SCF PERTURBATION THEORY OF NUCLEAR SPIN COUPLING CONSTANTS

A SELF-CONSISTENT-FIELD PERTURBATION THEORY
OF
NUCLEAR SPIN COUPLING CONSTANTS

by

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SCOPE AND CONTENTS:

The principal methods of calculating nuclear spin coupling constants by applying perturbation theory to molecular orbital wavefunctions for the electronic structure of molecules are discussed. A new method employing a self-consistent-field perturbation theory (SCFPT) is then presented and compared with the earlier methods.

In self-consistent-field (SCF) methods, the interaction of an electron with other electrons in a molecule is accounted for by treating the other electrons as an average distribution of negative charge. However, this charge distribution cannot be calculated until the electron-electron interactions themselves are known. In the SCF method, an initial charge distribution is assumed and then modified in an iterative calculation until the desired degree of self-consistency is attained. In most previous perturbation methods, these electron interactions are not taken into account in a self-consistent manner in calculating the perturbed wavefunction even when SCF wavefunctions are used to describe the unperturbed molecule.

The main advantage of the new SCFPT approach is that it treats the interactions between electrons with the same degree of self-consistency in the perturbed wavefunction as in the unperturbed wavefunction. The SCFPT method offers additional advantages due to its computational efficiency and the direct manner in which it treats the perturbations. This permits the theory to be developed for the orbital and dipolar contributions to nuclear spin coupling as well as for the more commonly treated contact interaction.

In this study, the SCFPT theory is used with the Intermediate Neglect of Differential Overlap (INDO) molecular orbital approximation to calculate a number of coupling constants involving ^{13}C and ^{19}F. The usually neglected orbital and dipolar terms are found to be very important in FF and CF coupling. They can play a decisive role in explaining the experimental trend of J_{CF} among a series of compounds. The orbital interaction is found to play a significant role in certain CC couplings.

Generally good agreement is obtained between theory and experiment except for J_{CF} and J_{FF} in oxalyl fluoride and the incorrect signs obtained for cis J_{FF} in fluorinated ethylenes. The nature of the theory permits the latter discrepancy to be rationalized in terms of computational details.

The value of J_{FF} in difluoracetic acid is predicted to be -235 Hz.

The SCFPT method is used with a theory of d_π - p_π bonding to predict in agreement with experiment that J_{CH} in acetylene will decrease when that molecule is bound in a transition metal complex.

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CHAPTER I. INTRODUCTION

1. Aim and Outline

The aim of this dissertation is to present a theoretical method which permits values for nuclear spin coupling constants in a molecule to be calculated from the molecular orbital (MO) description of its electronic structure. The method is based on a self-consistent-field (SCF) type of perturbation theory (SCFPT) and therefore, in contrast with most previous methods, is capable of making optimum use of the SCF nature of currently available MO wavefunctions. The recently published finite perturbation theory (FPT) of Pople, McIver and Ostlund(1,2,3) is also a self-consistent method but is somewhat less computationally efficient than the method presented here and, as with most other published coupling-constant theories, has been developed only for the least complicated of the three mechanisms which contribute to nuclear spin coupling.

In this study, the theory is developed for the usually neglected orbital and dipolar contributions as well as for the more commonly treated contact contribution. (These terms are defined in Section 3 (b) of this chapter.) The theory is applicable to SCF MO theories of any level of approximation. However, the method is developed in detail for one semi-empirical theory, the INDO (Intermediate Neglect of Differential Overlap) method due to Pople, Beveridge and Dobosh(4). Some numerical calculations are reported for couplings involving the C^{13} and F^{19} nuclei and it is shown that the usually neglected coupling mechanisms can be significant in these cases.

Chapters II and III describe earlier approaches to the calculation of nuclear spin coupling constants. Chapter II reviews the non-SCF method based on the conventional or sum-over-states (SOS) perturbation theory of Rayleigh and Schroedinger(5). Chapter III discusses the more recent FPT method and Chapter IV presents the SCFPT theory developed in this study. Chapter V contains an account of the numerical calculations performed using the SCFPT method. These calculations were used to investigate the relative importance of the three coupling mechanisms in C^{13} and F^{19} couplings and to support a theory of bonding of acetylene in transition metal complexes.

The remainder of this introduction briefly reviews the principles of nuclear magnetic resonance (NMR) spectroscopy so as to introduce certain definitions and nomenclature which will be used in subsequent chapters. This is followed by descriptive and mathematical accounts of the mechanisms by which the electrons in a molecule couple together pairs of nuclear spins to give rise to the splittings observed in the high resolution NMR spectra of fluids. Finally, the principles underlying the use of perturbation theory to calculate coupling constants are discussed to show the common background shared by the three theories presented later in detail.

2. Principles of NMR Spectroscopy

All of the material presented in this section is available in standard texts(6,7,8) on NMR to which the reader is referred for more details and applications. However, this brief outline is included here in order to provide some continuity between the theory comprising the bulk of this study and the experimental aspect of NMR which the theory seeks to interpret and predict. This account also serves to introduce certain fundamental symbols and definitions which will be used frequently in the remainder of the text.

A nucleus, N, with odd mass number possesses both spin and charge and therefore has a nuclear spin magnetic moment, $\mathbb{\mu}_N$,[1] given by:

$$\mathbb{\mu}_N = \gamma_N \hbar \mathbb{I}_N = g_N \beta_N \mathbb{I}_N \qquad [I\text{-}1]$$

where:[2]

$\mathbb{I}_N$ is the spin angular momentum operator for nucleus N, in units of $\hbar$;

γ_N is its magnetogyric ratio, in units of radians $\sec^{-1}$ gauss^{-1};

g_N is the nuclear g factor, a dimensionless constant; and

β_N is the nuclear magneton, in erg gauss^{-1}, given by:

$$\beta_N = e \hbar / 2 M c \qquad [I\text{-}2]$$

where:

e is the charge on a proton, in esu;

M is the mass of a proton, in gm; and

c is the speed of light, in cm $\sec^{-1}$.

The nuclear spin is quantized and has allowed components along any particular direction of $m_I\hbar$, where m_I is the magnetic quantum number which can take the values:

$$m_I = +I,\ (I-1), \ldots,\ -I \qquad [I\text{-}3]$$

where I is the nuclear spin quantum number.

In general there are many magnetic interactions which may occur among the various magnetic moments of the nuclei and electrons in a molecule. However, it is found experimentally that the main features of the NMR spectrum of a fluid may be explained using the following Hamiltonian:

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[1] The double lines in symbols such as $\mathbb{\mu}$ and $\mathbb{I}$ will be used to denote vector quantities and, in later sections, matrices.

[2] The values for these and other constants used in numerical calculations are given in Chapter V.

$$H = -\sum_{N} (1 - \sigma_N)\, \gamma_N\, \hbar\, \mathbb{H} \cdot \mathbb{I}_N + \sum_{A\,B} J_{AB}\, \mathbb{I}_A \cdot \mathbb{I}_B \qquad [I-4]$$

The first term corresponds to the nuclear Zeeman interaction between the applied uniform magnetic field, represented by the vector $\mathbb{H}$, and the spin angular momenta, $\mathbb{I}_N$, of the nuclei in the sample. It is responsible for the first-order splitting of the nuclear energy levels. The second term represents the isotropic nuclear spin-spin interactions between pairs of nuclei A and B in the system.

The two constants σ_N and J_{AB} are known, respectively, as the screening constant and the nuclear spin-coupling constant. They are characteristic of the nuclei and their chemical environment and are the source of much of the usefulness of NMR in chemistry. The screening constant expresses the fact that in a molecule the electrons will interact with the applied magnetic field in such a way as to cause nucleus N to experience an effective field $(1-\sigma_N)\,\mathbb{H}$ which in general will differ from $\mathbb{H}$. The nuclear spin-coupling constant is a measure of the extent to which pairs of nuclear spins interact with each other. It will be shown later that in fluid samples the direct dipolar interaction between pairs of nuclear magnetic moments averages to zero due to the random tumbling of the molecules. The remaining interaction takes place via the electrons in the molecule; therefore both σ and J give information about the electronic structure of molecules and conversely, if a mathematical description of the electronic structure of the molecule is known, both σ and J can in principle be calculated.

The way in which these interactions affect the NMR spectrum may be illustrated by taking as an example nucleus A to be a proton, the spin of which is $I = \frac{1}{2}$. The possible components of $\mathbb{I}_A$, along the direction specified by the magnetic field $\mathbb{H}$, are therefore $m_I = +\frac{1}{2}$ and $m_I = -\frac{1}{2}$, corresponding to a low energy nuclear spin state $|\alpha>$ (spin parallel to $\mathbb{H}$) and a higher energy state $|\beta>$ (antiparallel to $\mathbb{H}$), respectively. The energy of each of these states is obtained, to first-order, by averaging the first term of the Hamiltonian in Equation 4 over the wavefunction describing the state. This procedure permits an energy difference between the two states to be calculated as:

$$\Delta E = (1 - \sigma_A) \gamma_A \hbar H \qquad [I-5]$$

where H is the magnitude of the vector $\mathbb{H}$. Given a suitable mechanism for maintaining the population of protons of α-spin slightly greater than those of β-spin, then application of a suitably polarized oscillating electromagnetic field with frequency satisfying:

$$h\nu = (1 - \sigma_A) \gamma_A \hbar H \qquad [I-6]$$

will cause a resonance condition with net absorption of energy.

NMR spectra are usually obtained by holding the frequency, ν, constant and measuring the energy absorbed as a function of applied magnetic field strength, H. For a field of H = 15,000 gauss, the energy difference ΔE between the two spin states of a proton is about 10^{-6} kcal/mole. This corresponds to a frequency, ν, of approximately 100 MHz, i.e., in the radio frequency part of the electromagnetic spectrum. However, nuclei in different parts of a molecule will in general experience different electronic environments and hence will have different values for the screening constant, σ. These values are of the order of $\sigma = 10^{-5}$ for protons but can be as large as 10^{-2} for heavy atoms. At 15 Kgauss then, proton resonances in molecules may be shifted from the isolated proton value by the order of 1000 Hz. It is clear from Equation [I-6] that the magnitude of these shifts will be proportional to the strength of the applied magnetic field.

In general, the effect of the second term in the Hamiltonian is to impart a fine structure to the spectrum by causing the resonance line of a given nucleus to split into multiplets. For example if a proton A interacts with another proton B, then the resonance line of A will be split into a doublet with separation J_{AB} Hz. Values of coupling constants vary from over 1000 Hz (e.g., J_{PF} = 1400 Hz in PF_3) to the lower limits of experimental detection (∿0.01 Hz). The splitting is found to be independent of the strength of the applied magnetic field.

The detailed analysis of NMR spectra can be quite complicated. This is especially true in cases where the chemical shifts and coupling constants are of the same order of magnitude. This aspect of NMR spectroscopy will not be discussed further. Instead we turn now to the theory of nuclear spin coupling.

3. The Origin of Nuclear Spin-Spin Coupling

(a) The Direct Dipolar Interaction

The field-independent splitting of nuclear resonance lines was first reported independently by Proctor and Yu(9), Hahn and Maxwell(10,11), and Gutowsky, McCall, Slichter and McNeil(12,13,14) in 1950. The latter two groups of workers pointed out that the splitting could be interpreted empirically in terms of an energy of interaction between the spins, $\mathbb{I}_A$ and $\mathbb{I}_B$, of pairs of nuclei A and B, by the expression:

$$E_{AB} = h\, J_{AB}\, \mathbb{I}_A \cdot \mathbb{I}_B \qquad [I\text{-}7]$$

Now if the two nuclei are considered as small magnetic dipoles with magnetic moments $\boldsymbol{\mu}_A$, and $\boldsymbol{\mu}_B$, the energy of interaction between them is:

$$E_{AB} = \frac{(\boldsymbol{\mu}_A \cdot \boldsymbol{\mu}_B)}{R^3} - \frac{3(\boldsymbol{\mu}_A \cdot \mathbf{R})(\boldsymbol{\mu}_B \cdot \mathbf{R})}{R^3} \qquad [I\text{-}8]$$

where $\mathbb{R}$ is the vector with magnitude R joining the two nuclei. This may be written in terms of nuclear spins by use of Equation [I-1]:

$$E_{AB} = \gamma_A \gamma_B \hbar^2 \left[\frac{(\mathbb{I}_A \cdot \mathbb{I}_B)}{R^3} - \frac{3(\mathbb{I}_A \cdot \mathbb{R})(\mathbb{I}_B \cdot \mathbb{R})}{R^3}\right] \qquad \text{[I-9]}$$

This energy may be put in a form analogous to the experimental expression [I-7] by writing:

$$E_{AB} = h\, \mathbb{I}_A \cdot \mathbb{d} \cdot \mathbb{I}_B$$

Here $\mathbb{d}$ is a tensor which has the following form when expanded in terms of the cartesian components, x, y and z, of the vector R:

$$\mathbb{d} = \frac{h\gamma_A\gamma_B}{4\pi^2} \begin{vmatrix} (R^2 - 3x^2) & -3xy & -3xz \\ -3xy & (R^2 - 3y^2) & -3yz \\ -3xz & -3yz & (R^2 - 3z^2) \end{vmatrix} R^{-5}$$

The direct dipolar interaction is responsible for the very large splittings (of the order of KHz) which are observed in the broad line NMR of solids$^{(6)}$ and partially oriented molecules$^{(15)}$. However, in liquid or gaseous samples the molecules are randomly tumbling so that only the average value of $\mathbb{d}$ is observed. The average value of a symmetric tensor such as $\mathbb{d}$ is given by one third of its trace:

$$(\mathbb{d})_{ave} = \frac{1}{3}\left[(R^2 - 3x^2) + (R^2 - 3y^2) + (R^2 - 3z^2)\right]$$

which in this case is zero. The splitting observed in the NMR of fluids therefore cannot be due to the nuclear spins interacting directly with each other as magnetic dipoles, but instead is considered to be due to their interaction via the electrons in the molecule.

Before going on to the detailed mathematical description of the electron-nucleus interactions we will consider them in a qualitative way.

Ramsey$^{(16)}$ proposed that both the spin and orbital motion of the electrons would be involved and both aspects of the interactions are discussed in the following section.

(b) A Qualitative Description of the Nucleus-Electron Interactions

(i) The Orbital Interaction

The electron possesses angular momentum by virtue of its orbital motion about the nuclei and, since the electron also carries charge, there will be a magnetic moment associated with this orbital motion. This electron orbital magnetic moment will interact with the magnetic moment which a nucleus has due to its charge and spin. Hence the orbital motion of an electron will be affected by the magnetic field of a given nucleus. This means that the electron's orbital magnetic field will be modified by the nucleus and this will affect the electron's magnetic interaction with other nuclei in the molecule. In this way information about the spin of one nucleus is transferred by the electron's orbital motion to the other nuclei.

The orbital interaction affects the kinetic energy of the electrons so it will appear as a correction to the electron kinetic energy term in the appropriate Hamiltonian operator which will be given later. It should also be noted that this same mechanism produces magnetic shielding of the nuclei from an external magnetic field. The same term therefore appears in the Hamiltonian used for calculating chemical shifts in NMR$^{(17)}$.

(ii) The Spin Interaction

The second kind of angular momentum which the electron has is that due to its spin. This spin angular momentum together with the electron's charge gives the electron a spin magnetic moment which can interact with nuclear magnetic moments in the molecule. An electron, k, in the vicinity of a nucleus, A, will tend to have its spin, $\mathbf{S}_k$, aligned so that its spin magnetic moment, $\boldsymbol{\mu}_k$, lies antiparallel to the magnetic moment, $\boldsymbol{\mu}_A$, of the nucleus. In order to discuss the relative senses of the vectors $\mathbf{S}_k$ and $\boldsymbol{\mu}_k$ we examine the electronic equivalent to the nuclear Equations [I-1] and [I-2]:

$$\boldsymbol{\mu}_k = g\ \beta\ \mathbf{S}_k \tag{I-10}$$

$$\beta = e\hbar\ /\ 2\ m\ c \tag{I-11}$$

where now g is the electronic g factor (≈ 2);

β is the Bohr magneton;

e is the charge on an electron; and

m is the mass of an electron.

Since e is negative for an electron, these equations show that $\boldsymbol{\mu}_k$ will be antiparallel to $\mathbf{S}_k$. On the other hand, e in Equation [I-2] is positive. The relative sign of $\boldsymbol{\mu}_N$ and $\mathbf{I}_N$ is determined by the sign of γ_N (which has the same sign as g_N). For a pair of nuclei, A and B, with positive magnetogytic ratios, bound together by an electron-pair bond consisting of electrons k and j, the relative senses of the magnetic moment and spin vectors may be summarized in the following way:

$$\begin{array}{cccc} \Uparrow & \downarrow & \uparrow & \Downarrow \\ \boldsymbol{\mu}_A & \boldsymbol{\mu}_k & \boldsymbol{\mu}_j & \boldsymbol{\mu}_B \end{array} \qquad \begin{array}{cccc} \Uparrow & \uparrow & \downarrow & \Downarrow \\ \mathbf{I}_A & \mathbf{S}_k & \mathbf{S}_j & \mathbf{I}_B \end{array}$$

This explanation therefore predicts that the electron spin-nuclear spin interaction would tend to cause directly bonded nuclei to have their magnetic moments aligned antiparallel. If both nuclei have magnetogytic ratios of the same sign then their spin angular momentum vectors will also be antiparallel, a situation corresponding to a positive coupling constant. However, negative coupling constants have been observed between directly bonded nuclei which have magnetogyric ratios of the same sign$^{(18)}$. If such couplings are to be explained by the spin-spin interaction, the bonding scheme must be modified to include the possibility that the electron spins may be parallel.

A slightly different way of visualizing this same nuclear spin coupling mechanism is in terms of electron spin polarization. As indicated above, an electron in the vicinity of a nucleus will tend to have its spin aligned parallel to the magnetic moment of the nucleus. Since there is correlation between electron spins, the alignment of electron spin in a particular direction in the vicinity of a given nucleus will affect the distribution of electron spin in the rest of the molecule, i.e., there will be some polarization of electron spin. The other nuclei in the molecule will therefore experience an excess of positive or negative electron spin in their vicinity and will tend to have their spins aligned accordingly. Both positive and negative coupling constants can therefore be rationalized in this way.

(c) The Nuclear Spin Coupling Hamiltonians

In this study we wish to develop quantitative expressions from which nuclear spin coupling constants may be calculated. It was shown in Section 3 (a) of this chapter that the nuclear spin coupling observed in fluids can not be explained simply by the direct interaction between nuclear spins. Instead the problem must be approached in terms of indirect interaction via the electrons in the molecule, as described in Section 3 (b). The desired coupling constant expressions are therefore obtained by deriving equations for the electronic energy of the molecule taking into account magnetic interactions between the nuclei and the electrons. From these electronic energy expressions terms which are second order in the nuclear spins may be extracted and compared with Equation [I-7] defining E_{AB}, the nuclear spin interaction energy, to obtain expressions for the coupling constant, J_{AB}. In order to obtain the required electronic energy expressions, we need the Hamiltonian operators which quantitatively specify the nuclear-electronic interactions described in the previous section.

First consider the orbital interaction, that is the interaction between the magnetic moments of the nuclei and the magnetic moment which the electrons possess due to their orbital motion about the nuclei. The classical Hamiltonian for a particle with charge e and mass m moving with momentum $\mathbb{p}$ in an electromagnetic field specified by a vector potential $\mathbb{A}$ and a scalar potential ϕ may be written$^{(19)}$

$$\mathcal{H} = \frac{1}{2m} (\mathbb{p} - \frac{e}{c} \mathbb{A})^2 + e\phi \qquad [I\text{-}12]$$

where c is the speed of light.

In the particular case of the orbital motion of electrons in a molecule, this Hamiltonian takes the form:

$$\mathcal{H} = \frac{1}{2m} \sum_k (\mathbb{p}_k + \frac{e}{c} \mathbb{A}_k)^2 + V \qquad [I\text{-}13]$$

where:

$\mathbb{p}_k$ is the momentum of electron k;

e is the magnitude of the charge on an electron (i.e., a positive number);

$\mathbb{A}_k$ is the vector potential of the magnetic field created by the magnetic moments of all the nuclei in the molecule and evaluated in the region of electron k;

V (= $e\phi$) is the electrostatic potential energy of the electrons in the electrostatic field of the nuclei; and

the summation extends over all of the electrons in the molecule.

The vector potential due to the magnetic moments of the nuclei is given by:

$$\mathbb{A}_k = \sum_N \frac{\boldsymbol{\mu}_N \times \mathbb{r}_{kN}}{r_{kN}^3} \qquad [I\text{-}14]$$

where:

$\boldsymbol{\mu}_N$ is the magnetic moment vector of nucleus N;

$\mathbb{r}_{kN}$ is the vector from nucleus N to electron k, with magnitude r_{kN};

and the summation extends over all the nuclei in the molecule.

We now have to convert this classical Hamiltonian into the corresponding quantum mechanical operator. We then select those parts of the operator which will give terms of the appropriate form (i.e., second order in the nuclear spins) when averaged over suitable electronic wavefunctions.

In order to convert the classical Hamiltonian, $\mathcal{H}$, into the quantum mechanical Hamiltonian operator, H, we make the following substitutions:

$$\mathbb{p}_k \rightarrow \frac{\hbar}{i} \nabla_k \qquad [I\text{-}15]$$

$$\boldsymbol{\mu}_N \rightarrow \hbar\, \gamma_N\, \mathbb{I}_N \qquad [I\text{-}16]$$

where:

∇_k is the operator $\mathbb{i}(\partial/\partial x) + \mathbb{j}(\partial/\partial y) + \mathbb{k}(\partial/\partial z)$ for electron k;

$\mathbb{I}_N$ is the nuclear spin operator for nucleus N;

γ_N is the magnetogyric ratio for nucleus N;

x, y and z refer to the coordinates of electron k; and

$\mathbb{i}$, $\mathbb{j}$ and $\mathbb{k}$ are unit vectors in the x, y and z directions, respectively.

If we substitute Equations [I-14], [I-15] and [I-16] into the expression for the classical Hamiltonian [I-13], and retain only those terms containing the nuclear spin operator, we obtain the Hamiltonian operator:

$$H = \frac{1}{2m} \sum_k \left(\frac{\hbar}{i} \nabla_k + \frac{e}{c} \sum_N \frac{\hbar\gamma_N}{r_{kN}^3} \mathbb{I}_N \times \mathbb{r}_{kN}\right)^2 \qquad [I\text{-}17]$$

The summation $\sum_k$ extends over all the electrons of the molecule, and $\sum_N$ extends over all the nuclei of the molecule. The purely electrostatic term V has been omitted since it does not depend on the nuclear spin operator. When the square is expanded there are two terms which depend on the nuclear spins:

$$H_1^{(a)} = \frac{e^2\hbar^2}{2mc^2} \sum_{k,N,N'} \frac{\gamma_N\gamma_{N'}}{r_{kN}^3 r_{kN'}^3} (\mathbb{I}_N \times \mathbb{r}_{kN}) \cdot (\mathbb{I}_{N'} \times \mathbb{r}_{kN'}) \qquad [I\text{-}18]$$

$$= \frac{e^2\hbar^2}{2mc^2} \sum_{k,N,N'} \frac{\gamma_N\gamma_{N'}}{r_{kN}^3 r_{kN'}^3} [(\mathbb{I}_N \cdot \mathbb{I}_{N'})(\mathbb{r}_{kN} \cdot \mathbb{r}_{kN'}) - (\mathbb{I}_N \cdot \mathbb{r}_{kN'})(\mathbb{I}_{N'} \cdot \mathbb{r}_{kN})] \qquad [I\text{-}19]$$

where the triple summation runs over all the electrons, k, of the molecule, and all pairs of nuclei, N and N', in the molecule, and

$$H_1^{(b)} = \frac{e\hbar^2}{mci} \sum_{k,N} \frac{\gamma_N}{r_{kN}^3} (\mathbb{I}_N \times \mathbb{r}_{kN}) \cdot \nabla_k \qquad [I\text{-}20]$$

$$= \frac{e\hbar^2}{mci} \sum_{k,N} \frac{\gamma_N}{r_{kN}^3} \mathbb{I}_N \cdot (\mathbb{r}_{kN} \times \nabla_k) \qquad [I\text{-}21]$$

This term involves just a double summation over the electrons and nuclei of the molecule.

The quantum mechanical operator for the orbital angular momentum of electron k about nucleus N is given by the vector:

$$\mathbb{L}_{kN} = \frac{\hbar}{i} (\mathbb{r}_{kN} \times \nabla_k) \qquad [I\text{-}22]$$

so that $H_1^{(b)}$ may be written:

$$H_1^{(b)} = \frac{e\hbar^2}{mc} \sum_{k,N} \frac{\gamma_N}{r_{kN}^3} (\mathbb{I}_N \cdot \mathbb{L}_{kN}) \qquad [I-23]$$

$$= 2\beta\hbar \sum_{k,N} \frac{\gamma_N}{r_{kN}^3} (\mathbb{I}_N \cdot \mathbb{L}_{kN}) \qquad [I-24]$$

where β is the Bohr magneton,

$$\beta = \frac{eh}{4\pi mc} = \frac{e\hbar}{2mc} \qquad [I-25]$$

where e and m are the charge and mass of the electron, respectively. The operators $H_1^{(a)}$ and $H_1^{(b)}$ specify that part of the nuclear interaction which occurs via the orbital motion of the electrons. We now turn to the interaction via the electron spins.

The energy of interaction between two magnetic dipoles, μ_1 and μ_2, is given by:

$$E_{12} = \frac{3(\mu_1 \cdot \mathbb{r})(\mu_2 \cdot \mathbb{r})}{r^5} - \frac{(\mu_1 \cdot \mu_2)}{r^3} \qquad [I-26]$$

where $\mathbb{r}$ is the vector of length r, joining the two dipoles. In the present case the two magnetic dipoles are those which are associated with a nucleus, N, and an electron, k, by virtue of their charge and spin angular momentum. The energy of the dipolar interaction between the nuclear spin magnetic moment, μ_N, and the electron spin magnetic moment, μ_k, is therefore given by:

$$E_{kN} = \frac{3(\mu_N \cdot \mathbb{r}_{kN})(\mu_k \cdot \mathbb{r}_{kN})}{r_{kN}^5} - \frac{\mu_N \cdot \mu_k}{r_{kN}^3} \qquad [I-27]$$

where $\mathbb{r}_{kN}$ is the vector of length r_{kN} joining nucleus N and electron k. This may be written in terms of the nuclear and electron spin angular momentum operators, $\mathbb{I}_N$ and $\mathbb{S}_k$ respectively, by using the expressions:

$$\mu_N = \gamma\hbar\, \mathbb{I}_N \qquad [I-28]$$

and $$\boldsymbol{\mu}_k = 2\beta\hbar\mathbf{S}_k \qquad [I\text{-}29]$$

to give the Hamiltonian operator:

$$H_2 = 2\beta\hbar \sum_{k,N} \gamma_N \left[\frac{3(\mathbf{S}_k\cdot\mathbf{r}_{kN})(\mathbf{I}_N\cdot\mathbf{r}_{kN})}{r_{kN}^5} - \frac{\mathbf{S}_k\cdot\mathbf{I}_N}{r_{kN}^3}\right] \qquad [I\text{-}30]$$

We shall refer to this as the dipolar coupling Hamiltonian.

Some texts(20) state that relativistic arguments show that an additional operator, H_3, should be introduced here. However, we shall follow Abragam's treatment(21) in which H_3 is introduced as a consequence of certain complications arising from the use of H_2. The complications arise because the expression for H_2 given in equation [I-30] has a singularity at the point $r_{kN} = 0$. This point corresponds to electrons being at the position of the nucleus. This causes no problem for electrons in p-orbitals(21) since the probability of finding them at $r_{kN} = 0$ is zero. However, in s orbitals electrons have a finite density at the nucleus. In fact the part of the electron spin mechanism due to electron density at the nucleus produces the largest contribution to many nuclear spin coupling constants(22). In Abragam's treatment, the problem is resolved by dividing the atom into two regions and calculating the interaction energy separately in each. In the region relatively far from the nucleus, H_2 is used. For the region in the immediate vicinity of the nucleus, the new term, H_3, derived below is used. In the relativistic theory in which H_3 is introduced for other reasons, one is forced to say that the matrix elements of H_2 which are indeterminate must be set equal to zero.

This simplified derivation of the expression for H_3 is quoted in reference 7. Consider the nucleus enclosed by a sphere of radius R, where R is large compared with the size of the nucleus but small compared with the atomic radius. For the region $r_{kN} > R$ the electron spin-nuclear spin interaction is adequately described by H_2. The value of R is small enough that within the sphere the wave function for the electron may be considered to have a constant value, ψ_o. The electron density due to electron k within the sphere will then have the uniform value

$$\rho(o) = \langle\psi_o|\delta(r_{kN})|\psi_o\rangle \qquad [I-31]$$

Here the delta function $\delta(r_{kN})$ ensures that only the density at $r_{kN} = 0$ is included in the integral. The magnetisation due to electron k within the sphere is:

$$\mathbb{m}(o) = -\rho(o) \cdot 2\beta \mathbb{S}_k \qquad [I-32]$$

and the induced magnetic field at the nucleus is:

$$\mathbb{H}(o) = \frac{8\pi}{3}\mathbb{m}(o) = -\frac{16\pi}{3}\rho(o)\beta\mathbb{S}_k \qquad [I-33]$$

The interaction energy between this field and the nuclear magnetic moment, $\gamma\hbar\,\mathbb{I}_N$, is given by:

$$E_{kN}^{(o)} = \frac{16\pi\beta}{3}\rho(o)\gamma_N h \mathbb{S}_k \cdot \mathbb{I}_N \,. \qquad [I-34]$$

The Hamiltonian which corresponds to this interaction for all the electrons and nuclei in the system is:

$$H_3 = \frac{16\pi\beta\hbar}{3}\sum_{k,N}\gamma_N\,\delta(r_{kN})\,\mathbb{S}_k \cdot \mathbb{I}_N \qquad [I-35]$$

This type of treatment was first used by Fermi(23) to explain the hyperfine structure observed in the atomic spectra of atoms in s-states. Since the delta function picks out the value at $r_{kN} = 0$ in any integration over the coordinates of electron k, i.e., it depends on the properties of electrons at the nucleus, the interaction represented by H_3 is referred to as the "Fermi contact" interaction.

In more rigorous derivations of the contact Hamiltonian such as given by Abragam and Pryce(21) or Blinder(24) it is made clear that the contact interaction only refers to wave functions which are spherically symmetrical about the nucleus in question. Thus the contact Hamiltonian has non-zero matrix elements only between functions which are (a) non-zero at the nucleus and (b) have spherical symmetry about that nucleus. This point will be referred to later in discussing approximations which involve the neglect of certain integrals which occur in the theoretical expressions for J.

Coupling between the electrons and the nuclear spins is therefore described by the three Hamiltonian operators, H_1, H_2 and H_3. In the interest of brevity we shall refer to these as the "orbital", "dipolar" and "contact" Hamiltonians, respectively.

Ramsey showed(16) that there are no non-zero cross terms between the different nuclear spin coupling Hamiltonians providing that:

(a) there is rapid molecular tumbling;

(b) there is no significant coupling between the electron spin angular momentum and the orientation of the molecule; and

(c) there is no significant electron spin-orbit coupling.

Under these conditions, the total electron-nucleus interaction Hamiltonian may be treated as a sum of independent Hamiltonians each corresponding to one of the mechanisms described above, i.e.:

$$H = H_1^{(a)} + H_1^{(b)} + H_2 + H_3.$$

This will result in independent expressions for the contribution which each mechanism makes to the total coupling constant. A coupling constant between two nuclei A and B will then be obtained as a sum of independent terms, one from each coupling mechanism, i.e.:

$$J_{AB} = J_{AB}^{(1a)} + J_{AB}^{(1b)} + J_{AB}^{(2)} + J_{AB}^{(3)} .$$

4. The Perturbation Theory Approach to Nuclear Spin Coupling

In subsequent chapters we describe a number of perturbation theory methods which permit the electron-nucleus Hamiltonians just described to operate on electronic wavefunctions for a molecule so as to produce expressions which permit the calculation of numerical values for coupling constants. In this section we discuss some matters which are generally applicable to all of these different perturbation methods.

The general problem of going from Hamiltonian operators which describe electron-nucleus interactions to expressions for nucleus-nucleus interactions is handled as follows. First it is assumed that the Born-Oppenheimer approximation applies, so that the nuclei may be considered to remain fixed with respect to the instantaneous motion of the electrons. We may therefore consider the wavefunction for a molecule to be separable into a nuclear part and an electronic part. If, in evaluating matrix elements of the electron-nucleus Hamiltonians, we consider only operations which affect the electronic part of the wavefunction for the molecule, the nuclear spin operators, $\mathbb{I}_A$ and $\mathbb{I}_B$, may be carried as constant factors. The energy corresponding to a given Hamiltonian may then be obtained as a function of $\mathbb{I}_A$ and $\mathbb{I}_B$ by calculating the average value of the Hamiltonian over the electronic wavefunction for the system. It is then possible to select from the resulting energy expression terms which are proportional to the product $\mathbb{I}_A \cdot \mathbb{I}_B$. Comparison of such terms with Equation [I-7] yields expressions for J_{AB}.

In the following chapters we will consider in some detail two approaches which bear a fundamental relationship to the self-consistent perturbation method used for the numerical calculations in this study. These are the sum-over-states (SOS) perturbation theory due to Rayleigh and Schroedinger (see for example reference 19, Chapter VII) and the finite perturbation theory (FPT) of Pople, McIver and Ostlund(2). However we first describe in somewhat more detail the general approach outlined above in a way which shows the common basis shared by the three types of perturbation theory. The development is given in terms of nuclear magnetic moments, $\boldsymbol{\mu}$, rather than nuclear spins, $\mathbb{I}$, in order to make the notation more easily comparable with related derivations given by Pople et al(2).

In the perturbation method, the solution to the particular eigenvalue problem of interest:

$$H(\boldsymbol{\mu})\Psi(\boldsymbol{\mu}) = E(\boldsymbol{\mu})\Psi(\boldsymbol{\mu}) \qquad [I\text{-}36]$$

is sought in terms of the solutions to another, similar problem

$$H_o\Psi^{(o)} = E^{(o)}\Psi^{(o)} \qquad [I\text{-}37]$$

which it is assumed has already been solved. Here $\Psi^{(o)}$ represents the complete set of eigenfunctions and $E^{(o)}$ the complete set of eigenvalues of the unperturbed Hamiltonian operator, H_o. In the present problem, $\boldsymbol{\mu}$ represents the set of nuclear magnetic moments which are the source of the perturbation in the molecule of interest. Their effect is to slightly modify the unperturbed wavefunction, $\Psi^{(o)}$, and energy, $E^{(o)}$, for the molecule so that they become functions, $\Psi(\boldsymbol{\mu})$ and $E(\boldsymbol{\mu})$, of the nuclear magnetic moments.

We assume that the solutions to the perturbed and unperturbed problems are sufficiently close to each other that the perturbed quantities may be expanded as power series in the perturbation parameters μ_r, $r = 1,2,\ldots$, comprising the set $\boldsymbol{\mu}$:

$$E(\mu) = E^{(o)} + \sum_r \mu_r E_r^{(1)} + \frac{1}{2} \sum_r \sum_s \mu_r \mu_s E_{rs}^{(2)} + \ldots\ldots \qquad [I-38]$$

$$\Psi(\mu) = \Psi^{(o)} + \sum_r \mu_r \Psi_r^{(1)} + \frac{1}{2} \sum_r \sum_s \mu_r \mu_s \Psi_{rs}^{(2)} + \ldots\ldots \qquad [I-39]$$

where r and s refer to particular nuclei in the molecule, and where

$$E_r^{(1)} \equiv [\partial E(\mu)/\partial \mu_r]_o \qquad [I-40]$$

$$E_{rs}^{(2)} \equiv [\partial^2 E(\mu)/\partial \mu_r \partial \mu_s]_o \qquad [I-41]$$

$$\Psi_r^{(1)} \equiv [\partial \Psi(\mu)/\partial \mu_r]_o \qquad \text{etc.} \qquad [I-42]$$

These are the first-order, second-order, etc., corrections to the unperturbed energy, $E^{(o)}$, and wavefunction, $\Psi^{(o)}$. The subscripts o indicate that the partial derivatives are to be evaluated at $\mu = 0$.

We now seek expressions by which the effects of the perturbations may be calculated from a knowledge of the unperturbed problem and the nature of the perturbation Hamiltonian. Recall that the operator for the $H_1^{(a)}$ part of the orbital coupling mechanism is second-order in the nuclear spins (Equation [I-19]) while the operators for the other electron-nucleus coupling mechanisms are first-order in the nuclear spins. We therefore write the total Hamiltonian for the perturbed molecule in the general form:

$$H(\mu) = H_o + \sum_r \mu_r H_r + \sum_r \sum_s \mu_r \mu_s H_{rs} \qquad [I-43]$$

where H_{rs} represents the second-order part of the orbital mechanism and H_r represents the sum of the first-order nuclear spin perturbation operators. The summations run over all the nuclei r and s in the molecule and H_o is the Hamiltonian operator for the molecule in the absence of nuclear spin coupling. If this form for $H(\mu)$ together with the expansions [I-38] for $E(\mu)$ and [I-39] for $\Psi(\mu)$ are substituted into the perturbed eigenvalue Equation [I-36], an expression for $E_{rs}^{(2)}$ may be obtained. If we assume that both the perturbed and unperturbed wavefunctions are normalized:

$$<\Psi^{(o)}|\Psi^{(o)}> = 1 \qquad [I-44]$$

and $$<\Psi(\mu)|\Psi(\mu)> = 1 \qquad [I-45]$$

then the expression for $E_{rs}^{(2)}$ may be simplified to:

$$\frac{1}{2} E_{rs}^{(2)} = \frac{1}{2} <\Psi^{(o)}|H_{rs}|\Psi^{(o)}> + <\Psi^{(o)}|H_r|\Psi_s^{(1)}> \qquad [I-46]$$

The first term in this expression has a form analogous to a first-order perturbation energy in that the energy may be calculated simply from a knowledge of the perturbation operator and the unperturbed wavefunction. Since the $H_1^{(a)}$ orbital perturbation operator is second-order in the nuclear spins, this first term will be used to obtain the energy expression required for calculating that part of the orbital coupling constant, $J_{AB}^{1(a)}$. The remaining orbital $(H_1^{(b)})$, dipolar (H_2), and contact (H_3) coupling operators, given in Equations [I-24], [I-30], and [I-35] are only first-order in the nuclear spins. Expressions based on the second term in Equation [I-46] are therefore required in order to obtain the desired second-order energy equations. For these latter coupling mechanisms we may therefore write the perturbation energy due to the interaction between two nuclei r and s as:

$$\frac{1}{2} E_{rs}^{(2)} = <\Psi^{(o)}|H_r|\Psi_s^{(1)}> \qquad [I-47]$$

Recall that H_r is the operator expressing the perturbing effect of the magnetic moment, μ_r, of nucleus r and $\Psi_s^{(1)}$ is the first-order perturbation to $\Psi^{(o)}$ resulting from the magnetic moment, μ_s, of nucleus s. From the definition of $\Psi_s^{(1)}$ in Equation [I-42] we may write:

$$\frac{1}{2} E_{rs}^{(2)} = <\Psi^{(o)}|H_r|[\partial\Psi(\mu)/\partial\mu_s]_o> \qquad [I-48]$$

This equation and the first term in Equation [I-46] are the basis for the various perturbation theories of nuclear spin coupling constants to be discussed in the following chapters. It will be shown that the essential difference between the methods lies in their approach to evaluating the derivative in Equation [I-48].

In this study we perform the calculations outlined above by applying perturbation theory to molecular orbital wavefunctions and the following chapters give in some detail the theoretical background to such an approach. However, it should be mentioned that other fundamental approximation methods have been applied to the calculation of coupling constants, namely variational methods(25,26,27) rather than perturbation theory and valence-bond wavefunctions(28,29) rather than molecular orbital ones. However the perturbation theory-MO combination seems to predominate recent calculations, probably because of the ease with which such a method may be programmed for automatic solution by digital computer, and so only this type of approach will be described in detail.

CHAPTER II. THE SUM-OVER-STATES PERTURBATION METHOD

In this chapter we discuss the most widely used method for approximating the derivative in the second-order perturbation energy expression [I-48] derived in the preceding chapter. We then show how this method may be used to obtain tractable MO formulae for calculating nuclear spin coupling constants.

1. General Theory

The method is known as the Rayleigh-Schroedinger(5) or sum-over-states (SOS) method. It approximates the derivative, $\Psi_s^{(1)}$, in Equation [I-47] by expanding this perturbation in terms of wavefunctions which are solutions to the unperturbed problem. This is possible because of the general property that any arbitrary function can be expanded in a series of orthonormal functions which form a complete set and which satisfy the same boundary conditions as the original function(30). Accordingly we write:

$$\Psi_s^{(1)} = \sum_n A_{sn} \Psi_n^{(o)} \qquad [II\text{-}1]$$

In cases such as the present one in which the wavefunctions are those describing the electronic structure of molecules, we are usually interested in perturbations to the ground electronic state, i.e., $\Psi_s^{(1)}$ is a change in the ground state function. The subscript s refers to the nucleus which is the source of the perturbation. On the right hand side of Equation [II-1], the subscript n runs over the complete set of excited states of the unperturbed molecule taking values from 1 to ∞. In this notation, the unperturbed ground state wavefunction would be written $\Psi_o^{(o)}$ rather than $\Psi^{(o)}$ used in the previous chapter for simplicity. It is important to note that the selection of the $\Psi_n^{(o)}$

to be the excited states of the molecule is an arbitrary choice since any other complete, orthonormal set of functions satisfying the required boundary conditions could have been used. The excited states are the logical choice because in principle the unperturbed problem can be solved for the complete set of eigenfunctions of H_o. However, as will be shown later, this is virtually never the case for molecular systems and only poor approximations to the excited states are available.

An expression for the expansion coefficients A_{sn} in Equation [II-1] may be found by solving the first-order perturbation equation:

$$H_o\Psi_s^{(1)} + H_s\Psi_o^{(o)} = E_o^{(o)}\Psi_s^{(1)} + E_s^{(1)}\Psi_o^{(o)} \qquad [II\text{-}2]$$

This equation is obtained by substituting expansions in μ_s of the form [I-38] for $E(\mu)$ and [I-39] for $\Psi(\mu)$ into the perturbed eigenvalue Equation [I-36] and equating coefficients of the first power of μ_s. The expansion used for $H(\mu)$ in the derivation of [II-2] is that corresponding to just the first two terms in Equation [I-43]. The third term involving H_{rs} gives rise to that part of the second-order perturbation energy which may be calculated from a knowledge of just the ground state wavefunction (see Equation [I-46]). In Equation [II-2] subscript zeros have been added to distinguish the unperturbed ground state energy and wavefunction from the corresponding unperturbed excited state quantities.

With the expansion [II-1] for $\Psi_s^{(1)}$, Equation [II-2] may be solved for A_{sn} to give:

$$A_{sn} = \langle\Psi_n^{(o)}|H_s|\Psi_o^{(o)}\rangle/(E_o^{(o)} - E_n^{(o)}) \qquad n \neq 0 \qquad [II\text{-}3]$$

and so the first-order correction to the wavefunction due to the perturbing nuclear magnetic moment μ_s is:

$$\Psi_s^{(1)} = \sum_{n\neq 0}^{\infty} \frac{<\Psi_n^{(o)}|H_s|\Psi_o^{(o)}>}{(E_o^{(o)} - E_n^{(o)})} \Psi_n^{(o)} \qquad [II-4]$$

With this expression for the derivative in Equation [I-47] we obtain the familiar second-order perturbation energy expression:

$$\frac{1}{2} E_{rs}^{(2)} = \sum_{n\neq 0}^{\infty} \frac{<\Psi_o^{(o)}|H_r|\Psi_n^{(o)}><\Psi_n^{(o)}|H_s|\Psi_o^{(o)}>}{(E_o^{(o)} - E_n^{(o)})} \qquad [II-5]$$

2. Application to Nuclear Spin Coupling

In the present problem of calculating nuclear spin coupling constants, the unperturbed Hamiltonian, H_o, is taken to be the operator containing terms for the kinetic energy of the electrons and the coulomb interactions among the electrons and between the electrons and the nuclei. The unperturbed wavefunctions $\Psi_n^{(o)}$ are therefore the ground and excited electronic states of the molecule of interest. We are concerned with perturbations to the ground state due to the interactions between the nuclear spins and the electrons, so the perturbing operator is taken to be one of the electron-nucleus interaction Hamiltonians specified in the previous chapter. We will consider the application of SOS perturbation theory to each coupling mechanism in turn and derive expressions for the contribution each mechanism makes to the coupling constant J_{AB}.

(i) Electron Orbital Terms

It was shown earlier that the $H_1^{(a)}$ part of the orbital Hamiltonian is already second-order in the nuclear spins so that a nucleus-nucleus interaction energy of the desired form, i.e., second-order in the nuclear spins (Equation [I-7]), may be obtained by analogy with first-order perturbation theory. Accordingly we see from the first term in Equation [I-46] that the contribution to this part of the orbital interaction energy due to a pair of nuclei r and s is:

$$E^{1(a)}_{rs} = \langle\Psi^{(o)}|H^{1(a)}_{rs}|\Psi^{(o)}\rangle \qquad [II\text{-}6]$$

If we use the Hamiltonian expression [I-19]:

$$H^{(a)}_{1} = \frac{e^2\hbar^2}{2mc^2}\sum_{kNN'}\frac{\gamma_N\gamma_{N'}}{r_{kN}^{3}r_{kN'}^{3}}\left[(\mathbb{I}_N\cdot\mathbb{I}_{N'})(\mathbb{r}_{kN}\cdot\mathbb{r}_{kN'}) - (\mathbb{I}_N\cdot\mathbb{r}_{kN'})(\mathbb{I}_{N'}\cdot\mathbb{r}_{kN})\right] \qquad [II\text{-}7]$$

in place of $H^{1(a)}_{rs}$ in Equation [II-6], we obtain the sum of these energies for all pairs of nuclei in the molecule:

$$\sum_{N<N'} E^{1(a)}_{NN'} = \frac{e^2\hbar^2}{2mc^2}\sum_{k,N,N'}\gamma_N\gamma_{N'}\langle\Psi^{(o)}_{o}\left|\frac{(\mathbb{I}_N\cdot\mathbb{I}_{N'})(\mathbb{r}_{kN}\cdot\mathbb{r}_{kN'}) - (\mathbb{I}_N\cdot\mathbb{r}_{kN'})(\mathbb{I}_{N'}\cdot\mathbb{r}_{kN})}{r_{kN}^{3}r_{kN'}^{3}}\right|\Psi^{(o)}_{o}\rangle \qquad [II\text{-}8]$$

If we pick out the interaction for a particular pair of nuclei, A and B, then we obtain:

$$E^{1(a)}_{AB} = \frac{e^2\hbar^2}{mc^2}\gamma_A\gamma_B\sum_{k}\langle\Psi^{(o)}_{o}\left|\frac{(\mathbb{I}_A\cdot\mathbb{I}_B)(\mathbb{r}_{kA}\cdot\mathbb{r}_{kB}) - (\mathbb{I}_A\cdot\mathbb{r}_{kB})(\mathbb{I}_B\cdot\mathbb{r}_{kA})}{r_{kA}^{3}r_{kB}^{3}}\right|\Psi^{(o)}_{o}\rangle \qquad [II\text{-}9]$$

Note that a factor of 2 has appeared since the right hand side of Equation [II-8] contains terms in A and B twice. If Equation [II-9] is now averaged over all orientations of the molecule, the average interaction energy of nuclei A and B becomes[(31)]:

$$(E^{1(a)}_{AB})_{av} = \frac{2e^2\hbar^2}{3mc^2}\gamma_A\gamma_B\sum_{k}\langle\Psi^{(o)}_{o}\left|\frac{(\mathbb{I}_A\cdot\mathbb{I}_B)(\mathbb{r}_{kA}\cdot\mathbb{r}_{kB})}{r_{kA}^{3}r_{kB}^{3}}\right|\Psi^{(o)}_{o}\rangle \qquad [II\text{-}10]$$

Since $\Psi^{(o)}_{o}$ is a function of the coordinates of the electrons only, the factor $\mathbb{I}_A\cdot\mathbb{I}_B$ can be taken outside of the integral in [II-10]. Comparison with

Equation [I-7] then gives the following expression for the coupling constants between nuclei A and B due to the $H_1^{(a)}$ part of the orbital coupling mechanism:

$$J_{AB}^{1(a)} = \frac{1}{h} \quad \frac{2e^2\hbar^2}{3mc^2} \gamma_A\gamma_B \sum_k <\psi_o^{(o)} \left| \frac{\mathbf{r}_{kA}\cdot\mathbf{r}_{kB}}{r_{kA}^3 r_{kB}^3} \right| \psi_o^{(o)}> \qquad [II-11]$$

The $H_1^{(b)}$ part of the orbital interaction is only first order in the nuclear spins; therefore to obtain terms which are bilinear in the nuclear spins we use the second order perturbation energy Expression [II-5]. With the form of $H_1^{(b)}$ given in Equation [I-24], this yields:

$$\sum_{N\leq N'} E_{NN'}^{1(b)} = -4\beta^2\hbar^2 \sum_{\substack{k,N,N'\\ n\neq 0}} \gamma_N\gamma_{N'} \frac{<\psi_o^{(o)} \left| \frac{\mathbf{I}_N\cdot\mathbf{L}_{kN}}{r_{kN}^3} \right| \psi_n^{(o)}><\psi_n^{(o)} \left| \frac{\mathbf{I}_{N'}\cdot\mathbf{L}_{kN'}}{r_{kN'}^3} \right| \psi_o^{(o)}>}{(E_n - E_o)} \qquad [II-12]$$

If we now pick out the interaction for the pair of nuclei A and B, we obtain:

$$E_{AB}^{1(b)} = -8\beta^2\hbar^2 \gamma_A\gamma_B \sum_{k,n\neq 0} \frac{<\psi_o^{(o)} | (\mathbf{I}_A\cdot\mathbf{L}_{kA}) r_{kA}^{-3} | \psi_n^{(o)}><\psi_n^{(o)} | (\mathbf{I}_B\cdot\mathbf{L}_{kB}) r_{kB}^{-3} | \psi_o^{(o)}>}{(E_n - E_o)} \qquad [II-13]$$

where as before we pick up a factor of 2 because the sums over N and N' in Equation [II-12] both include A and B. Taking the average over all molecular orientations and making use of the assumption that the nuclear spin operators do not operate on the electronic wavefunctions, we obtain:

$$(E_{AB}^{1(b)})_{av} = \frac{-8}{3} \beta^2\hbar^2 \gamma_A\gamma_B \mathbf{I}_A\cdot\mathbf{I}_B \sum_{k,n\neq 0} \frac{<\psi_o^{(o)} | \mathbf{L}_{kA} r_{kA}^{-3} | \psi_n^{(o)}><\psi_n^{(o)} | \mathbf{L}_{kB} r_{kB}^{-3} | \psi_o^{(o)}>}{(E_n - E_o)} \qquad [II-14]$$

so that the expression for this contribution to the coupling constant is:

$$J_{AB}^{1(b)} = \frac{-8}{3} \frac{\beta^2}{h} \hbar^2 \gamma_A\gamma_B \sum_{k,n\neq 0} \frac{<\psi_o^{(o)} | \mathbf{L}_{kA} r_{kA}^{-3} | \psi_n^{(o)}><\psi_n^{(o)} | \mathbf{L}_{kB} r_{kB}^{-3} | \psi_o^{(o)}>}{[E_n - E_o)} \qquad [II-15]$$

The Electron Spin Dipolar Term

Since the Hamiltonian for the dipolar interaction between the nuclear spins and the electron spins is linear in $\mathbf{I}_N$, we again use second order perturbation theory with the operator H_2 specified in Equation [I-30] and obtain:

$$\sum_{N\leq N'} E^{(2)}_{NN'} = -4\beta^2\hbar^2 \sum_{k,N,N',n\neq 0} \frac{\gamma_N\gamma_{N'}}{(E_n-E_o)} \langle\Psi_o^{(o)}\left|\frac{3(\mathbf{S}_k\cdot\mathbf{r}_{kN})(\mathbf{I}_N\cdot\mathbf{r}_{kN})}{r_{kN}^5} - \frac{\mathbf{S}_k\cdot\mathbf{I}_N}{r_{kN}^3}\right|\Psi_n^{(o)}\rangle$$

$$\times \langle\Psi_n^{(o)}\left|\frac{3(\mathbf{S}_k\cdot\mathbf{r}_{kN'})(\mathbf{I}_{N'}\cdot\mathbf{r}_{kN'})}{r_{kN'}^5} - \frac{\mathbf{S}_k\cdot\mathbf{I}_{N'}}{r_{kN'}^3}\right|\Psi_o^{(o)}\rangle \qquad [II\text{-}16]$$

We now pick out the terms in A and B and average over the molecular orientations to obtain:

$$(E^{(2)}_{AB})_{av} = \frac{-8}{3}\beta^2\hbar^2\gamma_A\gamma_B\,\mathbf{I}_A\mathbf{I}_B \sum_{k,n\neq 0}(E_n-E_o)^{-1}\langle\Psi_o^{(o)}\left|\frac{3(\mathbf{S}_k\cdot\mathbf{r}_{kA})\mathbf{r}_{kA}}{r_{kA}^5} - \frac{\mathbf{S}_k}{r_{kA}^3}\right|\Psi_n^{(o)}\rangle$$

$$\times \langle\Psi_n^{(o)}\left|\frac{3(\mathbf{S}_k\cdot\mathbf{r}_{kB})\mathbf{r}_{kB}}{r_{kB}^5} - \frac{\mathbf{S}_k}{r_{kB}^3}\right|\Psi_o^{(o)}\rangle \qquad [II\text{-}17]$$

with corresponding coupling constant:

$$J^{(2)}_{AB} = \frac{-8}{3h}\beta^2\hbar^2\gamma_A\gamma_B \sum_{k,n\neq 0}(E_n-E_o)^{-1}\langle\Psi_o^{(o)}\left|\frac{3(\mathbf{S}_k\cdot\mathbf{r}_{kA})\mathbf{r}_{kA}}{r_{kA}^5} - \frac{\mathbf{S}_k}{r_{kA}^3}\right|\Psi_n^{(o)}\rangle$$

$$\times \langle\Psi_n^{(o)}\left|\frac{3(\mathbf{S}_k\cdot\mathbf{r}_{kB})\mathbf{r}_{kB}}{r_{kB}^5} - \frac{\mathbf{S}_k}{r_{kB}^3}\right|\Psi_o^{(o)}\rangle \qquad [II\text{-}18]$$

The Contact Term

By a procedure exactly analogous to that for the previous term we obtain the contact contribution to the coupling constant between two nuclei A and B as:

$$J_{AB}^{(3)} = \frac{-2}{3h}\left(\frac{16\pi\beta\hbar}{3}\right)^2 \gamma_A\gamma_B \sum_{j,k,n\neq 0} (E_n-E_o)^{-1}\langle\Psi_o^{(o)}|\delta(\mathbb{r}_{jA})\mathbb{S}_j|\Psi_n^{(o)}\rangle$$

$$\times \langle\Psi_n^{(o)}|\delta(\mathbb{r}_{kB})\mathbb{S}_k|\Psi_o^{(o)}\rangle \qquad [II-19]$$

3. Molecular Orbital Formulation

The next step in calculating the contributions to J_{AB} is to evaluate the matrix elements in Equations [II-11], [II-15], [II-18] and [II-19]. In order to do this we must specify the form of the electronic wavefunctions which of course will be many-electron functions. In previous work, both molecular-orbital(32) and valence-bond(28,29) wavefunctions have been employed. However, since we are concerned with the theoretical background to the molecular orbital method to be presented later, discussion of valence-bond methods will be omitted.

Molecular orbital methods currently find extremely wide use in chemistry and are described in detail at various levels of sophistication in a number of textbooks. Background material relevant to this dissertation may be found in the texts by Pilar(5), Eyring, Walter and Kimball(19), and particularly in the recent book by Pople and Beveridge(33) whose notation is fairly closely followed here. The present study does not attempt to compare molecular orbital theory with other theories of electronic structure, nor are the basic assumptions of the MO method examined in a critical way. Instead the theory is used as presented in the texts. In the following treatment the MO expressions are not derived. Instead, the intention is to state them in sufficient detail to make the notation and definitions of quantities clear.

In addition to making the Born-Oppenheimer approximation mentioned earlier, the molecular orbital method introduces another fundamental approximation known as the one-electron approximation. This assumes that we can represent the many-electron function, Ψ_o, by a product of functions, called molecular orbitals, each of which depends on the coordinates of only one electron. A wavefunction to represent a closed-shell molecule with 2N electrons may be obtained by taking N orthonormal orbitals, $\psi_1, \psi_2, \ldots, \psi_N$, each of which is a function of the space coordinates of one electron and which is associated with either an α or β electron spin function. These functions are then arranged in a determinant of the form:

$$\Psi_o(1,2,\ldots,2N) = [(2N)!]^{-1/2} \begin{vmatrix} \psi_1(1)\alpha(1)\psi_1(1)\beta(1)\psi_2(1)\alpha(1)\ldots\psi_N(1)\alpha(1)\psi_N(1)\beta(1) & \\ \psi_1(2)\alpha(2)\ldots\ldots & \vdots \\ \vdots & \vdots \\ \psi_1(2N)\alpha(2N)\ldots\ldots & \psi_N(2N)\alpha(2N)\psi_N(2N)\beta(2N) \end{vmatrix} \qquad \text{[II-20]}$$

which is commonly abbreviated as:

$$\Psi_o(1,2,\ldots,2N) = [(2N)!]^{-1/2} |\psi_1(1)\alpha(1)\psi_1(2)\beta(2)\ldots\ \ldots\psi_N(2N)\beta(2N)| \qquad \text{[II-21]}$$

The factor $[(2N)!]^{-1/2}$ ensures that Ψ_o is normalized.

This determinantal function has the necessary properties that:

(a) all the electrons are indistinguishable from each other; and

(b) the Pauli exclusion principle is automatically satisfied, since if any two electrons have the same space and spin functions, the determinant will become zero.

It does, however, have the undesirable property that electrons with opposite spins are not correlated. That is, it does not properly take account of the fact that at any instant, no two electrons may occupy the same position in space, even if they happen to have opposite spins. The effect of this feature of molecular orbital theory on the calculation of nuclear spin coupling constants will be discussed later in the section on "approximations".

Now that an approximate many-electron wavefunction has been specified we can proceed with the evaluation of the average values of the nuclear spin coupling operators which occur in the foregoing coupling constant expressions. First we make use of the fact that the operators are of the form:

$$H = \sum_{k} h(k)$$

where h(k) operates on the coordinates of one electron, k, only. This property, together with the facts that

(a) the electrons are indistinguishable from each other; and

(b) the molecular orbitals are orthonormal functions,

permits us to write each of the many-electron integrals as a sum of one-electron integrals, i.e.:

$$<\Psi|H|\Psi> = 2\sum_{i=1}^{occ} <\Psi_i(k)|h(k)|\Psi_i(k)> \qquad [II-22]$$

where k is any one of the electrons and i runs over the N doubly-occupied molecular orbitals. This expression assumes that H does not contain electron spin operators. When this is not the case, additional numerical factors will appear when the integration over the electron spin coordinates is carried out.

A characteristic feature of molecular orbital calculations is that they produce not only the N occupied MO's, $\psi_1, \psi_2, \ldots, \psi_N$, but also a number of "virtual" or unoccupied MO's, $\psi_{N+1}, \psi_{N+2}, \ldots$. Although these latter functions do not necessarily have any physical significance, they are often used to construct approximate wavefunctions for the electronic excited states of the molecule. Second order perturbation expressions may therefore be conveniently simplified by replacing the sum over excited electronic states, $\sum_{n\neq 0}$, by a sum over vacant MO's, $\sum_{j}^{vac}$. In this way, a many-electron second-order perturbation expression may be reduced to a sum over one-electron functions:

$$\sum_{n\neq 0} \frac{<\Psi_o|H|\Psi_n><\Psi_n|H|\Psi_o>}{(E_o-E_n)} = 2 \sum_{i}^{occ} \sum_{j}^{vac} \frac{<\Psi_i|h(k)|\Psi_j><\Psi_j|h(k)|\Psi_i>}{\Delta E_{i\to j}} \qquad [II-23]$$

where h(k) is written to emphasize that the operator is the one-electron version of H.

In this expression the denominator $\Delta E_{i\to j}$ is the excitation energy for the process of going from the ground electronic state to the excited state formed by exciting one electron from occupied MO i to vacant MO j. In this approximation for the excited states, the orthogonality of the molecular orbitals ensures that the only states which will make non-zero contributions to the summation are those in which a single electron is excited$^{(22)}$. Such an excitation leads to four wavefunctions which are components of a singlet state, ${}^1\Psi_{i\to j}$, and a triplet state, ${}^3\Psi_{i\to j}$. These wavefunctions may be written:

$${}^1\Psi_{i\to j} = \frac{1}{\sqrt{2}} [|\psi_1\cdots\psi_i\bar{\psi}_j\cdots| + |\psi_1\cdots\psi_j\bar{\psi}_i\cdots|]$$

$${}^3\Psi_{i\to j} = \begin{array}{l} |\psi_1\cdots\bar{\psi}_i\bar{\psi}_j\cdots| \\ \frac{1}{\sqrt{2}} [|\psi_1\cdots\psi_i\bar{\psi}_j\cdots| - |\psi_1\cdots\psi_j\bar{\psi}_i\cdots|] \\ |\psi_1\cdots\psi_i\psi_j\cdots| \end{array}$$

where, to simplify the notation of Equation [II-21] a bar is used to denote an electron of β-spin and we have omitted the normalization constant and the numbering of the electrons. The corresponding excitation energies will be denoted as ${}^1\Delta E_{i\to j}$ and ${}^3\Delta E_{i\to j}$.

For closed-shell molecules the ground state, Ψ_o, is a singlet. In such cases the only non-zero matrix elements for operators which contain the electron spin operator, such as H_2 and H_3, will be when the excited state is a triplet. For operators which do not contain $\mathbb{S}$, such as $H_1^{(b)}$, only singlet excited states will mix with the ground state.

When the approximation specified in Equation [II-23] is applied to Equations [II-11], [II-15], [II-18] and [II-19], the following molecular orbital perturbation theory expressions are obtained for the four contributions to the coupling constant between two nuclei A and B:

$$J_{AB}^{1(a)} = \frac{1}{h}\frac{4e^2\hbar^2}{3mc^2}\gamma_A\gamma_B \sum_i^{occ} \left<\psi_i\left|\frac{\mathbb{r}_A\cdot\mathbb{r}_B}{r_A{}^3 r_B{}^3}\right|\psi_i\right> \qquad \text{[II-24]}$$

$$J_{AB}^{1(b)} = -\frac{16}{3}\frac{\beta^2}{h}\hbar^2\gamma_A\gamma_B \sum_i^{occ}\sum_j^{vac} ({}^1\Delta E_{i\to j})^{-1}\left<\psi_i\right|r_A^{-3}\mathbb{L}_A\left|\psi_j\right>\left<\psi_j\right|r_B^{-3}\mathbb{L}_B\left|\psi_i\right> \qquad \text{[II-25]}$$

$$J_{AB}^{(2)} = -\frac{4}{3}\frac{\beta^2}{h}\hbar^2\gamma_A\gamma_B \sum_i^{occ}\sum_j^{vac} ({}^3\Delta E_{i\to j})^{-1}\left<\psi_i\left|\frac{3\mathbb{r}_{A\alpha}\mathbb{r}_{A\beta}-\mathbb{r}_A^2\delta_{\alpha\beta}}{r_A{}^5}\right|\psi_j\right>\left<\psi_j\left|\frac{3\mathbb{r}_{B\alpha}\mathbb{r}_{B\beta}-\mathbb{r}_B^2\delta_{\alpha\beta}}{r_B{}^5}\right|\psi_i\right> \qquad \text{[II-26]}$$

$$J_{AB}^{(3)} = \frac{-2}{3h}\left(\frac{16\pi\beta\hbar}{3}\right)^2\gamma_A\gamma_B \sum_i^{occ}\sum_j^{vac} ({}^3\Delta E_{i\to j})^{-1}\left<\psi_i\right|\delta(\mathbb{r}_A)\left|\psi_j\right>\left<\psi_j\right|\delta(\mathbb{r}_B)\left|\psi_i\right> \qquad \text{[II-27]}$$

In the case of the dipolar and contact terms, the presence of the electron spin operator, $\mathbb{S}$, in the perturbation Hamiltonians means that the process of reducing the many-electron functions [II-18] and [II-19] to the one-electron functions [II-26] and [II-27] is not trivial. Without going into excessive detail, we note that since it affects only spherically symmetric parts of the wavefunction, the contact term is by definition isotropic and the effect of the electron spin operators is simply to introduce a numerical factor 3/2 in going from Equation [II-19] to [II-27]. The dipolar interaction on the other hand is anisotropic and the different cartesian components of the electron spin operator must be considered in detail. The result shown in Equation [II-26] uses the tensor summation convention. The subscripts α and β denote the cartesian components of the electron position vectors, $\mathbf{r}_A$ and $\mathbf{r}_B$. In the summation convention the expression implies the sum of all the distinct terms obtained by allowing α and β to run over x, y and z. The Kronecker delta, $\delta_{\alpha\beta}$, is unity if $\alpha = \beta$ and zero otherwise.

We now introduce the LCAO (Linear Combination of Atomic Orbitals) expansion in which each molecular orbital, ψ_i, is written as a linear combination of a set of atomic orbitals, χ_σ:

$$\psi_i = \sum_{\sigma} \chi_\sigma C_{\sigma i} \qquad [II-28]$$

so that the problem of determining the wavefunction for a molecule becomes that of finding the coefficients $C_{\sigma i}$. In this representation, the coupling constant expressions become$^{(34)}$:

$$J_{AB}^{1(a)} = \frac{2\hbar\gamma_A\gamma_B e^2}{3\pi mc^2} \sum_{i}^{occ} \sum_{\lambda\sigma} C_{\lambda i} C_{\sigma i} <\chi_\lambda | \mathbf{r}_A \cdot \mathbf{r}_B \ r_A^{-3} r_B^{-3} | \chi_\sigma> \qquad [II-29]$$

$$J_{AB}^{1(b)} = -\frac{8\hbar\gamma_A\gamma_B\beta^2}{3\pi} \sum_{i}^{occ} \sum_{j}^{vac} ({}^1\Delta E_{i\to j})^{-1} \sum_{\lambda\sigma\nu\omega} C_{\lambda i} C_{\sigma j} C_{\nu j} C_{\omega i} <\chi_\lambda | r_A^{-3} \mathbf{L}_A | \chi_\sigma><\chi_\nu | r_B^{-3} \mathbf{L}_B | \chi_\omega> \qquad [II-30]$$

$$J_{AB}^{(2)} = -\frac{2\hbar\gamma_A\gamma_B\beta^2}{3\pi} \sum_{i}^{occ} \sum_{j}^{vac} ({}^3\Delta E_{i\to j})^{-1} \sum_{\lambda\sigma\nu\omega} |C_{\lambda i} C_{\sigma j} C_{\nu j} C_{\omega i} <\chi_\lambda | r_A^{-5} (3r_{A\alpha} r_{A\beta} - r_A^2 \delta_{\alpha\beta}) | \chi_\sigma>$$
$$\times <\chi_\nu | r_B^{-5} (3r_{B\alpha} r_{B\beta} - r_B^2 \delta_{\alpha\beta}) | \chi_\omega> \qquad [II-31]$$

$$J_{AB}^{(3)} = -\frac{64h\gamma_A\gamma_B\beta^2}{9} \sum_{i}^{occ} \sum_{j}^{vac} ({}^3\Delta E_{i\to j})^{-1} \sum_{\lambda\sigma\nu\omega} C_{\lambda i} C_{\sigma j} C_{\nu j} C_{\omega i} <\chi_\lambda | \delta(\mathbf{r}_A) | \phi_\sigma><\phi_\nu | \delta(\mathbf{r}_B) | \chi_\omega> \qquad [II-32]$$

In the case of the dipolar term, if the expression is written out explicitly then, taking note of the Kronecker delta $\delta_{\alpha\beta}$, we obtain:

$$
\begin{aligned}
J_{AB}^{(2)} = \frac{-2\hbar\gamma_A\gamma_B\beta^2}{3\pi} & \sum_i^{occ} \sum_j^{vac} ({}^3\Delta E_{i\rightarrow j})^{-1} \sum_{\lambda\sigma\nu\omega} C_{\lambda i}C_{\sigma j}C_{\nu j}C_{\omega i} \\
& \times [<\chi_\lambda|r_A^{-5}(3X_A^2 - r_A^2)|\chi_\sigma><\chi_\nu|r_B^{-5}(3X_B^2 - r_B^2)|\chi_\omega> \\
& + 2<\chi_\lambda|r_A^{-5}(3X_AY_A)|\chi_\sigma><\chi_\nu|r_B^{-5}(3X_BY_B)|\chi_\omega> \\
& + 2<\chi_\lambda|r_A^{-5}(3X_AZ_A)|\chi_\sigma><\chi_\nu|r_B^{-5}(3X_BZ_B)|\chi_\omega> \\
& + <\chi_\lambda|r_A^{-5}(3Y_A^2 - r_A^2)|\chi_\sigma><\chi_\nu|r_B^{-5}(3Y_B^2 - r_B^2)|\chi_\omega> \\
& + 2<\chi_\lambda|r_A^{-5}(3Y_AZ_A)|\chi_\sigma><\chi_\nu|r_B^{-5}(3Y_BZ_B)|\chi_\omega> \\
& + <\chi_\lambda|r_A^{-5}(3Z_A^2 - r_A^2)|\chi_\sigma><\chi_\nu|r_B^{-5}(3Z_B^2 - r_B^2)|\chi_\omega>] \qquad [II\text{-}33]
\end{aligned}
$$

Here we have used the following notation for the cartesian components of the position vector, $\mathbb{r}_N$, of an electron relative to a nucleus, N:

$$|\mathbb{r}_N| \equiv r_N = [X_N{}^2 + Y_X{}^2 + Z_N{}^2]^{1/2}$$

Equations [II-29] to [II-32] are the basic expressions for the sum-over-states LCAO MO method of calculating nuclear spin coupling constants. However, many calculations have employed further approximations and these will be discussed below. In Section 5 of this chapter on the SOS method we will review the major approximations which have been made in the light of their effect on the numerical values of J which the method yields.

4. Further Approximations

Straight-forward application of the coupling constant expressions just derived can result in very long calculations, particularly for large molecules. In order to make such calculations more tractable, further approximations may be introduced at this point in the development of the theory. We will describe here some of the more commonly used approximations, but evaluation of their effect on the calculated coupling constant values will be deferred to Section 5.

Perhaps the most drastic simplification commonly made is the "mean excitation energy" approximation. This was used by both Ramsey(16) and McConnell(32) in the papers which first set out the SOS theory of coupling constants described above. In this approximation the perturbation theory expressions such as [II-19] or [II-27] are simplified by replacing the excitation energies, $(E_n - E_o)$ or $\Delta E_{i \rightarrow j}$, with appropriate average values. In general, different values of the mean energy are used for different coupling mechanisms.

This approximation may be made before or after the one-electron approximation is made, that is before or after the type of wavefunction to be used in Equations [II-15], [II-18] and [II-19] is specified. The former procedure was used by McConnell(32) and simplifies the second-order perturbation theory expressions by removing the dependence of J_{AB} on the excited state wavefunctions. For example, the full expression for the contact contribution:

$$J_{AB}^{(3)} = -\frac{2}{3h}\left[\frac{16\pi\beta\hbar}{3}\right]^2 \gamma_A \gamma_B \sum_{n \neq 0}^{\infty} \frac{\langle \Psi_o | \sum_j \delta(\mathbb{r}_{jA}) \mathbb{S}_j | \Psi_N \rangle \langle \Psi_n | \sum_k \delta(\mathbb{r}_{kB}) \mathbb{S}_k | \Psi_o \rangle}{(E_n - E_o)} \qquad [II\text{-}34]$$

may be reduced by the mean energy approximation to:

$$J_{AB}^{(3)} = -\frac{2}{3h}\left[\frac{16\pi\beta\hbar}{3}\right]^2 \frac{\gamma_A \gamma_B}{\overline{\Delta E}} \langle \Psi o | \sum_{jk} \delta(\mathbb{r}_{jA}) \delta(\mathbb{r}_{jB}) \; \mathbb{S}_A \cdot \mathbb{S}_B | \Psi_o \rangle \qquad [II\text{-}35]$$

All that is required to evaluate coupling constants from this expression is a knowledge of the ground state electronic wavefunction and a value for the mean energy $\overline{\Delta E}$. Some form of Ψ_o is available for most molecules, whereas even approximate excited state wavefunctions and energies are known for only a few, and even in those cases by no means all of the states are known. Of course a rigorous calculation of the value of $\overline{\Delta E}$ would require a solution to just the problems which the mean energy was introduced to avoid. It is therefore necessary to choose a semi-empirical value for $\overline{\Delta E}$. The difficulty of making this choice and other drawbacks to the mean energy approximation will be discussed in Section 5.

Pople and Santry$^{(22)}$ chose not to make the mean energy approximation before the one-electron approximation. This permitted them to derive the LCAO expressions for J_{AB} shown in Equations [II-29] to [II-32]. For example, recall the expression for the contact contribution:

$$J_{AB}^{(3)} = \frac{-64h\gamma_A\gamma_B\beta^2}{9} \sum_i^{occ} \sum_j^{vac} ({}^3\Delta E_{i\to j})^{-1} \sum_{\lambda\sigma\nu\omega} C_{\lambda i} C_{\sigma j} C_{\nu j} C_{\omega i} \langle\chi_\lambda|\delta(\mathbf{r}_A)|\chi_\sigma\rangle\langle\chi_\nu|\delta(\mathbf{r}_B)|\chi_\omega\rangle \qquad \text{[II-36]}$$

At this stage the mean energy approximation could be made simply by replacing the triplet excitation energies, ${}^3\Delta E_{i\to j}$, with an average energy, $\overline{{}^3\Delta E}$, which is independent of the MO's i and j:

$$J_{AB}^{(3)} = \frac{-64h\gamma_A\gamma_B\beta^2}{9} (\overline{{}^3\Delta E})^{-1} \sum_i^{occ} \sum_j^{vac} \sum_{\lambda\sigma\nu\omega} C_{\lambda i} C_{\sigma j} C_{\nu j} C_{\omega i} \langle\chi_\lambda|\delta(\mathbf{r}_A)|\chi_\sigma\rangle\langle\chi_\nu|\delta(\mathbf{r}_B)|\chi_\omega\rangle \qquad \text{[II-37]}$$

The identical procedure may be performed for the other second-order contributions to J_{AB}.

The Expression [II-37] is also obtained by McConnell's$^{(32)}$ method if the one-electron, LCAO approximations are applied to Equation [II-35]. However, the advantage of the Pople-Santry method is that since Expression [II-36] is "exact" within the one-electron approximation, it permits one to calculate J_{AB} from a ground state MO wavefunction in the absence of the mean-energy approximation and so by comparing the results with those from Equation [II-37] determine the effect of that approximation on J_{AB}. Some discussion of such comparisons will be presented in Section 5 of this chapter.

A less severe approximation and one which is retained in the present study is the one-centre approximation$^{(22)}$. This is an attempt to simplify the quadruple sums over atomic orbitals which appear in the LCAO equations above.

From the LCAO expressions [II-29] to [II-32] for the various contributions to the coupling constant we see that the following types of integrals occur in quadruple summations over atomic orbitals:

from the orbital terms, $J_{AB}^{(1a)}$: $\langle\chi_\lambda|\mathbb{r}_A\cdot\mathbb{r}_B\ r_A^{-3}r_B^{-3}|\chi_\sigma\rangle$

$J_{AB}^{(1b)}$: $\langle\chi_\lambda|r_A^{-3}\ \mathbb{L}_A|\chi_\sigma\rangle$

from the dipolar term, $J_{AB}^{(2)}$: $\langle\chi_\lambda|r_A^{-5}(3r_{A\alpha}r_{A\beta} - r_A{}^2\delta_{\alpha\beta})|\chi_\sigma\rangle$

from the contact term, $J_{AB}^{(3)}$: $\langle\chi_\lambda|\delta(\mathbb{r}_A)|\chi_\sigma\rangle$

In their most general form these integrals may have $\lambda \neq \sigma$, i.e., be evaluated between different atomic orbitals, and these orbitals may be centred on different atoms.

Some of these integrals will be indentically zero. For example, if we assume that the electron orbital angular momentum about atom A, $\mathbb{L}_A$, is quantized in the z-direction, then since:

$$(\mathbb{L}_A)_z|s\rangle = 0$$

a number of the integrals in the expression for $J_{AB}^{(1b)}$ will be zero. Similarly, since $\delta(r_A)$ picks out values of the basis functions at nucleus A, $J_{AB}^{(3)}$ integrals involving non-s orbitals centred on atom A will be zero.

There remain, however, a large number of non-zero integrals in the quadruple summations. If a comparatively complete type of MO theory is being applied to a small molecule, all of these non-zero integrals are usually retained. However, in semi-empirical MO methods, which are applicable to larger molecules, it is common to increase computational efficiency by neglecting those integrals which are very small. One systematic way of doing this is to make the one-centre approximation which consists of retaining only those integrals which involve atomic orbitals centred on the same atom. Accordingly in the LCAO expressions [II-29] to [II-32] we require the atomic orbitals χ_λ and χ_σ to be both centred on atom A while χ_ν and χ_ω are both on atom B.

In order to show explicitly the simplification obtained from the one-centre approximation it is convenient to specify the set of atomic orbitals to be used as the basis for the MO description of the molecule. In the approximate MO method$^{(4)}$ used in the present study, bonding is described in terms of valence electrons and the inner electrons are treated as a non-polarizable core. Thus we use a 1s orbital to describe a hydrogen atom and the set 2s, $2p_x$, $2p_y$, $2p_z$ for the first-row atoms. This type of basis set leads to the following simplifications when the one-centre approximation is applied to molecules composed of atoms up to only fluorine in the periodic table.

Orbital terms:

The first part, $J_{AB}^{(1a)}$, may be neglected since whichever atom χ_λ and χ_σ are centred on there will always be a factor r^{-3} which will make each integral in the summation very small. For example, if χ_λ and χ_σ are on atom

A, then for typical distances between atoms, the quantity r_B^{-3} will be a small multiplying factor. This approximation will of course be best for indirectly bonded couplings and worst for couplings between directly bonded atoms with short bond lengths such as HF. However, even in the case of HF, Kato and Saika(34) found that the $J_{HF}^{(1a)}$ term contributed less than 1% to the total value. In the $J_{AB}^{(1b)}$ part, the orbital angular momentum operator ensures that the only non-zero terms are those in which χ_λ and χ_σ are both 2p orbitals on atom A while χ_ν and χ_ω must be 2p orbitals on atom B. Hence at this level of approximation, the orbital term will be zero if either atom A or B is hydrogen. If A and B are first-row atoms, then the only one-centre integrals in Equation [II-30] which are non-zero are:

$$\langle 2p_{y_A}|r_A^{-3}L_{A_x}|2p_{z_A}\rangle = -\langle 2p_{z_A}|r_A^{-3}L_{A_x}|2p_{y_A}\rangle = -i\langle r^{-3}\rangle_A \qquad \text{[II-38]}$$

$$\langle 2p_{z_A}|r_A^{-3}L_{A_y}|2p_{x_A}\rangle = -\langle 2p_{x_A}|r_A^{-3}L_{A_y}|2p_{z_A}\rangle = -i\langle r^{-3}\rangle_A \qquad \text{[II-39]}$$

$$\langle 2p_{x_A}|r_A^{-3}L_{A_z}|2p_{y_A}\rangle = -\langle 2p_{y_A}|r_A^{-3}L_{A_z}|2p_{x_A}\rangle = -i\langle r^{-3}\rangle_A \qquad \text{[II-40]}$$

plus an equivalent set for atom B.

The symbols L_{A_x}, L_{A_y} and L_{A_z} refer to the cartesian components of the operator for the electron angular momentum, $\mathbb{L}_A$, about atom A and $\langle r^{-3}\rangle_A$ stands for the average value of r^{-3} between valence-shell p-orbitals centred on atom A, where r is the magnitude of the position vector of the electron with respect to nucleus A. When the quadruple sum in Equation [II-30] is written out explicitly in terms of these non-zero integrals, the expression for the orbital coupling constant becomes:

$$J_{AB}^{1(b)} = \frac{-8\hbar\gamma_A\gamma_B\beta^2}{3\pi}\langle r^{-3}\rangle_A\langle r^{-3}\rangle_B\sum_i^{occ}\sum_j^{vac}({}^1\Delta E_{i\to j})^{-1}$$

$$\times\ [-C_{z_Ai}C_{y_Aj}C_{z_Bj}C_{y_Bi} + C_{y_Ai}C_{z_Aj}C_{y_Bj}C_{z_Bi}$$

$$+ c_{z_A i}c_{x_A j}c_{z_B j}c_{x_B i} - c_{x_A i}c_{z_A j}c_{x_B j}c_{z_B i} + c_{x_A i}c_{y_A j}c_{x_B j}c_{y_B i}$$

$$- c_{y_A i}c_{x_A j}c_{y_B j}c_{x_B i}] \qquad \text{[II-41]}$$

Thus use of the one-centre approximation with this basis set has reduced the quadruple sum to a sum of only six terms. In equation [II-41], $c_{z_A i}$ is the coefficient of the $2p_z$ atomic orbital of atom A in the ith occupied MO.

Dipolar term:

In this case also the only one-centre integrals which are non-zero are those in Equation [II-31] in which χ_λ and χ_σ are 2p orbitals on atom A and χ_ν and χ_ω are 2p orbitals on atom B. Hence in this approximation the dipolar contribution is zero if either A or B is hydrogen. For first-row atoms the non-zero matrix elements of the dipolar operator are shown in Appendix A. These elements may be used to expand the quadruple sum in Equation [II-31] resulting in a sum of 15 terms(22) rather than the 6 in the orbital case. However, the dipolar contribution to J_{AB} still turns out to be proportional to the product $\langle r^{-3}\rangle_A\langle r^{-3}\rangle_B$ as in the case of the orbital term.

Contact term:

Since a valence-shell basis-set is being considered, the only non-zero contributions to $J_{AB}^{(3)}$ in Equation [II-32] in the one-centre approximation come from the term in which χ_λ and χ_σ are both the valence s-orbital of atom A while χ_ν and χ_ω are the valence s-orbital of atom B. The contact term is therefore the only one in this approximation to contribute to couplings involving hydrogen. The expression for the contact coupling becomes:

$$J_{AB}^{(3)} = \frac{-64\, h\gamma_A\gamma_B\beta^2}{9} S_A^2(o)\, S_B^2(o) \sum_i^{occ} \sum_j^{vac} ({}^3\Delta E_{i\rightarrow j})^{-1} c_{s_A i}c_{s_A j}c_{s_B j}c_{s_B i} \qquad \text{[II-42]}$$

where $S_A^2(o) = \langle s_A|\delta(r_A)|s_A\rangle$, the density of the valence-shell s-electron at the nucleus of atom A.

If the mean energy approximation is introduced at this point, that is after the one-centre approximation, it permits further simplification of the notation in terms of the bond-order matrix, defined by:

$$P_{\sigma\nu} = 2 \sum_{i}^{occ} C^{*}_{\sigma i} C_{\nu i} \qquad \text{[II-43]}$$

If $\sigma = \nu$, $P_{\sigma\sigma}$ gives the electron density in the atomic orbital χ_σ. If σ and ν are on neighbouring atoms, $P_{\sigma\nu}$ gives a measure of the bonding between the orbitals χ_σ and χ_ν. In MO theory it is required that the molecular orbitals be orthonormal:

$$\langle\psi_i|\psi_j\rangle = \delta_{ij} \qquad \text{[II-44]}$$

In terms of the LCAO expansion (Equation [II-28]) this condition becomes:

$$\sum_{\sigma}\sum_{\nu} C^{*}_{\sigma i} C_{\nu j} \langle\chi_\sigma|\chi_\nu\rangle = \delta_{ij} \qquad \text{[II-45]}$$

If an orthonormal basis set is used, we have:

$$\langle\chi_\sigma|\chi_\nu\rangle = \delta_{\sigma\nu} \qquad \text{[II-46]}$$

so that the requirement [II-45] becomes:

$$\sum_{\sigma} C^{*}_{\sigma i} C_{\nu j} = \delta_{ij} \qquad \text{[II-47]}$$

The matrix, $\mathbb{C}$, of all the MO coefficients is an orthogonal matrix, so that [II-47] may be written:

$$\sum_{k}^{\substack{\text{all}\\ \text{MO's}}} C^{*}_{\sigma k} C_{\nu k} = \delta_{\sigma\nu} \qquad \text{[II-48]}$$

In particular:

$$\sum_{k}^{\substack{\text{all}\\ \text{MO's}}} C^{*}_{\sigma k} C_{\nu k} = 0 \quad \text{if } \sigma \neq \nu \qquad \text{[II-49]}$$

The sum over k in this equation may be written as two sums, one over occupied MO's, i, and another over vacant MO's, j, giving:

$$\sum_{i}^{occ} C^*_{\sigma i} C_{\nu i} + \sum_{j}^{vac} C_{\sigma j} C_{\nu j} = 0 \qquad \sigma \neq \nu \qquad [II\text{-}50]$$

Recalling the definition of $P_{\sigma\nu}$, Equation [II-43], it is clear that Equation [II-50] implies:

$$2 \sum_{j}^{vac} C^*_{\sigma j} C_{\nu j} = -P_{\sigma\nu} \qquad \sigma \neq \nu \qquad [II\text{-}51]$$

In the particular case that χ_σ and χ_ν are the valence-shell s-orbitals of atoms A and B, Equations [II-43] and [II-51] give:

$$2 \sum_{i}^{occ} C_{s_A i} C_{s_B i} = P_{s_A s_B} \qquad \text{and} \qquad 2 \sum_{j}^{vac} C_{s_A j} C_{s_B j} = -P_{s_A s_B} \qquad [II\text{-}52]$$

If these relationships are substituted into Equation [II-42] and the mean energy $\overline{^3\Delta E}$ is used in place of the excitation energies $^3\Delta E_{i\to j}$ we obtain:

$$J^{(3)}_{AB} = \frac{64 h \gamma_A \gamma_B \beta^2}{9} S^2_A(o) S^2_B(o) \; (\overline{^3\Delta E})^{-1} \; P^2_{s_A s_B} \qquad [II\text{-}53]$$

If the nuclei A and B have magnetogyric ratios γ_A and γ_B of the same sign, then this expression predicts that the coupling constant $J^{(3)}_{AB}$ will always be positive. This is because any reasonable average excitation energy for a molecule must clearly be positive. All the other factors in the expression, except γ_A and γ_B, are either squared or positive by definition.

Equation [II-53] represents the MO theory of coupling constants in its most approximate form. To the extent that the contact interaction is the dominant mechanism of the coupling, Equation [II-53] relates the coupling constant between two nuclei to the degree that s-orbitals are responsible for the bonding between them (the amount of "s-character" to the bond). The equation is therefore the basis for seeking simple relationships between hybridization and coupling constant values. However, it cannot explain most negative coupling constants and the severity of the approximations used in its derivation must always be born in mind. Pople and Santry(22) gave equivalent expressions in terms of the mean energy approximation and valence-shell bond-orders for the other two coupling mechanisms.

Before going on to discuss some of the results obtained with the SOS method it is appropriate to mention the problem of evaluating the $S_N^2(0)$ and $\langle r^{-3}\rangle_N$ integrals. When semi-empirical MO theories such as that used in the present study are employed, these integrals are not evaluated explicitly. Corresponding values from Hartree-Fock calculations on atoms may be used or else the integrals may be treated as parameters which are adjusted to optimize agreement between the theoretical and experimental values of J_{AB} in a series of molecules. Generally, the choice of treating the integrals as parameters, rather than using the calculated atomic values, is made for the following reasons:

(a) Electron density values at the position of the nucleus are difficult to obtain with good absolute accuracy. One reason for this is simply that the density values are very high near the nucleus and so a given percentage error in the calculation will result in a large absolute error in this region.

(b) Even if accurate atomic values were available, they would not take into account the possibility that in a molecule the integrals may well have values different from in the atom and furthermore one would expect these values to change from molecule to molecule.

(c) If these integrals are treated as parameters it is possible that some of the error introduced by making the one-centre approximation may be compensated for.

5. Evaluation of the SOS Method

The main disadvantage of the SOS perturbation theory is that it does not properly take into account the self-consistent field (SCF) nature of the electronic wavefunctions obtained from modern MO theories. In the development of the SOS equations it was assumed that the unperturbed wavefunction, $\Psi_o^{(o)}$, was an eigenfunction of a simple molecular Hamiltonian, $H^{(o)}$ (see Equations [I-37] and [II-2]). However, the many-electron determinantal wavefunctions, such as that specified in Equation [II-20] and used to obtain the MO expressions for coupling constants, are in fact eigenfunctions of a two-electron, Hartree-Fock Hamiltonian, F. This Hamiltonian depends in a self-consistent manner on the electron distribution in the molecule. In order to make proper use of SCF wavefunctions in perturbation theory methods, the perturbation theory itself should be of a self-consistent type.

In the next two chapters recent perturbation methods are presented which overcome the principle deficiency of the SOS method in that they are as self-consistent as the SCF wavefunctions to which they are applied. However, there are a number of other approximations, apart from the self-consistency question, which have been mentioned in connection with the SOS method. These approximations are further discussed in this section within the context of the SOS perturbation theory.

Let us first consider the mean energy approximation. This is the most severe approximation mentioned so far. It was introduced in the original papers of Ramsey(16) and McConnell(32) as a simple method for obtaining numerical estimates of the coupling constants predicted by their theories. This approximation leads to attractively simple formulae such as Equation [II-53] which suggests that coupling constants between directly bonded nuclei may be simply related to the degree of s-orbital character of the bond between them. The success of this simple approach led to the mean energy approximation being quite widely used(35) in coupling constant calculations. However, as more failures of this approach became apparent it fell under considerable criticism(36).

We have already mentioned the arbitrary nature of the choice of the $\overline{\Delta E}$ value to be used, but this would not be a serious fault if a value could be found empirically which would give good agreement between theory and experiment over a wide range of coupling constants. That such a choice is not possible is made clear by a consideration of the more serious criticisms of the approximation given below.

As was shown previously in connection with Equation [II-53] the mean energy approximation always leads to positive coupling constants for pairs of nuclei with gyromagnetic ratios of the same sign. Pople and Santry(22) showed that this is not the case for the more rigorous expressions and so explained the theoretical basis for the negative couplings observed in many such cases. In a short note(36) McLachlan pointed out that this is a general problem associated with use of the mean energy approximation in second-order perturbation theory. While each individual excitation energy is certainly positive, the corresponding product of matrix elements in the numerator of the complete perturbation theory expression for the second-order energy may well be negative and therefore the summation over the excited states may be negative. Karplus(37) has discussed the general type of bonding in which the numerator might be expected to be positive in which case the mean energy approximation would predict the correct sign for the coupling constant. However, recent theoretical studies of coupling constants have avoided the mean energy approximation by returning to the more complete expansions. In the present study, this alternative has been chosen and this approximation will not be discussed further.

The one-centre approximation is retained in the present study. This type of approximation is consistent with the semi-empirical MO theory which is used for the numerical calculations and in which a number of small integrals are neglected while others are treated as parameters. However, it is interesting to examine the effects of this approximation on coupling constants calculated from an ab initio MO theory in which there is no parametrization and the integrals are calculated explicitly from the basis set used.

Such a study was made by Barbier and Berthier(38). They found that in their ab initio calculations they obtained results much closer to experiment if they did not make the one-centre approximation and that this was particularly true for directly-bonded couplings. This is not a surprising result since the wavefunctions they used were themselves calculated without neglecting multi-centre integrals. It confirms the approach taken in the present study of using a perturbation theory which is at a level of approximation appropriate to that of the wavefunctions employed.

The coupling constant theory presented so far contains further approximations due to the manner in which the sum over excited states is calculated. In this regard, two approximations are inherent in Equations [II-29] to [II-32]:

(a) the infinite sum has been approximated by a finite sum over a set of excited states; and

(b) the states which have been included are described only very approximately by one-electron excitations from occupied to vacant MO's.

A number of ab initio studies have been undertaken to try to assess the relative effects of these approximations. The question is whether the perturbation expansion is poorly convergent, in which case approximation (a) above would be unreliable, or whether the individual excited states should be more accurately calculated than by approximation (b). We will describe below some attempts to answer this question. These studies used ab initio wavefunctions of varying degrees of complexity but avoided the mean energy and one-centre approximations.

A number of ab initio calculations have been made of the coupling in hydrogen fluoride. The experimental magnitude of this coupling constant is 521 Hz(39). Recent molecular beam experiments(40) have shown the sign to be positive. The most extensive calculation was by Kato and Saika(34) who calculated all four contributions to J_{HF} using a number of different wavefunctions. In all cases they found that the contact term was the dominant one, the first-order orbital term was negligible and the remaining terms amounted to 10% to 20% of the total coupling. They found that a wavefunction using a minimal basis set of 5 Slater-type orbitals (STO's) gave a value of -1277 Hz for the dominant contact term. Optimizing the exponents of this basis set gave -1483 Hz. Adam, Grimson and Sprangle(41) used an extended basis set of 9 STO's and obtained a much better value of +598 Hz. However, going to 14 STO's gave(34) +621 Hz, 16 STO's(41) gave +501 Hz, and 18 STO's(41) gave -270 Hz. From these results a number of conclusions were drawn:

(a) the value of the coupling constant calculated for HF is very sensitive to the type of basis set used; and

(b) simply increasing the size of the basis set does not necessarily improve the agreement between theory and experiment.

These conclusions are not difficult to rationalize. Calculated coupling constant values are very sensitive to electronic charge densities near the nuclei because of the delta function in the contact term and the r^{-3} factors in the orbital and dipolar terms. However, charge densities near the nuclei are among the most difficult properties to calculate accurately from MO theory. Furthermore, it is known that approximate wavefunctions which are better in terms of total energy, i.e., generally those with larger basis sets, do not necessarily lead to better descriptions of the electron charge distribution at the nucleus.

Further insight into the convergence question was obtained in these studies by examining the contribution to J_{HF} made by the individual excitations in the perturbation expansion. As the size of the basis set is increased a larger number of virtual orbitals is obtained from which approximate excited states may be constructed. When these higher states were included in the expansion the calculated higher terms were found(41) to be generally larger than the lower ones and to fluctuate in sign. A further conclusion is therefore:

(c) as higher excited states are included, the perturbation expansion shows no sign of convergence.

Nevertheless as Kato and Saika(34) pointed out, the excited state wavefunctions constructed from the virtual orbitals are not sufficiently accurate to decide whether or not the perturbation expansion itself really converges. Adam, Grimison and Sprangle(41), who used the largest basis set quoted above, agreed and suggested that configuration interaction (CI) should be used. This would bring in electron correlation effects, improve the description of the excited states and hopefully improve the agreement of the calculated J_{HF} with experiment. However, when Murrell, Turpin and Ditchfield(42) used CI with the 14 STO wavefunction they found not only a poorer agreement with experiment (+836 Hz) but also that the perturbation expansion appeared to be as poorly convergent as before.

The difficulties described above are not limited to the hydrogen fluoride molecule. For example ab initio calculations using a variety of wavefunctions available for the H_2 molecule have generally failed to reproduce the experimental coupling constant value of +278 Hz(43,44). Minimal basis set calculations by Ostlund, Newton, McIver and Pople(45) gave +992 Hz while calculations by Emanuel(46) using the most accurate wavefunctions available for the ground state and the first five excited states and averaging over the zeroth molecular vibration gave +163 Hz. Ostlund et al(45) and Hinchliffe and Cook(47) found similarly poor agreement with experiment for a number of other small molecules using minimal basis set wavefunctions.

In the present study we have taken the view that of the many approximations made in these recent theories of nuclear spin coupling, the lack of a self-consistent perturbation theory to match the SCF wavefunctions is one of the most important to investigate. After this fundamental weakness of the theory has been corrected is the appropriate stage to consider further refinements of the SCF wavefunctions such as the use of larger basis sets and configuration interaction.

In the following chapters we present two self-consistent perturbation methods: the finite perturbation theory (FPT) of Pople, McIver and Ostlund(1,2,3) and the SCF perturbation theory (SCFPT) developed as part of the present study.

CHAPTER III. FINITE PERTURBATION THEORY

1. Introduction

This a type of perturbation theory which is intermediate in development between the sum-over-states method just discussed and the self-consistent-field approach which is dealt with in the following chapter and on which the present study is based. The FPT method overcomes the main criticism of the SOS theory in that explicit account is taken of the SCF nature of the MO wavefunctions in the perturbation theory. In this sense the FPT method is a type of self-consistent perturbation theory. However, the SCFPT method to be described later is computationally more efficient and is generally applicable to even highly complex perturbations(48).

The FPT approach was developed for coupling constant calculations by Pople, McIver and Ostlund(1,2,3) from a method used for electrical polarizability calculations by Cohen and Roothaan(49,50) and by Schweig(51). The basic idea is to evaluate the derivative in the fundamental second-order perturbation energy expression, Equation [I-48], by direct calculation. To do this one calculates wavefunctions for a molecule in the presence of a finite perturbation (in the present context this would be a term representing one of the nucleus-electron coupling mechanisms) and then compares details of the electron density with the corresponding density for the unperturbed system. In other words, an additional term appropriate to the particular perturbation under consideration is added to the Hartree-Fock Hamiltonian for the molecule and then an otherwise normal MO calculation is performed. The perturbed SCF Hamiltonian yields a perturbed SCF wavefunction and hence a perturbed electron distribution. Comparison with the unperturbed electron distribution indicates the effect of the perturbation and permits the desired interaction energy to be calculated.

2. Mathematical Formulation

Although the FPT method is in principle as general as the conventional SOS theory it is difficult to give one formulation which is suitable for all types of perturbations. This is because it is necessary to specify the type of wavefunction (i.e., real or complex, open shell or closed shell) required for the particular perturbation at an early stage in the development of the equations. We shall therefore limit the description presented here to the case in which the perturbation is the Fermi contact part of the nuclear spin coupling interaction.

It was shown previously (Equation [I-35]) that the operator describing the contact interaction between the electrons, k, and the nuclei, N, in a molecule is:

$$H_3 = \frac{16\pi\beta\hbar}{3} \sum_{k,N} \gamma_N \delta(r_{kN}) \mathbf{S}_k \cdot \mathbf{I}_N \qquad \text{[III-1]}$$

where all quantities have been defined previously. For convenience we will re-write this operator in terms of nuclear magnetic moments, $\boldsymbol{\mu}_N$, rather than nuclear spins, $\mathbf{I}_N$. We will consider that part of H_3 which depends only on a particular nucleus, A, and will assume that its magnetic moment, μ_A, lies along the z-axis of the molecule. We then write:

$$\mu_A\, H_A = \frac{16}{3} \pi\beta\, \mu_A \sum_k \delta(r_{kA})\, S_{kz} \qquad \text{[III-2]}$$

Here, the operator H_A is a special case of the general perturbation operator, H_r, introduced in Equation [I-43] and S_{kz} is the z-component of the spin angular momentum operator for electron k. A similar operator, H_B, describes the contact interaction between the electrons and nucleus B.

The μ_A-dependence of the perturbation operator, $\mu_A H_A$, has been shown explicitly in order to simplify later expressions in which we wish to distinguish between the perturbation operator itself and its derivative with respect to μ_A. Showing the μ_A dependence of the operator explicitly permits the derivative to be conveniently written as H_A.

In order to calculate the contribution the nucleus-electron interactions make to the nuclear spin coupling constant we follow the general procedure outlined in Chapter I and seek an expression for $E_{AB}^{(2)}$, the second-order perturbation to the energy of the molecule due to these interactions. However, instead of beginning with Equation [I-48] it is more convenient to go back to the earlier definition of the second-order energy, Equation [I-41]:

$$\text{i.e., } E_{AB}^{(2)} = \left[\frac{\partial^2 E(\mu)}{\partial\mu_A \partial\mu_B}\right]_o \qquad \text{[III-3]}$$

$$\text{where: } E(\mu) = \langle\Psi(\mu)|\ H(\mu)\,|\Psi(\mu)\rangle \qquad \text{[III-4]}$$

is the total perturbed electron energy in terms of the perturbed wavefunction, $\Psi(\mu)$ and perturbed Hamiltonian, $H(\mu)$. The Hellman-Feynmann theorem$^{(52)}$ permits the first derivative of the energy to be written as the expectation value of the corresponding derivative of the Hamiltonian, i.e.:

$$\frac{\partial E(\mu)}{\partial\mu_B} = \langle\Psi(\mu)\left|\frac{\partial H(\mu)}{\partial\mu_B}\right|\Psi(\mu)\rangle \qquad \text{[III-5]}$$

The Hellman-Feynmann theorem is usually applicable only to exact wavefunctions. However, Pople et al$^{(2)}$ quote a proof due to Hurley$^{(53)}$ which shows that the theorem holds for the approximate wavefunctions obtained from LCAO-SCF-MO theory (such as one used in the present study) provided that the perturbation does not depend on the nuclear configuration.

If, as in the case of the contact perturbation, the perturbed Hamiltonian has the linear form:

$$H(\mu) = H_o + \sum_r \mu_r H_r \qquad [III-6]$$

where H_o is the unperturbed Hamiltonian, then the derivative in Equation [III-5] becomes:

$$\frac{\partial H(\mu)}{\partial \mu_B} = H_B \qquad [III-7]$$

The first derivative of the perturbed energy therefore becomes:

$$\frac{\partial E(\mu)}{\partial \mu_B} = <\Psi(\mu)|H_B|\Psi(\mu)> \qquad [III-8]$$

The required second-order energy, $E_{AB}^{(2)}$, may now be obtained as the first derivative of Equation [III-8] with respect to μ_A rather than the second derivative of the energy. Pople et al$^{(2)}$ showed that this derivative with respect to μ_A may be obtained numerically from the perturbed wavefunction, $\Psi(\mu_A)$, in which only the one perturbing magnetic moment, μ_A, is present. The function $\Psi(\mu_A)$ is the one obtained when only the μ_A term is used in the perturbed Hamiltonian, Equation [III-6]. The second order energy between nuclei A and B may then be written:

$$E_{AB}^{(2)} = [\frac{\partial}{\partial \mu_A} <\Psi(\mu_A)|H_B|\Psi(\mu_A)>]_{\mu_A=0} \qquad [III-9]$$

This is the fundamental equation of the FPT method. It now remains only to specify the molecular orbital expression for the integral of H_B between the perturbed wavefunction $\Psi(\mu_A)$ and for the derivative of that integral with respect to μ_A.

In order to obtain an expression for the integral in Equation [III-9] we must consider the form of the perturbed wavefunction, $\Psi(\mu_A)$. Since the perturbing Hamiltonian, H_A, contains the electron spin operator, S_{kz}, the contact perturbation will have a different effect on electrons of α-spin than on those of β-spin. In a molecule, this will produce a spin polarization of the electron distribution, i.e., there will be an uneven distribution of electrons with α and β spin. It is therefore necessary to use a wavefunction which is sufficiently flexible to accommodate this polarization. A suitable wavefunction is a many-electron, single determinantal function similar to that used in Chapter II for the SOS theory except that it must be unrestricted in the sense that the spatial part of a given molecular orbital, ψ_i, is allowed to be different for an electron of α-spin than for one of β-spin. The two spatial functions are denoted ψ_i^{α} and ψ_i^{β} respectively. In the abbreviated notation defined in Equation [II-21] this unrestricted wavefunction is written:

$$\Psi(1,2,\ldots,2N) = [(2N!)]^{-1/2} |\psi_1^{\alpha}(1)\alpha(1)\cdots\psi_N^{\alpha}(N)\alpha(N)\psi_{N+1}^{\beta}(N+1)\beta(N+1)\cdots\psi_{2N}^{\beta}(2N)\beta(2N)| \tag{III-10}$$

Although the perturbation causes electron spin polarization, we will be dealing with molecules which have closed-shell ground-states so that the total number, N, of electrons of α-spin is equal to the number of electrons of β-spin.

We now outline how this perturbed wavefunction is calculated and how the required derivative in Equation [III-9] is obtained from it. Details of the unrestricted MO theory have been given by Pople and Nesbet(54) and the main equations are summarized in Appendix B. We present here only those expressions necessary to define the FPT method.

The α- and β-MO's may be written as LCAO expansions similar to Equation [II-28]:

$$\psi_i^{\alpha} = \sum_{\sigma} \chi_{\sigma} C_{\sigma i}^{\alpha} \qquad \psi_i^{\beta} = \sum_{\sigma} \chi_{\sigma} C_{\sigma i}^{\beta} \tag{III-11}$$

The linear expansion coefficients, $C^{\alpha}_{\sigma i}$ and $C^{\beta}_{\sigma i}$, of the atomic orbitals, χ_{σ}, satisfy the matrix equations:

$$\mathbb{F}^{\alpha}\mathbb{C}_i^{\ \alpha} = \mathbb{S}\ \mathbb{C}_i^{\ \beta}\varepsilon_i^{\ \beta} \qquad\qquad \mathbb{F}^{\beta}\mathbb{C}_i^{\ \beta} = \mathbb{S}\ \mathbb{C}_i^{\ \beta}\varepsilon_i^{\ \beta} \qquad\qquad [\text{III-12}]$$

where $\mathbb{S}$ is the overlap matrix with elements:

$$S_{\sigma\nu} = \langle\chi_{\sigma}|\chi_{\nu}\rangle \qquad\qquad [\text{III-13}]$$

$\varepsilon_i^{\ \alpha}$ and $\varepsilon_i^{\ \beta}$ are orbital energies, and $\mathbb{F}^{\alpha}$ and $\mathbb{F}^{\beta}$ are the unrestricted Hartree-Fock matrices. We define α and β bond-order matrices, $\mathbb{P}^{\alpha}$ and $\mathbb{P}^{\beta}$, with elements:

$$P_{\lambda\sigma}^{\ \alpha} = \sum_{i}^{N} C^{\alpha *}_{\lambda i}\ C^{\alpha}_{\sigma i} \qquad\qquad P_{\lambda\sigma}^{\ \beta} = \sum_{i}^{N} C^{\beta *}_{\lambda i}\ C^{\beta}_{\sigma i} \qquad\qquad [\text{III-14}]$$

and a spin-density matrix, ρ, as:

$$\rho = \mathbb{P}^{\alpha} - \mathbb{P}^{\beta} \qquad\qquad [\text{III-15}]$$

The total bond-order matrix, $\mathbb{P}$, is

$$\mathbb{P} = \mathbb{P}^{\alpha} + \mathbb{P}^{\beta} \qquad\qquad [\text{III-16}]$$

The Fock matrices, $\mathbb{F}^{\alpha}$ and $\mathbb{F}^{\beta}$, are divided into a one-electron part, $\mathbb{H}$, which includes the kinetic energy of the electrons and the potential energy of their attraction for the nuclei, and two-electron parts, $\mathbb{G}^{\alpha}$ and $\mathbb{G}^{\beta}$, which describe the inter-electronic repulsions:

$$\mathbb{F}^{\alpha} = \mathbb{H} + \mathbb{G}^{\alpha} \qquad\qquad \mathbb{F}^{\beta} = \mathbb{H} + \mathbb{G}^{\beta} \qquad\qquad [\text{III-17}]$$

The elements of the two-electron matrices are:

$$G_{\sigma\nu}^{\ \alpha} = \sum_{\lambda\omega} [P_{\lambda\omega}\langle\sigma\nu|\lambda\omega\rangle - P^{\alpha}_{\lambda\omega}\langle\sigma\omega|\lambda\nu\rangle] \qquad G_{\sigma\nu}^{\ \beta} = \sum_{\lambda\omega} [P_{\lambda\omega}\langle\sigma\nu|\lambda\omega\rangle - P_{\lambda\omega}^{\ \beta}\langle\sigma\omega|\lambda\nu\rangle] \qquad [\text{III-18}]$$

The two-electron integrals, $\langle\sigma\nu|\lambda\omega\rangle$, are defined in Appendix B. The elements of the one-electron matrix, $\mathbb{H}$, are:

$$H_{\sigma\nu} = \langle\chi_\sigma|h|\chi_\nu\rangle \qquad [III\text{-}19]$$

where h contains all the one-electron operators for the molecule of interest. The self-consistent nature of the method may be seen from the fact that although the Fock matrices, $\mathbb{F}^\alpha$ and $\mathbb{F}^\beta$, are required in Equations [III-12] to solve for the coefficients, $\mathbb{C}^\alpha$ and $\mathbb{C}^\beta$, the Fock matrices themselves depend on the coefficients, through Equations [III-17], [III-18] and [III-14]. The equations are therefore solved by an iterative procedure in which initial coefficient matrices are guessed, then bond-order matrices calculated from [III-14] to give Fock matrices from [III-18] and [III-17] which are used in [III-12] to obtain new coefficient matrices. The process is repeated until a desired degree of self-consistency is obtained.

The FPT method consists of the same procedure as just outlined except that the one-electron part of the Fock matrix is modified by the addition of a one-electron form of the nuclear spin coupling Hamiltonian. It may be seen from Equation [III-2] that the perturbation operator, $\mu_A H_A$, is a sum of one-electron operators. It is inserted into the MO expressions by adding to $\mathbb{H}$ a one-electron perturbation matrix, $\mathbb{h}_A$, with elements:

$$h^A_{\sigma\nu} = (\pm\,\tfrac{1}{2})\,\frac{16\pi}{3}\,\beta\mu_A\langle\chi_\sigma|\delta(r_A)|\chi_\nu\rangle \qquad [III\text{-}20]$$

The factor $\frac{1}{2}$ comes from the electron spin operator in H_A which acts on the spin functions $\alpha(k)$ and $\beta(k)$ of Ψ. The positive sign applies when $\mathbb{h}_A$ is added to the α-Fock matrix and the negative sign when $\mathbb{h}_A$ is part of the β-Fock matrix. The elements of the perturbed Fock matrices used in the FPT calculation are therefore:

$$\begin{aligned} F^\alpha_{\sigma\nu} &= H_{\sigma\nu} + \frac{8\pi}{3}\,\beta\mu_A\langle\chi_\sigma|\delta(r_A)|\chi_\nu\rangle + G^\alpha_{\sigma\nu} \\ F^\beta_{\sigma\nu} &= H_{\sigma\nu} - \frac{8\pi}{3}\,\beta\mu_A\langle\chi_\sigma|\delta(r_A)|\chi_\nu\rangle + G^\beta_{\sigma\nu} \end{aligned} \qquad [III\text{-}21]$$

If, as in most cases, the unperturbed molecule has a closed-shell electronic structure, then in the absence of the perturbation ($\mu_A = 0$) there is no electron spin polarization ($\rho = 0$) and the α and β Fock matrices become identical. The solution is then just that for the unperturbed, closed-shell molecule. If the perturbation is present, the perturbed wavefunction, $\Psi(\mu_A)$, is obtained in terms of the perturbed MO coefficient matrices, $\mathbb{C}^\alpha$ and $\mathbb{C}^\beta$.

Now that we have obtained the wavefunction, $\Psi(\mu_A)$, for the system in the presence of the perturbation μ_A we consider the evaluation of the integral

$$<\Psi(\mu_A)|H_B|\Psi(\mu_A)> \qquad [III-22]$$

In this form both the wavefunction, $\Psi(\mu_A)$, and the operator, H_B, are many-electron functions. However, as explained above, the molecular orbital approach is to replace these functions with products of one-electron functions. When the wavefunction defined in Equation [III-10] is used, the integral becomes:

$$<\Psi(\mu_A)|H_B|\Psi(\mu_A)>= \sum_{i=1}^{N} [<\psi_i^\alpha|h_B|\psi_i^\alpha> - <\psi_i^\beta|h_B|\psi_i^\beta>] \qquad [III-23]$$

where $$h_B = \frac{8\pi}{3} \beta\delta(r_B) \qquad [III-24]$$

i.e., h_B is the one-electron version of H_B with the electron spin operation completed. If we now introduce the LCAO expansion and the definitions of the bond-order and spin density matrices given above we obtain:

$$<\Psi(\mu_A)|H_B|\Psi(\mu_A)> = \sum_{\sigma\nu} [P_{\sigma\nu}^{\alpha} - P_{\sigma\nu}^{\beta}]\, h_{\sigma\nu}^{B} \qquad [III-25]$$

$$= \sum \rho_{\sigma\nu}(\mu_A)\, h_{\sigma\nu}^{B} \qquad [III-26]$$

where $$h_{\sigma\nu}^{B} = <\chi_\sigma|h_B|\chi_\nu> \qquad [III-27]$$

$$= \frac{8\pi}{3} \beta <\chi_\sigma|\delta(r_B)|\chi_\nu> \qquad [III-28]$$

Here we have written $\rho_{\sigma\nu}(\mu_A)$ to emphasize that this factor contains all the μ_A dependence of Equation [III-25].

Following from Equation [III-9] we now take the derivative with respect to μ_A and write the energy we seek as:

$$E_{AB}^{(2)} = \frac{8\pi}{3} \beta \sum_{\sigma\nu} \langle\chi_\sigma|\delta(r_B)|\chi_\nu\rangle \left[\frac{\partial\rho_{\sigma\nu}(\mu_A)}{\partial\mu_A}\right]_{\mu_A = 0} \qquad \text{[III-29]}$$

This equation may be used to apply the FPT method with any unrestricted LCAO-SCF wavefunction. However, certain practical simplifications may be made in the case of semi-empirical wavefunctions such as the INDO(4) (Intermediate Neglect of Differential Overlap) method used in the present study (see Appendix B).

Under the INDO approximation, only valence-shell atomic orbitals are included in the basis set so that the integrals appearing in the FPT equations are zero except as follows:

$$\langle\chi_\sigma|\delta(r_A)|\chi_\nu\rangle = S_A^2(o) \text{ if } \sigma = \nu = \text{valence s-orbital of atom A} \qquad \text{[III-30]}$$

$$\langle\chi_\sigma|\delta(r_B)|\chi_\nu\rangle = S_B^2(o) \text{ if } \sigma = \nu = \text{valence s-orbital of atom B} \qquad \text{[III-31]}$$

where $S_N^2(o)$ is the density of the valence s-orbital of atom N evaluated at the nucleus. At this level of MO theory then, the perturbation matrix elements in Equations [III-20] and [III-21] are zero unless $\sigma = \nu =$ the valence s orbital of atom A, in which case the perturbation element $h_{\sigma\nu}^A$ becomes:

$$h^A = \frac{8\pi}{3} \beta\mu_A S_A^2(o) \qquad \text{[III-32]}$$

and the only element of the spin density matrix appearing in Equation [III-29] is $\rho_{s_B s_B}$, the diagonal element corresponding to the valence s orbital of atom B. To implement the perturbation, h^A is added to the diagonal element of the α-Fock matrix corresponding to the s orbital of atom A and $(-h^A)$ is added to the corresponding element of the β-Fock matrix.

It is now more convenient to write the derivative in Equation [III-29] as one with respect to the actual perturbation used, h^A, rather than μ_A. To do this we note:

$$\frac{\partial \rho_{s_B s_B}}{\partial \mu_A} = \left(\frac{\partial \rho_{s_B s_B}}{\partial h^A}\right)\left(\frac{\partial h^A}{\partial \mu_A}\right) \qquad [III-33]$$

and:

$$\frac{\partial h^A}{\partial \mu_A} = \frac{8\pi}{3}\beta\, S_A^2(o) \qquad [III-34]$$

so that:

$$\left[\frac{\partial \rho_{s_B s_B}(\mu_A)}{\partial \mu_A}\right]_{\mu_A=0} = \frac{8\pi}{3}\beta\, S_A^2(o)\left[\frac{\partial \rho_{s_B s_B}(h^A)}{\partial h^A}\right]_{h^A=0} \qquad [III-35]$$

Substitution of [III-30], [III-31] and [III-35] into Equation [III-29] yields:

$$E_{AB}^{(2)} = \left[\frac{8\pi}{3}\beta\right]^2 S_A^2(o)\, S_B^2(o)\left[\frac{\partial \rho_{s_B s_B}(h^A)}{\partial h^A}\right]_{h^A=0} \qquad [III-36]$$

The final simplification introduced by Pople, McIver and Ostlund(3) was to calculate the derivative in Equation [III-36] using a finite difference method. They derived from the Newton-Stirling formula(55) the approximate expression:

$$\left[\frac{\partial \rho(h)}{\partial h}\right]_{h=0} \approx \frac{\rho(h) - \rho(-h)}{h - (-h)} \qquad [III-37]$$

However, the spin density is an odd function of the contact perturbation, i.e.

$$\rho(h) = -\rho(-h) \qquad [III-38]$$

so that:

$$\left[\frac{\partial \rho(h)}{\partial h}\right]_{h=0} \approx \frac{\rho(h)}{h} \qquad [III-39]$$

The final expression for the perturbation energy is therefore approximated by:

$$E_{AB}^{(2)} = \left[\frac{8\pi\beta}{3}\right]^2 S_A^2(o)\, S_B^2(o)\left[\frac{\rho_{s_B s_B}(h^A)}{h^A}\right] \qquad [III-40]$$

The validity of the finite difference approximation is discussed in detail in reference 2. The value of the perturbation, h^A, must be chosen so that it is small enough for the approximation to be valid but large enough so that rounding errors which occur when the difference is taken are negligible. The other computational factor to be considered is the degree of convergence to be required of the SCF procedure so that errors in the calculated spin density are negligible. The criterion of convergence used was that the root-mean-square difference between two successive density matrices of dimension N:

$$\sum_{\sigma}^{N} \sum_{\nu}^{N} [P_{\sigma\nu} - P'_{\sigma\nu}]^{1/2}/N$$

should be less than a quantity Δ. Pople and coworkers found optimum values of $h^A = 10^{-3}$ and $\Delta = 10^{-9}$. For proton-proton couplings these values gave an error of about 10^{-4} Hz with slightly larger values for heavier nuclei. A further check of the computational accuracy was obtained by calculating the coupling constant between a given pair of nuclei A and B by first placing the perturbation on nucleus A and then on nucleus B. The discrepancy in the derivative $\rho(h)/h$ in the two calculations was found to be less than 10^{-6}.

3. Comparison with the SOS Method

The chief advantages of the finite perturbation method over the SOS approach are:

(a) The FPT method recognizes the SCF nature of the MO wavefunctions in a consistent manner. Hence the perturbed wavefunction which is obtained includes the desirable features of electron-electron repulsion to the same level of approximation as the corresponding unperturbed wavefunction.

(b) The method is computationally more powerful in that a single SCF calculation gives values for the coupling constants between a given nucleus and all the other nuclei in the molecule. In the SOS method a separate calculation is required for each pair of nuclei.

A comparison between the SOS and FPT methods was performed by Ditchfield, Ostlund, Murrell and Turpin(56). They found that the FPT and SOS methods could give quite different numerical results for the same property. To seek the source of this disagreement they took the FPT equations and from them derived an expression for the second-order energy which could be directly compared with the SOS expression. They concluded that the difference between the two methods was equivalent to including some doubly excited as well as singly excited states in the SOS expansion. They also found that the magnitude of the difference in numerical values given by the two methods depends on the molecule and the property being considered and is large when configuration interaction (CI) is important in describing the unperturbed wavefunction.

Ditchfield et al made numerical comparisons between the SOS and FPT methods by calculating the electrical polarizability and nuclear spin coupling constant for the hydrogen molecule using the extended basis set MO wavefunction of Fraga and Ransil(57). They obtained a polarizability value much closer to the accurate value (from an extensive variational calculation(58)) with the FPT approach than with the SOS method, even when the latter was used with configuration interaction. On the other hand, the coupling constant of H_2 calculated by FPT was intermediate in accuracy (with respect to the experimental value) between the SOS values with and without CI.

These results indicate that both configuration interaction and the use of a self-consistent perturbation theory can lead to improved agreement between theory and experiment for properties calculated by second-order perturbation theory. In the present study our approach is to seek further improvements to and extensions of the perturbation theory.

CHAPTER IV. SELF-CONSISTENT PERTURBATION THEORY

1. Introduction

In this chapter we present the self-consistent-field perturbation theory (SCFPT) which forms the basis for the numerical coupling constant calculations which were performed in this study. The method combines certain desirable features of the FPT and SOS theories described previously and adds a considerable improvement in computational efficiency. Like the FPT approach, the SCFPT method is a truely self-consistent type of perturbation theory but instead of evaluating the derivative in the second-order energy expression [III-9] by a numerical method as does FPT, it follows the rather more elegant approach of the SOS theory by using an explicit expression for the energy in terms of the unperturbed wavefunction and the perturbation Hamiltonian. This explicit energy expression avoids some important computational difficulties inherent in the FPT method but, unlike the SOS method, takes proper account of the SCF nature of the MO wavefunctions employed.

Due to the rather complicated nature of the SCFPT theory presented in this chapter we give below a general outline of the derivation procedure which will be followed. The complication arises partly because the equations defining the method are quite involved and partly because the theory is applied in detail to all three nuclear spin coupling mechanisms.

Expressions for the coupling constant, J_{AB}, will be obtained, as in the FPT and SOS methods, by comparing expressions for the second-order perturbation energy, $E_{AB}^{(2)}$, with the equation defining J_{AB}, Equation [I-7]. Expressions for $E_{AB}^{(2)}$ will be obtained in two steps:

(i) For each coupling mechanism the general expression for the second-order energy, Equation [III-9], will be cast into molecular orbital form. In each case this involves first considering what effect the particular perturbation will have on the electronic wavefunction for the molecule and then choosing a form for the MO wavefunction which will be able to accommodate that perturbation. For example it has already been shown that the contact interaction induces polarization of the electron spins and so a spin-unrestricted MO wavefunction is necessary. Once the form the the wavefunction has been decided, the many-electron integral in Equation [III-9] can be re-written in MO notation. For each coupling mechanism, $E_{AB}^{(2)}$ will be written as a function of the unperturbed MO coefficients, $\mathbb{C}^{(0)}$, and the first-order perturbation, $\mathbb{C}^{(1)}$, to these coefficients.

(ii) As the second step, detailed equations will be given which permit $\mathbb{C}^{(1)}$ to be calculated from a knowledge of $\mathbb{C}^{(0)}$ and the Hamiltonian operator for each coupling mechanism. These equations will be given in terms of the INDO molecular orbital method.

In step (ii) use will be made of a general expression relating $\mathbb{C}^{(1)}$ to $\mathbb{C}^{(0)}$. This expression is independent of the type of MO theory and of the particular coupling mechanism. It can therefore serve as the basis for an SCF perturbation theory using, for example, ab initio MO wavefunctions and can be applied to any problem susceptible to study by perturbation theory. It may be regarded as the fundamental equation of the SCFPT method and is derived in the following section.

2. The Basic Formulation

In this section a general expression is derived which permits the first-order perturbation to a set of self-consistent-field molecular orbitals to be obtained from the unperturbed orbitals and orbital energies. First, however, we give the definitions and notation used to describe the unperturbed molecule in MO terms.

We will assume that in its unperturbed form, the molecule is in its electronic ground state with a closed-shell electron configuration, that is one with 2N electrons in N doubly-occupied molecular orbitals (MO's), each with an electron of α- and β-spin. The MO's, $\psi_1, \psi_2, \ldots, \psi_N$, are arranged in a single determinantal wavefunction, Ψ, explicitly shown in Equation [II-20]. Each MO is expressed as a linear combination of m atomic orbital (AO) basis functions, $\chi_1, \chi_2, \ldots, \chi_m$.

i.e., $$\psi_j = \sum_{\sigma=1}^{m} \chi_\sigma C_{\sigma j}^{(0)} \qquad \text{[IV-1]}$$

or, in matrix notation:

$$\boldsymbol{\psi} = \boldsymbol{\chi}\, \mathbb{C}^{(0)} \qquad \text{[IV-2]}$$

where: $\boldsymbol{\psi}$ and $\boldsymbol{\chi}$ are row vectors of length N and m respectively;

$\mathbb{C}^{(0)}$ is an mxm matrix of the coefficients $C_{\sigma j}^{(0)}$;

σ is a row index labelling the basis function; and

j is a column index labelling the MO.

Unless otherwise stated, the subscripts i and j will be reserved for labelling MO's and the Greek subscripts, σ, ν, λ, ω for labelling the basis functions.

The MO coefficients are obtained as solutions to the SCF eigenvalue equations

$$\mathbb{F}^{(0)}\, \mathbb{C}^{(0)} = \mathbb{S}\, \mathbb{C}^{(0)}\, \mathbb{E}^{(0)} \qquad \text{[IV-3]}$$

where: $\mathbb{E}^{(0)}$ is the diagonal matrix of orbital energies, $\varepsilon_j^{(0)}$;

$\mathbb{S}$ is the overlap matrix, with elements $S_{\sigma\nu} = \langle\chi_\sigma|\chi_\nu\rangle$ [IV-4]

$\mathbb{F}^{(0)}$ is the Hartree-Fock Hamiltonian matrix, with elements

$$F_{\sigma\nu}^{(0)} = H_{\sigma\nu}^{(0)} + G_{\sigma\nu}^{(0)} \qquad \text{[IV-5]}$$

$$H^{(0)}_{\sigma\nu} = \langle\chi_\sigma|h|\chi_\nu\rangle \qquad \text{[IV-6]}$$

$$G^{(0)}_{\sigma\nu} = \sum_\lambda \sum_\omega P^{(0)}_{\lambda\omega}[\langle\sigma\nu|\lambda\omega\rangle - \frac{1}{2}\langle\sigma\omega|\lambda\nu\rangle] \qquad \text{[IV-7]}$$

$$P^{(0)}_{\lambda\omega} = 2 \sum_i^{occ} C^{(0)*}_{\lambda i} C^{(0)}_{\omega i} \qquad \text{[IV-8]}$$

$$\langle\sigma\nu|\lambda\omega\rangle = \iint \chi^*_\sigma(1)\chi_\nu(1)(1/r_{12})\chi^*_\lambda(2)\chi_\omega(2)d\tau_1 d\tau_2 \qquad \text{[IV-9]}$$

h represents those operators in the Hamiltonian which are functions of one electron only (i.e., the electron kinetic energy, and the electron-nucleus attraction potential);

$\mathbb{G}^{(0)}$ represents the repulsive interaction between pairs of electrons; and

$\mathbb{P}^{(0)}$ is referred to as the bond-order or density matrix.

In the following development we will assume that the AO basis functions form an orthonormal set, so that the overlap matrix becomes the unit matrix, $\mathbb{I}$

$$S_{\sigma\nu} = \langle\chi_\sigma|\chi_\nu\rangle = \delta_{\sigma\nu} \quad \text{[IV-10]} \quad \text{i.e., } \mathbb{S} = \mathbb{I} \qquad \text{[IV-11]}$$

This does not detract from the generality of the theory since any basis set of atomic orbitals can always be transformed into an orthonormal set. However, this assumption does simplify the notation and permits the orthonormality condition for the MO's to be concisely stated.

For any occupied MO's i and j we require:

$$\langle\psi_i|\psi_j\rangle = \delta_{ij} \qquad \text{[IV-12]}$$

Introduction of the expansion [IV-1] yields:

$$\sum_\sigma \sum_\nu \langle\chi_\sigma C^{(0)}_{\sigma i}|\chi_\nu C^{(0)}_{\nu j}\rangle = \delta_{ij} \qquad \text{[IV-13]}$$

$$\therefore \sum_\sigma \sum_\nu C^{(0)*}_{\sigma i} S_{\sigma\nu} C^{(0)}_{\nu j} = \delta_{ij} \qquad \text{[IV-14]}$$

or, in matrix notation,

$$\mathbb{C}^{(0)\dagger}_i \mathbb{S}\, \mathbb{C}^{(0)}_j = \delta_{ij} \qquad \text{[IV-15]}$$

so that if condition [IV-11] holds, the orthonormality condition for the MO's is simply:

$$\mathbb{C}_i^{(0)\dagger}\ \mathbb{C}_j^{(0)} = \delta_{ij} \qquad [\text{IV-16}]$$

Also, with this assumption, the SCF eigenvalue equations become:

$$\mathbb{F}^{(0)}\ \mathbb{C}^{(0)} = \mathbb{C}^{(0)}\ \mathbb{E}^{(0)} \qquad [\text{IV-17}]$$

Since $\mathbb{F}^{(0)}$ depends on $\mathbb{C}^{(0)}$ through $\mathbb{P}^{(0)}$, these equations are solved by iteration, yielding a set of unperturbed molecular orbitals and orbital energies.

In the presence of the perturbing nuclear spins, a corresponding set of SCF equations may be written in terms of the perturbed quantities:

$$\mathbb{F}\ \mathbb{C} = \mathbb{C}\ \mathbb{E} \qquad [\text{IV-18}]$$

As in the development of the SOS perturbation theory we expand all the perturbed quantities of interest as power series in a perturbation parameter μ.

e.g., $$\mathbb{C} = \mathbb{C}^{(0)} + \mu\ \mathbb{C}^{(1)} + \ldots.. \qquad [\text{IV-19}]$$

with similar expansions for $\mathbb{F}$, $\mathbb{P}$ and $\mathbb{E}$. When these expansions are substituted into [IV-18] and coefficients of the first power of μ are equated we obtain the first-order perturbation equation:

$$\mathbb{F}^{(0)}\ \mathbb{C}^{(1)} + \mathbb{F}^{(1)}\ \mathbb{C}^{(0)} = \mathbb{C}^{(0)}\ \mathbb{E}^{(1)} + \mathbb{C}^{(1)}\ \mathbb{E}^{(0)} \qquad [\text{IV-20}]$$

Since our aim is to calculate the second-order change in the energy, we shall need only to consider first-order perturbations, $\mathbb{C}^{(1)}$, to the MO coefficient matrix (reference 59). We shall seek an expression for $\mathbb{C}^{(1)}$ as a linear combination of the zero-order MO's:

$$\mathbb{C}^{(1)} = \mathbb{C}^{(0)}\ \mathbb{A} \qquad [\text{IV-21}]$$

where $\mathbb{A}$ is a matrix of expansion coefficients.

The first step in finding an expression for $\mathbb{A}$ is to examine the consequences of the orthogonality condition [IV-16]. Applied to the matrix of perturbed MO coefficients this requires that:

$$\mathbb{C}^{\dagger}\mathbb{C} = \mathbb{I} \qquad \text{[IV-22]}$$

where $\mathbb{I}$ is the unit matrix.

If we substitute the expansion [IV-19] into [IV-22] and equate corresponding powers of μ, we obtain,

for the zero-order case: $\mathbb{C}^{(0)\dagger}\mathbb{C}^{(0)} = \mathbb{I}$ [IV-23]

and the first-order condition: $\mathbb{C}^{(1)\dagger}\mathbb{C}^{(0)} + \mathbb{C}^{(0)\dagger}\mathbb{C}^{(1)} = 0$ [IV-24]

and so: $\mathbb{A}^{\dagger} + \mathbb{A} = 0$ [IV-25]

From [IV-25] it is clear that $\mathbb{A}$ is a skew symmetric matrix with

$$A_{ij} = -A_{ji}^{*} \qquad \text{[IV-26]}$$

To satisfy the condition [IV-26], we set

$$A_{ii} = 0 \qquad \text{[IV-27]}$$

The elements of $\mathbb{A}$ may be calculated from the first-order perturbation equation [IV-20]. Substitution of [IV-21] into [IV-20] and rearranging terms gives:

$$\mathbb{C}^{(0)}\,\mathbb{E}^{(0)}\,\mathbb{A} - \mathbb{C}^{(0)}\,\mathbb{A}\,\mathbb{E}^{(0)} = \mathbb{C}^{(0)}\,\mathbb{E}^{(1)} - \mathbb{F}^{(1)}\,\mathbb{C}^{(0)} \qquad \text{[IV-28]}$$

Multiply on the left by $\mathbb{C}^{(0)\dagger}$ and simplify by means of [IV-17] and [IV-23] to obtain:

$$\mathbb{E}^{(0)}\,\mathbb{A} - \mathbb{A}\,\mathbb{E}^{(0)} = \mathbb{E}^{(1)} - \mathbb{C}^{(0)\dagger}\,\mathbb{F}^{(1)}\,\mathbb{C}^{(0)} \qquad \text{[IV-29]}$$

Since $\mathbb{E}^{(0)}$ and $\mathbb{E}^{(1)}$ are diagonal matrices and $A_{ii} = 0$, we may obtain from this equation the relationship:

$$A_{ij} = \frac{-f_{ij}^{(1)}}{(\epsilon_i^{(0)} - \epsilon_j^{(0)})} \qquad i \neq j \qquad \text{[IV-30]}$$

where
$$f_{ij}^{(1)} = \sum_{\lambda}\sum_{\nu} C_{\lambda i}^{(0)*} F_{\lambda\nu}^{(1)} C_{\nu j}^{(0)} \qquad \text{[IV-31]}$$

$$= \mathbb{C}_i^{(0)\dagger}\, \mathbb{F}^{(1)}\, \mathbb{C}_j^{(0)} \qquad \text{[IV-32]}$$

From [IV-21] and [IV-27] we have:

$$C_{\sigma j}^{(1)} = {\sum_i}' C_{\sigma i}^{(0)} A_{ij} \qquad \text{[IV-33]}$$

where the prime indicates that the summation is to exclude the term in which $i = j$. Now from [IV-30] it is clear that A_{ij} is indefinite when $\varepsilon_i^{(0)} = \varepsilon_j^{(0)}$. A simple way to ensure that this singularity never causes difficulty is to restrict the summation in [IV-33] to vacant MO's i. The expression for the coefficients of the first-order perturbation to an occupied MO j then becomes:

$$C_{\sigma j}^{(1)} = -\sum_i^{\mathrm{vac}} C_{\sigma i}^{(0)} \sum_{\lambda}\sum_{\nu} \frac{C_{\lambda i}^{(0)*} F_{\lambda\nu}^{(1)} C_{\nu j}^{(0)}}{(\varepsilon_i^{(0)} - \varepsilon_j^{(0)})} \qquad j \text{ occ} \qquad \text{[IV-34]}$$

or
$$\mathbb{C}_j^{(1)} = \sum_i^{\mathrm{vac}} \left[\frac{\mathbb{C}_i^{(0)}\, \mathbb{C}_i^{(0)\dagger}}{(\varepsilon_j^{(0)} - \varepsilon_i^{(0)})}\right] \mathbb{F}^{(1)}\, \mathbb{C}_j^{(0)} \qquad j \text{ occ} \qquad \text{[IV-35]}$$

Restriction of the summation in these expressions to vacant orbitals i corresponds to neglect of the mixing between occupied orbitals. Such mixing among occupied orbitals corresponds to a transformation among them and does not change the values calculated for first-order properties of the system. For example, consider the first-order bond-order:

$$P_{\sigma\nu}^{(1)} = 2 \sum_j^{\mathrm{occ}} [C_{\sigma j}^{(1)*} C_{\nu j}^{(0)} + C_{\sigma j}^{(0)*} C_{\nu j}^{(1)}] \qquad \text{[IV-36]}$$

If we substitute the full expansion [IV-33] for the first order MO coefficients we obtain:

$$\begin{aligned} P^{(1)}_{\sigma\nu} &= 2 \sum_{j}^{occ} \sum_{i}{}' \, [C^{(0)*}_{\sigma i} C^{(0)}_{\nu j} + C^{(0)*}_{cj} C^{(0)}_{\nu i}] A_{ij} \\ &= 2 \sum_{j}^{occ} \sum_{i}^{vac} [C^{(0)*}_{\sigma i} C^{(0)}_{\nu j} + C^{(0)*}_{\sigma j} C^{(0)}_{\nu i}] A_{ij} \\ &+ 2 \sum_{j}^{occ} \sum_{i}^{occ} [C^{(0)*}_{\sigma i} C^{(0)}_{\nu j} A_{ij} + C^{(0)*}_{\sigma j} C^{(0)}_{\nu i} A_{ij}] \\ &= 2 \sum_{j}^{occ} \sum_{i}^{vac} [C^{(0)*}_{\sigma i} C^{(0)}_{\nu i} + C^{(0)*}_{\sigma j} C^{(0)}_{\nu i}] A_{ij} \\ &+ 2 \sum_{j}^{occ} \sum_{i}^{occ} C^{(0)*}_{\sigma i} C^{(0)}_{\nu j} \, [A_{ij} + A_{ji}] \end{aligned} \qquad [IV-37]$$

But from [IV-25] we have $A_{ij} + A_{ji} = 0$ [IV-38]

and so

$$P^{(1)}_{\sigma\nu} = 2 \sum_{j}^{occ} \sum_{i}^{vac} [C^{(0)*}_{\sigma i} C^{(0)}_{\nu j} + C^{(0)*}_{\sigma j} C^{(0)}_{\nu i}] A_{ij} \qquad [IV-39]$$

Therefore, if we restrict the summation in [IV-33] to vacant orbitals only we still obtain the correct expression for the first-order bond-order. A somewhat more general consideration of this restricted summation in terms of projection operators has been given by McWeeny(59).

Equation [IV-35] is the fundamental equation of our first-order SCF perturbation theory. Given an unperturbed set of molecular orbitals, $\mathbb{C}_j^{(0)}$, and orbital energies, $\varepsilon_j^{(0)}$, and a specific form for a one-electron perturbation, equation [IV-35] may be used as the basis for an iterative calculation of the first-order perturbation to the wavefunction. Note that the matrix in square brackets in [IV-35] is independent of the perturbation and therefore need not be re-calculated at each iteration.

In the following sections of this chapter we apply second-order SCF perturbation theory to the three nuclear spin coupling mechanisms described in Chapter I. However, before continuing there are a few general remarks which may appropriately be made at this point.

The perturbation operators given in Chapter I were written as sums of operators each acting on the coordinates of one electron only and were also summed over all the nuclei, N, in the molecule. In the treatments which follow we shall need to deal with the individual one-electron operators and to specify individual nuclei giving rise to the perturbation. The one-electron perturbation operators and corresponding matrix elements will be indicated by lower case letters and the nuclei will be indicated by the letter N as a subscript or superscript. Thus a one-electron perturbation operator describing the interaction between an electron and a nucleus N will be represented as

$$\mu_N h_N \qquad [IV\text{-}40]$$

where μ_N is the magnetic moment of nucleus N and will be used as the perturbation parameter. Under the influence of this perturbation, the one-electron part, $\mathbb{H}$, of the Fock matrix, $\mathbb{F}$, becomes:

$$\mathbb{H} = \mathbb{H}^{(0)} + \mu_N \mathbb{h}_N \qquad [IV\text{-}41]$$

where the elements of $\mathbb{h}_N$ are given by:

$$h^N_{\sigma\nu} = \langle\chi_\sigma|h_N|\chi_\nu\rangle \qquad [IV\text{-}42]$$

The Fock matrix for the perturbed molecule is then

$$\mathbb{F} = \mathbb{H} + \mathbb{G} \qquad [IV\text{-}43]$$

where the elements of $\mathbb{G}$ will now be functions of the perturbed bond-order matrix.

It is worth noting here that the perturbation makes itself felt in two ways in an SCF treatment. First, through h_N, by directly modifying the

Hamiltonian for each electron, and secondly through $\mathbb{G}$, since the perturbation modifies the average electronic field, as reflected by the density matrix, experienced by any given electron. This is of course the fundamental reason for using self-consistent perturbation theory and is essentially the same reason that an SCF method is used for the unperturbed system.

In the following sections we use the SCFPT expression [IV-35] for $\mathbb{C}_j^{(1)}$ in the scheme outlined at the beginning of this chapter to obtain expressions for the three contributions to the coupling constant.

3. The Contact Interaction

Since this interaction was used to illustrate the FPT method in Chapter III, some of the equations which follow have already been given. However, they are repeated here to make the presentation complete and to serve as a model for the succeeding derivations.

We seek an expression for the contribution to the coupling constant, J_{AB}, between two nuclei, A and B, caused by the Fermi contact interaction between the spins of these nuclei and the spins of the electrons in the molecule. To do this we first obtain an expression for the second-order interaction energy, $E_{AB}^{(2)}$, in terms of the first-order perturbation, $\mathbb{C}^{(1)}$, to the MO coefficient matrix. We then show in detail how $\mathbb{C}^{(1)}$ may be obtained using the basic SCFPT equation [IV-35], the contact perturbation operator and the INDO molecular orbital method.

If we consider the perturbing spin magnetic moment, μ_A, of nucleus A to be in the z-direction, then the perturbation operator for the contact interaction is given by equation [III-2]:

$$\mu_A H_A = \frac{16\pi}{3} \beta\mu_A \sum_k \delta(\mathbb{r}_{kA}) S_{kz} \qquad \text{[IV-44]}$$

where β is the Bohr magneton, $\delta(\mathbf{r}_{kA})$ is a Dirac delta function which restricts the summation to electrons, k, in contact with nucleus A, and S_{kz} is the z-component of the spin angular momentum operator for electron k. Now since this operator will induce electron-spin polarization in the wavefunction for the molecule, we write Ψ in the unrestricted form:

$$\Psi = (2n!)^{-1/2}|\psi_1^{\alpha}(1)\alpha(1)\cdots\psi_n^{\alpha}(n)\alpha(n)\psi_1^{\beta}(n+1)\beta(n+1)\cdots\psi_n^{\beta}(2n)\beta(2n)| \qquad [IV\text{-}45]$$

Here Ψ is a product of molecular spin orbitals (MSO), each of which is a product of a space orbital, ψ_i^{α} or ψ_i^{β}, and a spin orbital, α or β. In order to accommodate the contact perturbation, we permit the spatial molecular orbitals, ψ_i^{α} and ψ_i^{β}, belonging to a given MSO, to be different. However, for a closed-shell molecule, the total number, n, of electrons with α-spin remains equal to the total number of electrons with β-spin.

The function specified above may be substituted for $\Psi(\mu_A)$ in equation [III-9] to obtain an MO expression for $E_{AB}^{(2)}$. If we take account of the indistinguishability of the electrons and operate with S_{kz} on the spin parts of the orbitals, the many-electron integral in equation [III-9] reduces to:

$$\langle\Psi(\mu_A)|\ H_B|\Psi(\mu_A)\rangle = \sum_{i=1}^{n}[\langle\psi_i^{\alpha}|h_B|\psi_i^{\alpha}\rangle - \langle\psi_i^{\beta}|h_B|\psi_i^{\beta}\rangle] \qquad [IV\text{-}46]$$

Here the MO's ψ_i^{α} and ψ_i^{β} describe the electronic structure of the molecule in the presence of the perturbation due to nucleus A and are therefore functions of μ_A. The operator, h_B, is the one-electron version of H_B with the electron spin operation completed. Hence from [IV-44]:

$$h_B = \frac{8\pi}{3}\beta\ \delta(\mathbf{r}_B) \qquad [IV\text{-}47]$$

we now introduce the LCAO expansions:

$$\psi_j^{\alpha} = \sum_{\sigma}\chi_{\sigma}C_{\sigma j}^{\alpha} \qquad \psi_j^{\beta} = \sum_{\sigma}\chi_{\sigma}\ C_{\sigma j}^{\beta} \qquad [IV\text{-}48]$$

where the χ_σ are atomic orbital basis functions, and we define α and β electron density matrices:

$$P^{\alpha}_{\sigma\nu} = \sum_{j=1}^{n} C^{\alpha *}_{\sigma j} C^{\alpha}_{\nu j} \qquad P^{\beta}_{\sigma\nu} = \sum_{j}^{n} C^{\beta *}_{\sigma j} C^{\beta}_{\nu j} \qquad [IV\text{-}49]$$

When these quantities are substituted into equation [IV-46] we obtain:

$$<\Psi(\mu_A)|\ H_B|\Psi(\mu_A)> = \sum_{\sigma\nu} [P^{\alpha}_{\sigma\nu} - P^{\beta}_{\sigma\nu}]\ h^{B}_{\sigma\nu} \qquad [IV\text{-}50]$$

where $$h^{B}_{\sigma\nu} = <\chi_\sigma|h_B|\chi_\nu> \qquad [IV\text{-}51]$$

The quantity $P^{\alpha}_{\sigma\nu} - P^{\beta}_{\sigma\nu}$ is an element, $\rho_{\sigma\nu}$, of the spin density matrix, i.e.:

$$\mathbb{\rho} = \mathbb{P}^{\alpha} - \mathbb{P}^{\beta} \qquad [IV\text{-}52]$$

and contains all the μ_A dependence of equation [IV-50]. Therefore in the case of the contact interaction, equation [III-9] for the second-order energy becomes:

$$E^{(2)}_{AB} = \sum_{\sigma\nu} h^{B}_{\sigma\nu} \left(\frac{\partial\rho_{\sigma\nu}}{\partial\mu_A}\right)_{\mu_A=0} \qquad [IV\text{-}53]$$

In order to complete step (i) of the derivation scheme for this section we need to write the derivative in equation [IV-53] in terms of $\mathbb{C}^{(1)}$, the first-order perturbation to the MO coefficient matrix. First we note that from the definition [IV-52]:

$$\left(\frac{\partial\mathbb{\rho}}{\partial\mu_A}\right)_{\mu_A=0} = \left(\frac{\partial\mathbb{P}^{\alpha}}{\partial\mu_A}\right)_{\mu_A=0} - \left(\frac{\partial\mathbb{P}^{\beta}}{\partial\mu_A}\right)_{\mu_A=0} \qquad [IV\text{-}54]$$

We expand the perturbed α and β density matrices to first-order in the perturbation μ_A:

$$\mathbb{P}^{\alpha} = \mathbb{P}^{(0)} + \mu_A\ \mathbb{P}^{\alpha(1)} \qquad [IV\text{-}55]$$

$$\mathbb{P}^{\beta} = \mathbb{P}^{(0)} + \mu_A\ \mathbb{P}^{\beta(1)} \qquad [IV\text{-}56]$$

where by definition:

$$\mathbb{P}^{\alpha(1)} = \left(\frac{\partial \mathbb{P}^{\alpha}}{\partial \mu_A}\right)_{\mu_A=0} \quad \text{and} \quad \mathbb{P}^{\beta(1)} = \left(\frac{\partial \mathbb{P}^{\beta}}{\partial \mu_A}\right)_{\mu_A=0} \qquad [\text{IV-57}]$$

so that we may write:

$$\left(\frac{\partial \rho}{\partial \mu_A}\right)_{\mu_A=0} = \mathbb{P}^{\alpha(1)} - \mathbb{P}^{\beta(1)} \qquad [\text{IV-58}]$$

From the symmetry of the perturbation operator, H_A, it is clear that the α and β perturbations differ only in sign, so that:

$$\mathbb{P}^{\alpha(1)} = - \mathbb{P}^{\beta(1)} \qquad [\text{IV-59}]$$

and hence:

$$\left(\frac{\partial \rho}{\partial \mu_A}\right)_{\mu_A=0} = 2\, \mathbb{P}^{\alpha(1)} \qquad [\text{IV-60}]$$

so that it is only necessary to solve the equations for the α part of the perturbation. Finally we expand the perturbed α coefficient matrix:

$$\mathbb{C}^{\alpha} = \mathbb{C}^{(0)} + \mu_A \; \mathbb{C}^{\alpha(1)} \qquad [\text{IV-61}]$$

and substitute this with the expansion [IV-55] for $\mathbb{P}^{\alpha}$ into equation [IV-49] defining $\mathbb{P}^{\alpha}$ and equate terms first-order in μ_A to obtain:

$$P^{\alpha(1)}_{\sigma\nu} = \sum_{i=1}^{n} [C^{\alpha(1)*}_{\sigma i} \; C^{(0)}_{\nu i} + C^{(0)*}_{\sigma i} \; C^{\alpha(1)}_{\nu i}] \qquad [\text{IV-62}]$$

Note that in the above expansions, the superscript α has been omitted from the zero-order quantities because these correspond to the absence of any perturbation in which case there is no electron-spin polarization and the α and β coefficient matrices are identical.

Equations [IV-53], [IV-60] and [IV-62] permit the second-order energy $E^{(2)}_{AB}$ due to the contact interaction to be calculated from a knowledge of

$\mathbb{C}^{\alpha(1)}$, the first-order perturbation to the MO coefficient matrix. We now turn to the details of how $\mathbb{C}^{\alpha(1)}$ and $h^{B}_{\sigma\nu}$ are obtained in the particular approximations to MO theory used in the present study.

In this study we use the INDO molecular orbital method$^{(4)}$ and the one-centre approximation discussed in Chapter II. INDO employs an LCAO basis set containing only valence-shell atomic orbitals. The one-centre approximation includes in the perturbation expressions only those integrals evaluated between basis functions centred on the same atom. Under these restrictions, the only non-zero matrix elements of the type $h^{B}_{\sigma\nu}$ are those in which χ_σ and χ_ν in equation [IV-51] are valence orbitals of atom B. Furthermore, the delta function in [IV-47] ensures that these must be s-orbitals. The only non-zero contribution to $h^{B}_{\sigma\nu}$ is therefore:

$$h_{s_B s_B} = \frac{8\pi}{3} \beta \, S_B^2(0) \qquad \text{[IV-63]}$$

where $S_B^2(0)$ is the density of the valence shell s-electron at nucleus B.

In order to calculate $\mathbb{C}^{\alpha(1)}$ we make use of the basic SCFPT equation [IV-35]. In this expression all the zero-order quantities are obtained from a straightforward INDO calculation of the ground state electronic structure of the unperturbed molecule. It remains only to specify the elements of $\mathbb{F}^{\alpha(1)}$, the first-order perturbation to the α-Fock matrix.

From equation [IV-42], the general form for the perturbation to the one-electron part of $\mathbb{F}$ due to the presence of μ_A is

$$h^{A}_{\sigma\nu} = \langle\chi_\sigma|h_A|\chi_\nu\rangle$$

If we use the same reasoning as for $h^{B}_{\sigma\nu}$, the only non-zero elements of this form are:

$$h_{s_A s_A} = \frac{8\pi}{3} \beta \, S_A^2(0)$$