given, unless the figure is followed by an asterisk, in which case it is the number of configurations of  $\pi$ -symmetry only. Where known, both figures have been given.

CI1 = calculation including all single and necessary double excitations.

CI2 = calculation including all single, double, and necessary triple excitations.

TABLE II

CI calculations for the NH<sub>2</sub> radical  
[Energies in Hartree, couplings in Gauss]

<u>BASIS SET</u>	<u>CALCULATION</u>	<u>ENERGY</u>	<u>a(N)</u>	<u>a(H)</u>	<u>NO. OF CONFIGURATIONS</u>
2s p/2s	UHF	-55.5325433	8.58	-19.07	
	CI1	-55.5331418	20.32	-34.44	57
	CI2	-55.583687	20.14	-39.83	753
4s p/1s	UHF	-55.5295986	6.37	-21.90	
	CI1	-55.530403	9.02	-40.22	57
	CI2	-55.595795	10.61	-45.29	299*, 753
2s p/3s	UHF	-55.5353052	8.90	-14.19	
	CI1	-55.5359324	21.07	-24.66	83
4s p/3s	UHF	-55.5399283	4.92	-14.79	
	CI1	-55.5404737	6.43	-25.00	109
7s p/3s	UHF	-55.5415684	5.65	-14.80	
	CI1	-55.5421161	9.05	-25.00	148
9s p/3s	UHF	-55.5415692	5.61	-14.80	
	CI1	-55.5421170	8.98	-25.00	174
2s p/4s	UHF	-55.5359087	8.74	-14.67	
	CI1	-55.5365020	20.67	-25.76	109
3s2p/3s	UHF	-55.5299930	5.91	-13.99	
	CI1	-55.5307149	9.11	-24.43	135
4s2p/2s	UHF	-55.538567	4.65	-19.92	
	CI1	-55.5391455	5.77	-35.53	122
4s2p/3s	UHF	-55.5414930	4.79	-14.63	
	CI1	-55.5421151	6.01	-24.79	148

Orbitals for nitrogen and hydrogen as used in NH<sub>2</sub> calculations

Huzinaga gaussian exponents	Number of orbitals formed					
	9	7	4	3		
5909.44	1s					
887.451	2s	1s				
204.749	3s		1s			1s
59.8376	4s	2s				
19.9981	5s	3s				
7.19274	6s	4s				
2.68598	7s	5s	2s			2s
0.70004	8s	6s	3s			3s
0.21329	9s	7s	4s			4s

<u>Nitrogen p-orbitals</u>	
26.786	2p
5.95635	
1.7074	3p
0.53136	
0.16537	

<u>Hydrogen s-orbitals</u>	
124.223	1s
18.6743	
4.27646	2s
1.22713	
0.409443	3s
0.14984	

TABLE IV

Results for the isotropic coupling constants of the NH<sub>2</sub> radical  
[in Gauss]

In each case, upper figure is a(N) and lower figure is a(H)

<u>No. of hydrogen s-orbitals in basis</u>	<u>No. of nitrogen s-orbitals in basis</u>								
	2	3	4	5	6	7	8	9	
1	22.26 -19.75	21.39 -21.92		8.48 -21.97	8.79 -21.99	9.22 -21.99			
2	21.79 -22.74	21.65 -23.99	12.12 -24.02	8.69 -24.05	8.99 -24.06	9.41 -24.06	9.64 -24.06	9.18 -24.06	
3	21.64 -26.96	22.65 -27.73	13.20 -22.77	9.29 -27.78	9.27 -27.78	9.49 -27.78	9.62 -27.78	9.70 -27.78	
4	22.34 -26.21	22.75 -26.77	12.87 -26.79	8.98 -26.80	8.96 -26.80	9.19 -26.80	9.32 -26.80	9.41 -26.80	
5	22.34 -25.71	22.74 -26.11	12.85 -26.13	8.97 -26.14	8.95 -26.14	9.17 -26.14	9.31 -26.14	9.39 -26.14	
6	22.34 -25.50	22.74 -25.81			8.94 -25.83	9.17 -25.83	9.30 -25.83	9.38 -25.83	

TABLE V

Results for the energy of the NH<sub>2</sub> radical [in Hartree]

<u>No. of hydrogen s-orbitals in basis</u>	<u>No. of nitrogen s-orbitals in basis</u>								
	2	3	4	5	6	7	8	9	
1	-55.4683341	-55.4814481		-55.4820276	-55.4822183	-55.4822676			
2	-55.4951159	-55.5023789	-55.5025067	-55.5028317	-55.5030054	-55.5030522	-55.5030610	-55.5030620	
3	-55.5319492	-55.5374758	-55.5375935	-55.5378272	-55.5379386	-55.5379701	-55.5379759	-55.5379765	
4	-55.5372415	-55.5425183	-55.5427044	-55.5429345	-55.5430446	-55.5430757	-55.5430814	-55.5430820	
5	-55.5382909	-55.5435292	-55.5437171	-55.5439452	-55.5440550	-55.5440859	-55.5440916	-55.5440922	
6	-55.5384271	-55.5436800			-55.5441859	-55.5442168	-55.5442225	-55.5442232	

## The $\text{BH}_3^-$ , $\text{CH}_3$ , and $\text{NH}_3^+$ Radicals

Having found an approach which yielded reasonable results for the  $\text{NH}_2$  radical, it was now applied to the  $\text{BH}_3^-$ ,  $\text{CH}_3$ , and  $\text{NH}_3^+$  radicals. These radicals have been investigated using the Unrestricted Hartree-Fock with spin annihilation (UHFAA) method, giving satisfactory results for  $\text{NH}_3^+$  [18] and for  $\text{CH}_3$  [19], but  $\text{BH}_3^-$  was calculated to be bent by 9 degrees with an associated very large isotropic hyperfine coupling constant,  $a(\text{B})$  [19]. However, further calculations by Overill including orbitals appropriate to the boron anion gave the experimentally inferred planar geometry and improved isotropic coupling constants [20]. It was intended to duplicate this work on these radicals with the RHF + CI method.

The basis sets used for the RHF + CI calculations were the Huzinaga gaussian expansions, 9s-type and 5p-type for the heavy atoms and 6s-type for hydrogen, with additional 5p-type gaussian expansions for the anion or cation of the heavy atoms as given in reference 20. New s-orbitals were formed by breaking up the original expansions as had been done for  $\text{NH}_2$ . The bond lengths and hydrogen atomic orbital exponents were taken as 2.35 and 1.15 respectively for  $\text{BH}_3^-$ , 2.05 and 1.4 for  $\text{CH}_3$ , and 1.95 and 1.6 for  $\text{NH}_3^+$ , these being the optimised values for a minimal basis set calculation. All single and the necessary double excitation configurations were included in each of the calculations.

These radicals are generally considered to be planar and in this conformation only an indirect coupling mechanism is operative. However, out-of-plane vibrations will introduce direct coupling and so augment the coupling constant for the planar radical; the extent of this effect can be seen from the calculated isotropic coupling constants of  $\text{BH}_3^-$ , the direct and indirect terms of which are given in Table VII. The

estimation of the vibrational contributions to hyperfine coupling constants involves the calculation of total energies and hyperfine coupling constants at non-equilibrium nuclear conformations.

It is assumed that the zero-point energy vibrational modes execute simple harmonic motion:

$$\psi_{\text{vib}} = (\alpha/\pi)^{1/4} \exp(-\alpha x^2/2)$$

where  $x$  is the displacement from the equilibrium conformation and

$$\alpha = 2 \mu E_{\text{vib}}^{\circ}$$

where  $\mu$  is the reduced mass and  $E_{\text{vib}}^{\circ}$  is the zero-point energy for the vibration:

$$E_{\text{vib}} = (v + \frac{1}{2}) (k/\mu)^{1/2} \quad v = 0, 1, 2 \dots$$

$k$  being the force constant of the vibration defined by

$$E = E_0 + \frac{1}{2} k x^2$$

$E_0$  and  $E$  are the calculated energies at zero and non-zero displacements respectively.

The general variation of the isotropic hyperfine coupling constant,  $a$ , with  $x$  is

$$a = \sum_{n=0}^{\infty} C_n x^n$$

If it is assumed that terms with  $n > 2$  can be neglected, and noting that for an harmonic oscillator terms with odd powers of  $x$  disappear, then this reduces to:

$$a = C_0 + C_2 x^2$$

where  $C_0$  is the coupling constant calculated at the equilibrium nuclear conformation. Then  $\langle a \rangle$ , the vibrationally corrected hyperfine coupling constant, is the mean value of the calculated coupling constants over the displacements sampled during the execution of the zero-point vibration, as is given by

$$\langle a \rangle = \langle \psi_{\text{vib}} | a | \psi_{\text{vib}} \rangle = C_0 + C_2 / (2\alpha)$$

The estimates obtained from this equation may not be satisfactory in situations where the simple harmonic approximation is unreasonable, for example with large displacements or small force constants.

The RHF + CI results incorporating zero-point out-of-plane vibrational corrections for the  $\text{BH}_3^-$ ,  $\text{CH}_3$  and  $\text{NH}_3^+$  radicals are given in Tables VI, VII, and IX respectively. Table X is a summary of these results, comparing them with the UHFAA results of Overill using the contracted Huzinaga 9s 5p/6s gaussian set with the addition of anionic and cationic 5p expansions and with the experimentally determined values.

In general the isotropic coupling constants determined by the RHF + CI method are in excellent agreement with experiment, and offer an improvement over the UHFAA results, the exception to this is the anomalously high value for the carbon coupling constant of  $\text{CH}_3$ . The inclusion of an anionic p-orbital is seen to have a significant effect in  $\text{BH}_3^-$  giving a reduction in the boron isotropic coupling constant from 22.56 to 7.7 G, which gives with the addition of the considerable vibronic contribution a value which is quite close to the experimentally determined one. On the other hand, the inclusion of anionic and cationic orbitals has little importance for the  $\text{NH}_3^+$  and  $\text{CH}_3$  radicals.

The case of  $\text{BH}_3^-$  can be explained by supposing that the unpaired

electron is held relatively close to the boron nucleus, using only orbitals appropriate to the neutral atom, causing considerable inter-electronic repulsion with the B-H  $\sigma$ -bonding electrons. This could only be relieved by the adoption of a pyramidal conformation in which the bonds were directed away from the non-bonding electron. This is remedied by inclusion of the more diffuse anionic orbital which allows the unpaired electron to be held further from the boron nucleus. The interelectronic repulsion with the bonding orbitals is reduced and the radical becomes planar.

TABLE VI

C.I. Results for the BH<sub>3</sub><sup>-</sup> radical

Energies in hartrees; couplings in gauss  
force constant in a.u. (=1544 Nm<sup>-1</sup>)

Basis	$\theta$	Energy	a(B)	a(H)	No. of configurations
6s p <sup>o</sup> /3s	0	-26.3283894	22.56	-23.22	174
6s p <sup>o</sup> p <sup>-</sup> /2s	0	-26.3452886	7.70	-18.12	174
	1	-26.3452687	7.89	-18.10	
	2	-26.3452087	8.46	-18.03	
	5	-26.3447794	12.42	-17.56	
	10	-26.3430991	26.24	-15.89	
	15	-26.3397557	47.78	-13.30	
	20	-26.3334386	74.64	-10.33	
6s p <sup>o</sup> p <sup>-</sup> /2s	a(B)	Calculated value		7.70	
		Vibronic correction		15.39	
		Corrected value		23.09	
	a(H)	Calculated value		-18.12	
		Vibronic correction		1.87	
		Corrected value		-16.25	
	Force constant			0.02359	

TABLE VII

The direct and indirect contributions to the isotropic coupling constants of the  $\text{BH}_3^-$  radical at various angles of bending (in Gauss)

Angle (degrees)	a(B)		a(H)		Total
	Indirect	Direct	Indirect	Direct	
0	7.70	0.00	-18.12	0.00	-18.12
0.5	7.71	0.04	-18.12	0.00	-18.12
1	7.72	0.17	-18.12	0.02	-18.10
2	7.78	0.68	-18.10	0.07	-18.03
5	8.17	4.25	-18.00	0.44	-17.56
10	9.19	17.05	-17.57	1.68	-15.89
15	10.24	37.54	-16.75	3.45	-13.30
20	11.64	63.00	-15.69	5.36	-10.33

TABLE VIII

C.I. Results for the CH<sub>3</sub> radical

Energies in Hartree; couplings in Gauss;  
force constant in a.u. (=1544 Nm<sup>-1</sup>)

Basis	$\theta$	Energy	a(C)	a(H)	No. of configurations
6s p <sup>o</sup> /3s	0	-39.5527517	35.46	-27.22	174
	2	-39.5526285	36.82	-27.00	
	5	-39.5519738	43.82	-25.85	
	10	-39.5494872	67.08	-22.19	
6s p <sup>o</sup> p <sup>+</sup> p <sup>-</sup> /3s	0	-39.5580702	30.86	-26.30	252
	2	-39.5579806	32.13	-26.08	
	5	-39.5574887	38.69	-24.97	
	10	-39.5546892	54.82	-10.44	

		6s p <sup>o</sup> /3s	6s p <sup>o</sup> p <sup>+</sup> p <sup>-</sup> /3s
a(C)	Calculated value	35.46	30.86
	Vibronic correction	25.42	27.68
	Corrected value	60.88	58.54
a(H)	Calculated value	-27.22	-26.30
	Vibronic correction	4.23	4.73
	Corrected value	-22.99	-21.57
Force constant		0.0480	0.0347

TABLE IX

C.I. Results for the NH<sub>3</sub><sup>+</sup> radical

Energies in Hartree; couplings in Gauss;  
force constant in a.u. (=1544 Nm<sup>-1</sup>)

Basis	$\theta$	Energy	a(N)	a(H)	No. of configurations
6s p <sup>o</sup> /3s	0	-55.8725836	15.56	-27.84	174
	2	-55.8723074	16.04	-27.65	
	5	-55.8708487	18.56	-26.68	
	10	-55.8655372	27.24	-23.45	
8s p <sup>o</sup> /4s	0	-55.8756110	15.75	-29.97	239
	2	-55.8753443	16.23	-29.77	
	5	-55.8739355	18.11	-28.78	
	10	-55.8687972	27.28	-25.47	
6s p <sup>o</sup> p <sup>+</sup> p <sup>-</sup> /3s	0	-55.8753672	16.43	-28.25	252
	2	-55.8751309	16.91	-28.05	

		6s p <sup>o</sup> /3s	8s p <sup>o</sup> /4s	6s p <sup>o</sup> p <sup>+</sup> p <sup>-</sup> /3s
a(N)	Calculated value	15.56	15.75	16.43
	Vibronic correction	6.29	6.32	6.8
	Corrected value	21.85	22.07	23.2
a(H)	Calculated value	-27.84	-29.97	-28.25
	Vibronic correction	2.48	2.56	2.8
	Corrected value	-25.36	-27.40	-25.5
Force constant		0.1188	0.1149	0.112

TABLE X

Summary of Results for the  $\text{BH}_3^-$ ,  $\text{CH}_3$ , and  $\text{NH}_3^+$  radicals[Energies in Hartree; couplings in Gauss; force constants in a.u. ( $=1544 \text{ Nm}^{-1}$ )]

	Energy	a(X)			a(H)		
		Calculated Value	Vibronic Correction	Total	Calculated Value	Vibronic Correction	Total
$\text{BH}_3^-$							
6s $p^0p^-/2s$	-26.3452886	7.70	15.39	23.09	-18.12	1.87	-16.25
UHF	-26.338893	15.50	14.5	30.0	-13.81	1.7	-12.1
Expt [21]				20.7			(-)15.1
$\text{CH}_3$							
6s $p^0/3s$	-39.5527517	35.46	25.42	60.88	-27.22	4.23	-22.99
6s $p^0p^+p^-/3s$	-39.5580702	30.86	27.68	58.54	-26.30	4.73	-21.57
UHF	-39.543904	25.98	23.2	49.2	-22.06	3.9	-18.2
Expt [22]				38.0			(-)23.0
$\text{NH}_3^+$							
6s $p^0/3s$	-55.8725836	15.56	6.29	21.85	-27.84	2.48	-25.36
6s $p^0p^+p^-/3s$	-55.8753672	16.43	6.77	23.19	-28.25	2.77	-25.47
8s $p^0/4s$	-55.8756110	15.75	6.32	22.07	-29.97	2.56	-27.40
UHF	-55.856935	10.80	5.9	16.7	-23.24	2.6	-20.6
Expt [23]				19.5			(-)25.8

TABLE XI

Orbitals for  $\text{BH}_3^-$ ,  $\text{CH}_3$ , and  $\text{NH}_3^+$  radical calculations

Heavy atom s-orbitals

		No. of gaussians for orbital expansions							
		1s	2s	3s	4s	5s	6s	7s	8s
Total no. of orbitals formed	6	3	2	1	1	1	1		
	8	2	1	1	1	1	1	1	1

Hydrogen s-orbitals

		No. of gaussians for orbital expansions		
		1s	2s	3s
Total no. of orbitals formed	3	3	2	1
	2	3	3	

Gaussians with the lowest exponents went to form the highest orbitals

## The BeOH Radical

Brom and Weltner have recently obtained the ESR spectrum of the isolated BeOH radical in an argon matrix. The reported hyperfine coupling constants were:

$$\begin{array}{ll} a(\text{Be}) = -94.3 \text{ G} & B(\text{Be}) = -1.4 \text{ G} \\ a(\text{H}) = <1.8 \text{ G} & B(\text{H}) = \sim 0.4 \text{ G} \end{array}$$

The ESR spectrum was characteristic of a linear molecule [14].

RHF + CI calculations were carried out for this  $\sigma$ -radical using a basis set consisting of Huzinaga gaussian expansions, 9s-type for beryllium, 9s-type and 5p-type for oxygen, and 6s-type for hydrogen, with the addition of a STO-5G expansion [27] for the beryllium p-orbital. The geometry and scaling factors for the exponents of the beryllium p-orbital and hydrogen s-orbital were optimised for the contracted basis, including all single, double, and necessary triple excitation configurations in the calculations (CI2). These confirmed the presumed linear structure for the radical and yielded optimum values of  $R(\text{Be-O}) = 2.6$  a.u.,  $R(\text{O-H}) = 1.8$  a.u.,  $\xi_{\text{H}} = 1.45$ , and  $\xi_{\text{Be}(p)} = 1.1$ ; details are given in Table XII.

A single calculation was performed with the s-orbitals uncontracted so as to give a (5s p/5s p/2s) basis. In the case of beryllium and oxygen, the four gaussians with the lowest exponents were released from the Huzinaga 1s-expansions to form new orbitals, leaving a set of five gaussians which have coefficients in much the same proportions to one another in both the Huzinaga 1s and 2s-orbitals (see Table XIV). This is probably a much better basis, for its size, than the more haphazard ones used for earlier calculations. This calculation included all single and necessary double excitations (CI1).

The CI results obtained with the two basis sets are compared with experiment in Table XIII. It can be seen that the CI1 calculation employing the (5s p/5s p/2s) basis gave very gratifying results for the coupling constants, the isotropic terms agreeing with the observed values to within the limits of experimental accuracy, while the anisotropic terms are quite reasonable remembering that the basis was not set up with these in mind. Included in the table are the direct contributions to the couplings obtained from the uncorrelated RHF wavefunction. These in general form a substantial proportion of the total and are much the same for both basis sets. Clearly it is in describing the indirect contribution that the (5s p/5s p/2s) proves superior to the (2s p/2s p/1s) basis.

TABLE XII

CI optimization of the BeOH radical  
 [Energies in Hartree; couplings in Gauss]

R(Be-O)	R(O-H)	Be-O-H	$\xi_H$	$\xi_{Be(p)}$	Energy	a(Be)	a(O)	a(H)
2.6	1.80	0	1.4	1.1	-90.1295725	-79.25	-13.85	4.05
*2.6	1.80	0	1.45	1.1	-90.1299653	-79.20	-13.85	4.34
2.6	1.80	0	1.5	1.1	-90.1296362	-79.14	-13.80	4.50
2.6	1.75	0	1.45	1.1	-90.1278622	-79.07	-13.72	4.01
2.6	1.85	0	1.45	1.1	-90.1298760	-79.29	-13.94	4.50
2.55	1.80	0	1.45	1.1	-90.12928919	-78.45	-13.80	3.95
2.65	1.80	0	1.45	1.1	-90.1294372	-79.91	-13.93	4.65
2.6	1.80	2	1.45	1.1	-90.1299482	-79.19	-13.84	4.29
2.6	1.80	5	1.45	1.1	-90.1298589	-79.15	-13.80	4.25
2.6	1.80	0	1.45	1.0	-90.1283301	-76.29	-11.41	5.51
2.6	1.80	0	1.45	1.2	-90.1261089	-81.69	-18.22	3.34
2.6	1.80	0	1.45	**	-89.845361	-62.51	-204.99	33.88

\* Minimum energy geometry.

\*\* Calculation with no boron p-orbital.

TABLE XIII

CI results for the BeOH radical at optimum geometry  
 [Energies in Hartrees; couplings in Gauss]

Basis	Source	Energy	a(Be)	a(O)	a(H)	B(Be)	B(O)	B(H)	No. of $\sigma$ -symmetry configurations
2sp/2sp/1s	Direct		-78.96	-16.31	1.22	-1.298	-0.576	0.914	
	CI1	-90.0672317	-79.22	-13.13	2.32	-1.158	-1.974	0.171	37
	CI2	-90.1299653	-79.20	-13.85	4.29	-1.054	-2.488	0.128	493
5sp/5sp/2s	Direct		-78.82	-16.38	1.52	-1.243	-0.572	0.903	
	CI1	-90.0726307	-94.32	-17.69	1.76	-1.106	-1.917	0.111	128
	Expt		-94.3		<1.8	-1.4		~0.4	

TABLE XIV

S-orbitals as used in (5sp/5sp/2s) basis for the BeOH radical

<u>HUZINAGA GAUSSIAN EXPONENTS</u>		<u>ORBITALS</u>
Be	O	
1741.38	7816.54	}
262.139	1175.82	
60.3255	273.188	
17.6239	81.1696	
5.93258	27.1836	
2.18473	9.53223	2s
0.85895	3.41364	3s
0.18062	0.93978	4s
0.05835	0.28461	5s

<u>HUZINAGA GAUSSIAN EXPONENTS</u>		<u>ORBITALS</u>
H		
143.306	}	1s
21.5433		
4.93347		
1.41566		
0.472348		
0.172861		2s

## The BeH Radical

Calculations were performed for the BeH radical employing Huzinaga gaussian expansions, 9s-type for beryllium and 6s-type for hydrogen, with the addition of p-orbitals consisting of a single gaussian function with an exponent of 0.3 for beryllium and 0.75 for hydrogen. The range of basis sets, for which results are presented in Table XV, were constructed by releasing successively the gaussians with the lowest exponents from the beryllium 2s and hydrogen 1s-orbitals. The exception was the (5sp/4sp) basis for which the gaussians were released from the 1s-orbital on beryllium, the original 2s-orbital being dispensed with. In each case a value of 2.538 a.u. was taken for  $R(\text{Be-H})$ . The results may be compared with the experimentally observed hyperfine coupling constants:

$$\begin{array}{ll} a(\text{Be}) = -71 \text{ G} & B(\text{Be}) = -1.6 \text{ G} \\ a(\text{H}) = 69 \text{ G} & B(\text{H}) = 1.2 \text{ G} \quad [34] \end{array}$$

The calculated coupling constants for this range of basis sets show a convergence towards the experimental values, accompanied by a lowering in the energy, on moving to more extensive bases. However, there remains a discrepancy even with the (5sp/4sp) basis, the most extensive set used, and this is probably due to the inadequacy of the beryllium p-orbital, the importance of which can be clearly recognised from the table.

Of particular interest are the calculations performed allowing different levels of excitation in the configuration interaction, the most comprehensive series of results being for the (4sp/2sp) basis. These show close to 95% of the correlation energy being provided by inclusion of the double and triple excitations consequent upon going

from the CI1 to the CI2 type of calculation. Looking now at the isotropic coupling constants, it can be seen that the hydrogen is affected to a greater extent than the beryllium coupling by truncating the CI. However, if only the indirect contribution is considered, the behaviour of both atoms' couplings show some similarity; broadly speaking the CI1 brings the contribution to within around 35%, the CI2 to within 10%, and the CI3 to within 1% of the complete CI values. Hopefully calculations of this type can give an indication of the errors incurred when truncating the CI, which becomes a necessity if fairly extensive basis sets are to be used.

TABLE XV

## CI results for the BeH Radical

[Energies in Hartree, couplings in Gauss]

Basis	Calculation	Energy	a(Be)	a(H)	B(Be)	B(H)	No. of configurations
3s/1s	RHF	-15.0274833	-25.84	454.15	-0.618	-0.026	
	Fu11 CI	-15.0298257	-23.30	454.31	-0.625	-0.132	24
4s/2s	RHF	-15.0570829	-38.80	153.27	-0.300	0.860	
	Fu11 CI	-15.0856200	-38.98	205.46	-0.389	0.724	300
5s/3s	RHF	-15.0593015	-39.85	128.46	-0.307	0.836	
	Fu11 CI	-15.0893949	-40.18	190.63	-0.388	0.734	1568
6s/3s	RHF	-15.0593166	-39.06	128.48	-0.307	0.839	
	CI3	-15.0899108	-38.31	190.77	*	*	1599
	Fu11 CI	-15.0900523	-38.33	190.66	-0.388	0.736	3024
2sp/1s	RHF	-15.1003661	-58.04	101.52	-1.224	2.853	
	Fu11 CI	-15.1165318	-49.76	167.70	-1.233	1.987	
2sp/1sp	RHF	-15.1033966	-58.37	98.34	-1.239	2.853	
	Fu11 CI	-15.1300294	-52.48	158.14	-1.231	1.991	760; 3024
3sp/1sp	RHF	-15.1084235	-57.63	97.75		*	
	CI2	-15.1376184	-52.08	155.97	*	*	198; 598
	Fu11 CI	-15.1380186	-51.81	159.72			1408; 5400
2sp/2sp	RHF	-15.1180032	-63.68	42.88		*	
	Fu11 CI	-15.1498016	-56.97	112.25	*	*	1408; 5400

\* No anisotropic couplings available

TABLE XV (continued)

Basis	Calculation	Energy	a(Be)	a(H)	B(Be)	B(H)	No. of configurations
4sp/2sp	RHF	-15.1273969	-59.63	33.82	-0.900	2.247	
	CI1	-15.1291304	-68.79	79.77	-0.914	1.727	38; 64
	CI2	-15.1734542	-67.04	87.18	-0.918	1.664	390; 966
	CI3	-15.1739206	-66.64	93.00	-0.919	1.614	1640; 5016
	Full CI	-15.1742129	-66.58	93.39	-0.919	1.611	4144; 14520
5sp/4sp	RHF	-15.1281362	-62.05	39.94	-0.917	2.288	
	CI1	-15.1298308	-70.14	79.28	-0.934	1.769	59; 87
	CI2	-15.1768755	-68.92	86.41	-0.934	1.713	843; 1539

NB: Where two figures are given in the 'No. of configurations' column, the first is the number of interacting,  $\sigma$ -symmetry configurations and the second is the total of  $\sigma$  and  $\pi$ -symmetry configurations.

## Section Four

The Calculation of Nuclear Magnetic  
Resonance Coupling Constants

## Theory

Nucleus-nucleus coupling involves the direct dipole-dipole interaction of the magnetic moments and also an indirect interaction by way of the electrons. In such a system as a liquid, where there is no fixed orientation for the molecules, the direct couplings are averaged to zero. There are three mechanisms for the indirect interaction: the Fermi contact, spin-dipolar and orbital contributions.

The Fermi contact interaction, which describes the coupling between the nuclear moments and the electron spins in contact with that nucleus, has the Hamiltonian operator

$$H^F = \frac{8\pi}{3} g_e \beta_e \sum_A \sum_k \delta(\Gamma_{kA}) \mu_A \cdot S_k \quad (4.1)$$

where  $g_e$  is the electronic g-value,

$\beta_e$  is the Bohr magneton,

$\mu_A$  is the magnetic moment of nucleus A,

$S_k$  is the spin angular momentum operator for electron k,

and  $\delta(\Gamma_{kA})$  is the three-dimensional Dirac delta function for electron k at nucleus A, which has the property that

$$\int f(\Gamma_k) \delta(\Gamma_{kA}) d\Gamma_k = f(\Gamma_A)$$

where  $f(\Gamma_k)$  is an arbitrary function of the co-ordinates of electron k

and  $\Gamma_{kA} = \Gamma_k - \Gamma_A$ .

The operator for the dipole interaction between the nuclear moments and the electron spins, is given by

$$H^D = g_e \beta_e \sum_A \sum_k [3 (\mu_A \cdot \Gamma_{kA}) (S_k \cdot \Gamma_{kA}) \Gamma_{kA}^{-5} - (\mu_A \cdot S_k) \Gamma_{kA}^{-3}]. \quad (4.2)$$

The nuclear moment - electron orbital interaction has an operator of the form

$$H^o = 2 \beta_e \sum_A \sum_k (\mu_A \cdot L_{kA}) \Gamma_{kA}^{-3} \quad (4.3)$$

where  $L_{kA}$  is the orbital angular momentum operator for electron  $k$  about nucleus  $A$ .

Of the cross-terms between these interactions, the spin-dipolar - Fermi contact cross-term is averaged to zero in liquids, whilst the spin dipolar - orbital and Fermi contact - orbital cross-terms are likely to be negligible unless the electron spin-orbital coupling is strong. In any event these cross-terms have not been evaluated in this work.

The observed nuclear spin-spin coupling interaction is of the form

$$E_{AB} = h J_{AB} I_A I_B \quad (4.4)$$

where  $E_{AB}$  is the interaction energy between the nuclei  $A$  and  $B$  with spins  $I_A$  and  $I_B$ ,  $h$  is Plank's constant and  $J_{AB}$  is the observed nuclear spin-spin coupling constant between  $A$  and  $B$ . The magnetogyric ratio relates  $\mu_A$  and  $I_A$  by

$$\gamma_A = \mu_A / (I_A \hbar)$$

so that equation (4.4) can be rewritten as

$$J_{AB} = E_{AB}^2 \gamma_A \gamma_B h / 2\pi \quad (4.5)$$

where  $E_{AB}^2$  is the second order energy of interaction of the nuclear magnetic moments  $\mu_A$  and  $\mu_B$ ,

$$E_{AB}^2 = \left[ \frac{\delta^2 E_{AB}}{\delta \mu_A \delta \mu_B} \right]_{\mu_A = \mu_B = 0} \quad (4.6)$$

To obtain theoretical values of  $J_{AB}$ , we form a matrix which comprises the calculated Hamiltonian matrix with an added first row and column, as shown below.

$H_{00}$	$V_{0i}^B$ ----- $V_{0i}^B$
$V_{10}^A$	$H_{11}$ ----- $H_{ii}$
⋮	⋮ ----- ⋮
$V_{i0}^A$	$H_{i1}$ ----- $H_{ii}$

Here  $H_{00}$  is the energy of the unperturbed wavefunction  $\Psi = \sum c_j \phi_j$  and

$$V_{0i} = \sum_j c_j \langle \phi_j | V_{op} | \phi_i \rangle .$$

Using partitioned matrix techniques and following Lowdin, such a matrix can be solved to obtain

$$E = H_{00} + \sum_i \sum_j V_{0i} (\tilde{H} - H_{00} \tilde{I})_{ij}^{-1} V_{j0} \quad (4.7)$$

Since  $V_{0i}$  and  $V_{j0}$  are sums of contributions from each nucleus, these may be evaluated separately (and then have the superscript A, B, etc.), when the relevant expression for the interaction energy between nuclei A and B is

$$\sum_i \sum_j [V_{0i}^A (\tilde{H} - H_{00} \tilde{I})_{ij}^{-1} V_{j0}^B + V_{0i}^B (\tilde{H} - H_{00} \tilde{I})_{ij}^{-1} V_{j0}^A] \quad (4.8)$$

since terms involving  $\mu_A \cdot \mu_A$  and  $\mu_B \cdot \mu_B$  can be neglected from equation (4.6).

The matrix inversion was carried out using the biorthogonalisation

technique of Prosser and Hagstrom [26]. An iterative scheme would seem to be more generally suitable, and such a method can be formulated using the following equation

$$C_i^{\text{new}} (E - H_{ii}) = V_i + \sum_{i \neq j} H_{ij} C_j^{\text{old}} \quad (4.9)$$

where  $v_i$  is defined as  $v_{oi}$  above, and then

$$E_{AB}^{(2)} = \sum_i (C_i^A V_i^B + C_i^B V_i^A) . \quad (4.10)$$

Unfortunately this method was found to run into convergence problems when an attempt was made to make use of it in the calculations presented here.

## Results

The RHF + CI method was used to calculate nuclear spin-spin coupling constants for the series of molecules CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O, and HF, the Fermi contact, electron orbital, and spin-dipolar contributions being evaluated in each case. The optimised minimal basis sets consisted of both SCF 9s, 5p/6s atomic orbital expansions [15] and Slater-type orbitals in the STO-6G expansion [27]. Details of the molecular geometries and atomic orbital exponents are given in Table I and are identical to those used by Overill for SCFPM calculations [20]. The results are presented in Tables I and II, where the CI couplings are compared with the relevant SCFPM and observed values.

As might be expected using only a minimal basis set, the calculated couplings are in poor agreement with experiment, however, a number of features are worthy of notice. The importance of the different contributions to the couplings are in the order Fermi contact > electron orbital > spin-dipolar. It has been quite usual to evaluate only the Fermi contact term, but it can be seen that the electron orbital term can be of significance and this is particularly so for the H-F coupling. Though the other terms are fairly stable, the Fermi contact contribution to the X-H couplings show a marked divergence between the STO and SCF bases on descending the series CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O, HF.

To obtain improved results more extensive basis sets have to be used. This has been done by Overill using the SCFP method and excellent X-H couplings have resulted, though the H-H couplings are still much too large [20]. It would seem that an accurate description of the electronic correlation is important here, and better values have been obtained by Roos et al. [24,25] using a large configuration interaction.

Molecular geometries, basis sets, and numbers of configurations included in CI calculations

<u>MOLECULE</u>	<u>BASIS</u>	<u>GEOMETRY</u>	<u>ORBITAL EXPONENTS</u>	<u>NO. OF CONFIGURATIONS</u>
CH <sub>4</sub>	SCFAO	R = 2.05	H: $\xi(1s) = 1.40$	441(CIIS)
		$\theta = 109.45$		
	STO-6G	R = 2.0665	H: $\xi(1s) = 1.17$	
		$\theta = 109.45$	C: $\xi(1s) = 5.68$ , $\xi(2s) = \xi(2p) = 1.76$	
NH <sub>3</sub>	SCFAO	R = 1.9162	H: $\xi(1s) = 1.40$	256(CIIS)
		$\theta = 106.73$		
	STO-6G	R = 1.9162	H: $\xi(1s) = 1.234$	
		$\theta = 106.73$	N: $\xi(1s) = 6.672$ , $\xi(2s) = 1.966$ , $\xi(2p) = 1.931$	
H <sub>2</sub> O	SCFAO	R = 1.8111	H: $\xi(1s) = 1.40$	121(CIIS), 441(Fu11 CI)
		$\theta = 104.45$		
	STO-6G	R = 1.8111	H: $\xi(1s) = 1.27$	
		$\theta = 104.45$	O: $\xi(1s) = 7.66$ , $\xi(2s) = 2.25$ , $\xi(2p) = 2.21$	
HF	SCFAO	R = 1.7328	H: $\xi(1s) = 1.50$	36(Fu11 CI)
	STO-6G	R = 1.7328	H: $\xi(1s) = 1.3163$	
			F: $\xi(1s) = 8.6533$ , $\xi(2s) = 2.5551$ , $\xi(2p) = 2.5498$	

CIIS indicates that all total configurations that could be derived from the one excitation spin-configurations were included in the calculation.

TABLE II

Results for the coupling constants in some polyatomic molecules  
using optimised minimal STO basis sets (in Hertz)

<u>Molecule</u>	<u>A-B</u>	<u>Source</u>	<u>Contact</u>	<u>Dipolar</u>	<u>Orbital</u>	<u>Total</u>
CH <sub>4</sub>	C-H	SCFPM	249.7	0.0	-0.1	249.6
		CI1S	189.5	0.6	0.04	190.1
		Expt [28]				125
	H-H	SCFPM	- 34.1	0.0	0.8	- 33.3
		CI1S	19.9	0.1	0.7	- 19.1
		Expt [29]				- 12.4
NH <sub>3</sub>	N-H	SCFPM	58.3	- 0.1	0.4	58.6
		CI1S	47.9	0.0	0.3	48.2
		Expt [30]				±43.6
	H-H	SCFPM	- 35.4	0.6	1.5	- 33.3
		CI1S	- 26.5	- 0.1	1.5	- 25.1
		Expt [30]				±10.4
H <sub>2</sub> O	O-H	SCFPM	- 1.4	1.3	-5.1	- 5.2
		CI1S	- 0.4	- 0.11	-4.8	- 5.3
		Full CI	6.2	0.09	-4.8	1.5
		Expt [31]				±79.0
	H-H	SCFPM	- 37.5	1.0	3.6	- 32.9
		CI1S	- 39.7	0.84	3.8	- 35.0
Full CI		- 23.2	0.9	4.1	- 18.2	
Expt [32]				± 7.2		
HF	F-H	SCFPM	-931.5	-27.3	217.4	-741.4
		Full CI	-725	-30.8	152.1	-604.5
		Expt [33]				530

TABLE III

Results for the coupling constants in some polyatomic molecules  
using optimised minimal SCFAO basis sets (in Hertz)

<u>Molecule</u>	<u>A-B</u>	<u>Source</u>	<u>Contact</u>	<u>Dipolar</u>	<u>Orbital</u>	<u>Total</u>
CH <sub>4</sub>	C-H	SCFPM	223.5	0.0	-0.1	223.4
		CI1S	186.5	0.4	-0.1	186.8
		Expt [28]				125
	H-H	SCFPM	-65.3	0.2	0.5	-64.6
		CI1S	-34.8	0.0	0.52	-34.3
		Expt [29]				-12.4
NH <sub>3</sub>	N-H	SCFPM	77.8	-0.2	0.4	78.0
		CI1S	66.9	0.0	0.4	67.3
		Expt [30]				±43.6
	H-H	SCFPM	-52.4	0.4	1.0	-51.0
		CI1S	-39.1	0.0	0.9	-38.2
		Expt [30]				±10.4
H <sub>2</sub> O	O-H	SCFPM	-92.7	1.5	-5.6	-96.8
		CI1S	-78.6	0.16	-5.3	-83.7
		Full CI	-72.6	0.14	-5.4	-77.9
		Expt [31]				±79.0
	H-H	SCFPM	-42.9	0.6	1.9	-40.4
		CI1S	-46.1	-0.5	1.9	-44.7
Full CI		-26.9	-0.5	2.0	-25.4	
Expt [32]				± 7.2		
HF	F-H	SCFPM	150.8	-26.9	174.9	298.8
		Full CI	80.4	-27.7	119.4	172.1
		Expt [33]				530

## Appendix

Compass Instructions

APPENDIX: COMPASS INSTRUCTIONS [5]

Logical Product Instruction

This instruction forms the logical product (AND function) of 60-bit words from operand registers  $X_j$  and  $X_k$  and places the product in operand register  $X_i$ . Bits of register  $X_i$  are set to 1 when the corresponding bits of the  $X_j$  and  $X_k$  registers are 1 as in the following example:

$$\begin{array}{r} (X_j) = 0\ 1\ 0\ 1 \\ (X_k) = \underline{1\ 1\ 0\ 0} \\ (X_i) = 0\ 1\ 0\ 0 \end{array}$$

Logical Sum Instruction

This instruction forms the logical sum (inclusive OR) of 60-bit words from operand registers  $X_j$  and  $X_k$  and places the sum in operand register  $X_i$ . A bit of register  $X_i$  is set to 1 if the corresponding bit of the  $X_j$  or  $X_k$  registers is a 1 as in the following example:

$$\begin{array}{r} (X_j) = 0\ 1\ 0\ 1 \\ (X_k) = \underline{1\ 1\ 0\ 0} \\ (X_i) = 1\ 1\ 0\ 1 \end{array}$$

Logical Difference Instruction

This instruction forms the logical difference (exclusive OR) of 60-bit words from operand registers  $X_j$  and  $X_k$  and places the result in operand register  $X_i$ . A bit of the result is set to 1 if the corresponding bits in the  $X_j$  and  $X_k$  registers are unlike as in the following example:

$$\begin{array}{r} 0\ 1\ 0\ 1 \\ \underline{1\ 1\ 0\ 0} \\ 1\ 0\ 0\ 1 \end{array}$$

### Complement Instruction

This instruction sets all bits of a 60-bit word in an X-register to 1 which were 0 and vice versa.

### Mask

This instruction clears an X-register and forms a mask in it. It defines a number of 1's in the mask as counted from the highest order bit in the X-register. The completed masking word consists of 1's in the high order bit positions of the word and 0's in the remainder of the word.

### Logical Shift

This instruction shifts the 60-bit word in an X-register left circular a number of places. Bits shifted off the left end of the X-register replace those shifted from the right end.

### Population Count

This instruction counts the number of 1 bits in an X-register and stores the count in another X-register.

### Normalize

This instruction normalizes the floating point quantity in an X-register. Normalizing consists of shifting the coefficient to the left the minimum number of positions required to make bit 47 different from 59. This places the most significant bit of the coefficient in the highest order position of the coefficient portion of the word. The exponent portion of the word is then decreased by the number of bit positions shifted. The number of shifts required to normalize the quantity is entered in a B-register.

## REFERENCES

1. J. C. Slater, Phys. Rev., 34 (1929) 1293 and 38 (1931) 1109.
2. R. K. Nesbet, J. Chem. Phys., 43 (1965) 311.
3. I. Shavitt, J. Comp. Phys., 6 (1970) 124.
4. Fortran Extended Version 4 Reference Manual, Control Data Corp.
5. Compass Version 3 Reference Manual, Control Data Corp.
6. C. F. Bender and E. R. Davidson, J. Phys. Chem., 70 (1966) 2675.
7. R. J. Buenker and S. D. Peyerimhoff, Theoret. Chim. Acta, 35 (1974) 33.
8. B. Roos, Chem. Phys. Letts., 15 (1972) 153.
9. R. F. Hausman Jr., S. D. Bloom and C. F. Bender, Chem. Phys. Letts., 32 (1975) 483.
10. E. R. Davidson, J. Comp. Phys., 17 (1975) 87.
11. C. Lanczos, J. Res. Nat. Bur. Stand., 45 (1950) 255.
12. P. D. Dacre, Theoret. Chim. Acta, 43 (1976) 197.
13. E. Platt, Ph.D. Thesis, University of Leicester (1976).
14. J. M. Brom, Jr. and W. Weltner, Jr., J. Chem. Phys., 64 (1976) 3898.
15. S. Huzinaga, J. Chem. Phys., 42 (1965) 1293.
16. J. R. Morton and D. R. Smith, Can. J. Chem., 44 (1966) 1951.
17. T. Cole, J. Chem. Phys., 35 (1961) 1169.
18. T. A. Claxton and N. A. Smith, Trans. Faraday Soc., 66 (1970) 1825.
19. T. A. Claxton, M. J. Godfrey and N. A. Smith, J.C.S. Faraday II, 68 (1972) 181.
20. R. E. Overill, Ph.D. Thesis, University of Leicester (1976).
21. E. D. Sprague and F. Williams, Molec. Phys., 20 (1971) 375.
22. R. W. Fessenden, J. Phys. Chem., 71 (1967) 74.

23. M. C. R. Symons and K. V. S. Rao, J. Chem. Soc. A, (1971) 263.
24. J. Kowalewski, B. Roos, P. Siegbahn and R. Vestin, Chem. Phys., 9 (1975) 29.
25. *ibid.*, 3 (1974) 70.
26. F. Prosser and S. Hagstrom, Int. J. Quant. Chem., II (1968) 89.
27. W. J. Helre, R. F. Stewart and J. A. Pople, J. Chem. Phys., 87 (1969) 2657.
28. N. Muller and D. E. Pritchard, J. Chem. Phys., 31 (1959) 768.
29. R. A. Bernheim and J. Lavery, J. Chem. Phys., 42 (1965) 1464.
30. R. A. Bernheim and H. Batiz-Hernandez, J. Chem. Phys., 40 (1964) 3446.
31. A. E. Flarin and M. Alei, J. Chem. Phys., 47 (1967) 4268.
32. J. R. Holmes, D. Kilveson and W. C. Drinkard, J. Chem. Phys., 37 (1962) 150.
33. J. S. Muentzer and W. Klemperer, J. Chem. Phys., 52 (1970) 6033.
34. L. B. Knight, Jr., J. M. Brom, Jr. and W. Weltner, Jr., J. Chem. Phys., 56 (1970) 1152.

Configuration Interaction and the Calculation of ESR and NMR  
Coupling Constants - B. Burton

A scheme is presented for a computer program using the Configuration Interaction method. To make the program as flexible as possible, lists of spin-configurations over RHF molecular orbitals are kept. These separate configurations for the alpha and beta spins can be combined to give the total configurations as and when necessary. It is shown how advantage may be taken of the internal bit structure of a computer word so as to store the spin-configurations as a binary pattern, which provides economical storage, and how information can then be extracted from them by means of the computer's logical machine instructions.

The Configuration Interaction method is applied to the calculation of magnetic resonance properties. The Electron Spin Resonance hyperfine coupling constants of the  $\pi$ -radicals  $\text{NH}_2$ ,  $\text{BH}_3^-$ ,  $\text{CH}_3$  and  $\text{NH}_3^+$  and the  $\sigma$ -radicals  $\text{BeOH}$  and  $\text{BeH}$  are studied using a range of basis sets and allowing various levels of excitations to be included in the CI. Rather more tentative results are presented for the Nuclear Magnetic Resonance coupling constants of  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{HF}$  using only minimal basis sets.