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*Volume 11*

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*Progress in*  
NUCLEAR MAGNETIC  
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*Volume 11*

### **Some Forthcoming Papers**

**Nuclear Magnetic Relaxation in Coupled Spin Systems** ROBERT L. VOLD  
and REGITZE R. VOLD

**Conformations of Nucleosides and Nucleotides** DAVID B. DAVIES

**NMR of Vinyl Polymers** E. KLESPER

**The NMR Spectroscopy of Carbanions and Carbocations** R. N. YOUNG

**Boron-11 NMR and Related Studies of Boron Compounds** L. J. TODD

**Tritium NMR Spectroscopy and Applications** J. A. ELVIDGE

**Broad Band Excitation Methods in NMR** D. ZIESSOW

## PREFACE

THIS complete edition of volume 11 of our review series is the first example of the format which will be adopted for future editions. The aim of the series continues to be the provision of in-depth reviews of all aspects of NMR spectroscopy, as illustrated by the articles in this volume. Thus, the articles by Dr. Kowalewski on coupling constants, and Drs Ebraheem and Webb on chemical shifts are concerned with the relationships between these NMR parameters and electronic structure, whilst articles by Dr. Mann, by Drs Aime and Milone, and by Dr. Petrosyan deal with applications of NMR to inorganic and organic chemistry. Dr. Shoolery contributes a timely article on the use of  $^{13}\text{C}$  NMR to the quantitative analysis of mixtures, particularly of naturally-occurring substances of commercial importance. The volume is fittingly completed by a review by Drs Smith, Mantsch and Saitô of the developing subject of deuterium NMR, which covers applications in physics, chemistry and biochemistry.

NMR spectroscopy is at present experiencing an exciting period of development as new experimental methods are introduced, and in future volumes in this series we will include articles by leading NMR spectroscopists describing the new techniques and their applications in chemistry, physics and biology.

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# CALCULATIONS OF NUCLEAR SPIN-SPIN COUPLING CONSTANTS

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## GLOSSARY OF ABBREVIATIONS

AO	Atomic Orbital	GTO	Gaussian Type Orbital
CGTO	Contracted Gaussian Type Orbital	INDO	Intermediate Neglect of Differential Overlap
CHF	Coupled Hartree-Fock	LCAO	Linear Combination of Atomic Orbitals
CI	Configuration Interaction	MO	Molecular Orbital
CNDO	Complete Neglect of Differential Overlap	MBPT	Many-Body Perturbation Theory
EHT	Extended Hückel Theory	PCILO	Perturbative Configuration Interaction with Localized Orbitals
FPT	Finite Perturbation Theory	PPP	Pariser-Pople-Parr



SCF	Self-Consistent Field
SCPT	Self-Consistent Perturbation Theory
SOS	Sum Over States
SOT	Sum Over Triplets
SPPA	Self-Consistent Polarization Propagator Approximation
STO	Slater Type Orbital
TDHF	Time Dependent Hartree-Fock
VB	Valence Bond

## 1. INTRODUCTION

The discovery of field-independent splittings in the NMR lines of liquids, made independently by Gutowsky *et al.*<sup>(1,2)</sup> and Hahn and Maxwell,<sup>(3,4)</sup> dates back to the initial days of nuclear magnetic resonance. They expressed the interaction energy giving rise to this fine structure as

$$E_{NN'} = h J_{NN'} \mathbf{I}_N \cdot \mathbf{I}_{N'} \quad (1.1)$$

This phenomenon has subsequently been referred to as indirect nuclear spin-spin coupling.  $J_{NN'}$  in eq (1.1) is the coupling constant between the nuclei N and N', having nuclear spins  $\mathbf{I}_N$  and  $\mathbf{I}_{N'}$ .

Not many years passed before Ramsey<sup>(5)</sup> formulated the theory of this effect in terms of the electron-coupled interactions between nuclear spins. Ramsey's estimate of the coupling constant in the HD molecule agreed well with the experimental value. A few years later McConnell<sup>(6)</sup> estimated the proton coupling constant in the CH<sub>2</sub> group as negative, using Ramsey's<sup>(5)</sup> theory and the Dirac vector model. Soon afterwards, simple computational schemes applicable to larger molecules were presented by McConnell<sup>(7)</sup> within the framework of the molecular orbital (MO) theory and by Karplus and Anderson<sup>(8,9)</sup> using the valence bond (VB) method. A considerable number of papers developing methods and reporting the results of applications were soon to follow. The achievements of this early period in calculating nuclear spin-spin coupling constants have been reviewed by Barfield and Grant.<sup>(10)</sup> In the mid-sixties Pople and Santry<sup>(11)</sup> improved the method for calculating coupling constants within the framework of MO theory by presenting a way to discard the most serious approximation inherent in the method of McConnell.<sup>(7)</sup> In the following years considerable progress was made with the MO method itself, the independent electron model being gradually replaced by the non-empirical and semi-empirical self-consistent field procedures. These new methods were soon to find their way into the area of spin-spin coupling constants. The work of the late sixties has been reviewed by Murrell.<sup>(12)</sup> Since the appearance of Murrell's review the rapidly expanding volume of reported work in this field has been reviewed on an annual basis by Grinter.<sup>(13)</sup> The purpose of the present review is to provide a complete survey of developments occurring subsequent to Murrell's paper.

The structure of the present review differs somewhat from that of its predecessors. We start by discussing the basic theory and computational methods

for calculations of coupling constants in Sections 2 and 3. Section 4 covers applications to diatomic molecules: the hydrogen and hydrogen fluoride molecules. Chapters 5 to 8 are devoted to applications for larger systems. Generally, the primary criterion for the Section division is the number of chemical bonds between the coupled nuclei—a classification used often in reviewing the experimental data. Further subdivision of the Sections is based on either the nuclear species involved or the chemical situation. The drawback of such a division is that different parts of the same paper are often mentioned in different Sections. Still, I believe that this scheme is the most tractable possible. Certain problems are too specific to be accommodated within the framework of Sections 5–8 and these are reviewed in Section 9 as special topics. Section 10 contains brief and general concluding remarks—when appropriate conclusions of a more specific nature appear in the text.

In order to facilitate comparison with experimental values, all the calculated coupling constants quoted in text and tables are given in Hertz (Hz) units. In certain cases, however, it is more appropriate to work in terms of the reduced coupling constant,<sup>(11)</sup>  $K_{NN'}$ , related to  $J_{NN'}$  by the following expression

$$K_{NN'} = 4\pi^2 J_{NN'} / h\gamma_N\gamma_{N'} \quad (1.2)$$

where  $\gamma_N$  and  $\gamma_{N'}$  are magnetogyric ratios of the N and N' nuclei. The reduced coupling constants are especially useful when comparisons are made between couplings involving different nuclei. The reduced coupling constants are given in the SI units.

As a rule, experimental values are quoted without giving references. In almost all cases the experimental data are taken from the theoretical papers in connection with which they are quoted and thus the references can be traced through these. Few exceptions to this rule are made, e.g. when all experimental data quoted in a table have been reported in a single paper. I hope that the authors of the experimental papers will excuse this procedure. The reason for adopting it is fairly obvious: it is to keep the already long reference list from becoming unwieldy.

This review covers the period from 1969. When in context, some papers from the preceding years have also been mentioned, the exclusion of other papers, reviewed previously by Barfield and Grant<sup>(10)</sup> and Murrell<sup>(12)</sup> was necessitated by the constraint of space. The coverage of the period 1969–1975 should be reasonably complete. Nevertheless, certain papers may have been overlooked, for which I apologize. The review was completed in the spring of 1976.

## 2. THE THEORY OF NUCLEAR SPIN-SPIN COUPLING

### 2.1. Basic Interactions

Following Ramsey,<sup>(5)</sup> the electron coupled interactions between the nuclear spins in molecules can be described in terms of the following Hamiltonian

$$\hat{H} = \hat{H}_{1a} + \hat{H}_{1b} + \hat{H}_2 + \hat{H}_3 \quad (2.1)$$

The first and the second terms describe the interaction between the nuclear magnetic moments and the orbital motion of the electrons and are given by the following equations

$$\hat{H}_{1a} = \frac{e\hbar}{c} \beta \sum_{N,N'} \gamma_N \gamma_{N'} \sum_k r_{kN}^{-3} r_{kN'}^{-3} \times [(\hat{\mathbf{I}}_N \cdot \hat{\mathbf{I}}_{N'}) (\mathbf{r}_{kN} \cdot \mathbf{r}_{kN'}) - (\hat{\mathbf{I}}_N \cdot \mathbf{r}_{kN'}) (\hat{\mathbf{I}}_{N'} \cdot \mathbf{r}_{kN})] \quad (2.2)$$

$$\hat{H}_{1b} = \frac{2\beta\hbar}{i} \sum_N \gamma_N \hat{\mathbf{I}}_N \cdot \sum_k r_{kN}^{-3} (\mathbf{r}_{kN} \times \nabla_k) \quad (2.3)$$

where  $\beta$  is the Bohr magneton and  $\mathbf{r}_{kN}$  is the radius vector from electron  $k$  to nucleus  $N$ .

The dipole-dipole interaction between the nuclear and electron spins is given in the following form

$$\hat{H}_2 = 2\beta\hbar \sum_N \gamma_N \sum_k [3(\hat{\mathbf{S}}_k \cdot \mathbf{r}_{kN})(\hat{\mathbf{I}}_N \cdot \mathbf{r}_{kN}) r_{kN}^{-5} - (\hat{\mathbf{S}}_k \cdot \hat{\mathbf{I}}_N) r_{kN}^{-3}] \quad (2.4)$$

where  $\hat{\mathbf{S}}_k$  denotes the spin of electron  $k$ . Equation (5) describes the interaction between the nuclear spin and electrons outside the nucleus. The electrons may, however, have a finite probability of being at the nucleus. The interaction between the nuclear and electron spin at the site of the nucleus is called the Fermi contact interaction and is given by

$$\hat{H}_3 = \frac{16\pi\beta\hbar}{3} \sum_N \gamma_N \sum_k \delta(\mathbf{r}_{kN}) \hat{\mathbf{S}}_k \cdot \hat{\mathbf{I}}_N \quad (2.5)$$

where  $\delta(\mathbf{r}_{kN})$  is the Dirac delta function and expresses the property of  $\hat{H}_3$  of operating on the wavefunction at the nucleus only.

It may be of interest to discuss the origin of these three types of interactions in somewhat more detail. All of them can be obtained in a natural way from the relativistic Dirac eqn for an electron in an external field (cf. Blinder<sup>(14)</sup>) under the assumption that the vector potential of a nucleus is that of a point dipole

$$\mathbf{A}_N = \gamma_N \frac{\hat{\mathbf{I}} \times \mathbf{r}_N}{r_N^3} \quad (2.6)$$

The orbital terms may also be derived non-relativistically by replacing the square of the momentum vector  $\hat{\mathbf{p}}^2$  in the electrostatic Hamiltonian by

$$\hat{\pi}^2 = \left( \hat{\mathbf{p}} + \frac{e}{c} \mathbf{A} \right)^2 \quad (2.7)$$

The term quadratic in  $\mathbf{A}_N$  leads to  $\hat{H}_{1a}$  and the cross term between  $\hat{\mathbf{p}}$  and  $\mathbf{A}_N$  gives rise to  $\hat{H}_{1b}$ . The electron-spin dependent terms can be obtained non-relativistically by considering the magnetic interaction between the magnetic dipole of a spinning electron and the field arising from the vector potential (2.6).

$$\mathbf{B}_N = \nabla \times \mathbf{A}_N \quad (2.8)$$

TABLE 1. Hydrogen-like relativistic corrections  $B(n,z)$  for  $s$ -states of some atoms<sup>(20,21)</sup>

Atom	Nuclear charge	Principal quantum number	$B(n,z)$
C	6	2	1.004
Si	14	3	1.023
Ge	32	4	1.125
Sn	50	5	1.348
Pb	82	6	2.592

For the details of the derivation the reader is referred to Hameka.<sup>(15)</sup> It should be noted that eqns (2.4) and (2.5) are obtained by setting the magnetic dipole moment due to electron spin to  $\mu = -2\beta\hbar$  instead of the correct  $-g_e\beta\hbar$ , where  $g_e = 2.0023$ .

The form of the magnetic dipole hyperfine Hamiltonian is correct for a point nucleus at the non-relativistic limit. The relativistic corrections of  $\hat{H}_3$  were first discussed in 1930 by Breit<sup>(16)</sup> who already pointed out that the correction factor is 3.9 for the  $2s$  shell of uranium. In Breit's original idea the hydrogen-like correction factors  $B(n,Z)$  were dependent on the principal quantum number  $n$  and nuclear charge  $Z$ . This was subsequently generalized for arbitrary  $n$ <sup>(17,18)</sup> and later also for arbitrary  $l$  and  $j$  (thus including  $\hat{H}_1$  and  $\hat{H}_2$ ).<sup>(19,20)</sup> These corrections enter calculations of the matrix elements of the magnetic dipole hyperfine Hamiltonian as simple multiplicative factors.

Despite their large magnitude for heavier elements, cf. Table 1, these corrections have been largely overlooked in the NMR literature, probably because of the paucity of theoretical calculations for the heavier elements. For example, it has been established<sup>(21)</sup> that the experimental trend for  $J_{\text{HX}}$  in the series  $\text{CH}_4$  to  $\text{PbH}_4$  can only be reproduced when relativistic corrections are included. A minor point that should be mentioned is that these relativistic corrections are calculated for the diagonal matrix elements of the hyperfine Hamiltonian, while the calculations of the spin-spin coupling constants require, strictly speaking, the off-diagonal elements between the electronic ground state and excited states.

Some confusion regarding the form of the Fermi contact interaction has been caused by the diverging second-order correction to the energy of a hydrogen atom perturbed by (2.5) (self-coupling energy,  $E_{\text{HH}}^{(2)}$ ), which was first discussed by Schwartz.<sup>(22)</sup> The consequences of this fact for the calculation of spin-spin coupling constants will be discussed in detail in connection with the presentation of variational calculations for the hydrogen molecule. Since the discussion regards the form of one of the basic interactions, it seems appropriate to review some of the problems involved here.

The first problem is to determine the correct order of magnitude of  $E_{\text{HH}}^{(2)}$ . Gregson *et al.*<sup>(23)</sup> found that

a finite value could be obtained by using an exponential approximation to the function

$$\frac{r_0}{4\pi r^2(r + r_0)^2} \quad (2.9)$$

appearing in Blinder's derivation<sup>(14)</sup> of the contact operator.  $r_0$  in (2.9) is of the order of the nuclear dimensions. A similar calculation using (2.9) was carried out by Power and Pitzer.<sup>(24)</sup> However, Moore and Moss<sup>(25)</sup> found that use of the 'Blinder operator', eqn (2.9), alone is not correct since it does not reproduce the relativistic results. Latvamaa *et al.*<sup>(26)</sup> considered the same problem at the Dirac and quantum electrodynamic levels of approximation and found that the Gregson self-coupling energies are over 100 times too large and totally unphysical. The reason is that the self-coupling energy of the hydrogen atom is dominated by contributions from the high energy (ultrarelativistic) continuum intermediate states, which precludes non-relativistic treatment.

The next problem is to determine the size of the effect of these high energy intermediate states, corresponding to a sharp structure in the perturbed wave function, on the spin-spin coupling constants. According to the summary of Pyykkö,<sup>(27)</sup> these effects are less than  $10^{-3}$  of the total value for several X-H and X-X coupling constants. Sängner and Voitländer<sup>(28)</sup> also find using variational method that the self-coupling and hetero-coupling energies are independent of each other to the order  $0(10^{-6})$ . We thus conclude that the self-coupling energy is not a relevant quantity in the present context and the form of Fermi contact interaction given by equation (2.5) may safely be used, at least for perturbation calculations, provided the relativistic corrections are taken into account for heavier nuclei.

## 2.2. The Rayleigh-Schrödinger Perturbation Theory of Nuclear Spin-spin Coupling Constants

All the interactions expressed by eqns (2.2)–(2.5) are small compared with the molecular electrostatic Hamiltonian and, thus, may be dealt with using perturbation theory. The terms which are bilinear in the coupled nuclear spins can then be selected from the perturbation expansion of the energy and equated to the phenomenological energy expression given by eqn (1.1). The electronic structure dependent factor in front of the scalar product  $\mathbf{I}_N \cdot \mathbf{I}_{N'}$  may be identified with  $hJ_{NN'}$ .

The first part of the orbital interaction,  $\hat{H}_{1a}$ , will immediately give the expression of desired form as the first-order perturbation correction to the energy; the other terms, or their combinations, will contribute in the form of second-order energy terms. A general form for this sort of second-order energy term, involving the nuclear spins  $\mathbf{I}_N$  and  $\mathbf{I}_{N'}$ , may be written as

$$E_{NN'}^{AB} = k_{NN'}^{AB} \sum_n \frac{\langle 0 | \mathbf{A}_N \cdot \mathbf{I}_N | n \rangle \langle n | \mathbf{B}_{N'} \cdot \mathbf{I}_{N'} | 0 \rangle}{E_0 - E_n} \quad (2.10)$$

where the superscript  $AB$  refers to the combination of mechanisms giving rise to the energy term.  $k_{NN'}^{AB}$  is a constant. Vector operators  $\mathbf{A}_{N'}$  and  $\mathbf{B}_{N'}$  depend on the electronic coordinates, momenta and spins and their exact form may be derived from eqns (2.3)–(2.5) for any combination of perturbations involved. The summation is carried out over all the excited states of the molecule,  $\Psi_n$  or  $|n\rangle$  with corresponding energies  $E_n$ . The symbols  $|0\rangle$  and  $E_0$  denote the ground state wavefunction  $\Psi_0$  and energy, respectively.

Equation (2.10) is not exactly of the form (1.1) but rather

$$E_{NN'} = h\mathbf{I}_N \cdot \mathbf{J}_{NN'} \cdot \mathbf{I}_{N'} \quad (2.11)$$

where it is assumed that the integrations implied by eqn (2.10) involve electron spins and coordinates only, allowing the nuclear spins to be factored out. Moreover, in going from (2.10) to (2.11) the matrix elements of vector operators  $\mathbf{A}_N$  and  $\mathbf{B}_{N'}$  are treated as vectors and the second rank coupling tensor  $\mathbf{J}_{NN'}$  is obtained by outer multiplication following the general relation

$$(\mathbf{A}_N \cdot \mathbf{I}_N)(\mathbf{B}_{N'} \cdot \mathbf{I}_{N'}) = \mathbf{I}_N \cdot (\mathbf{A}_N \mathbf{B}_{N'}) \cdot \mathbf{I}_{N'} \quad (2.12)$$

Actually, eqn (2.11) is the correct form of the electron coupled nuclear spin-spin interaction in anisotropic liquids, e.g. for samples partially oriented in nematic liquid crystals. In the absence of a preferred direction, the free tumbling of molecules will average out the eventual anisotropy, leading to the type of interaction energy expressed by eqn (1.1) with

$$J = \frac{1}{3}(J_{xx} + J_{yy} + J_{zz}) \quad (2.13)$$

When this is done expression (2.10) can be formulated in terms of the separate scalar product of nuclear spin operators and the matrix elements of operators  $\mathbf{A}_N$  and  $\mathbf{B}_{N'}$

$$E_{NN'}^{AB} = \frac{1}{3}k_{NN'}^{AB} \left( \sum_n \frac{\langle 0 | \mathbf{A}_N | n \rangle \cdot \langle n | \mathbf{B}_{N'} | 0 \rangle}{E_0 - E_n} \right) \mathbf{I}_N \cdot \mathbf{I}_{N'} \quad (2.14)$$

and each of the different contributions to  $J_{NN'}$  may be written

$$J_{NN'}^{AB} = \frac{2k_{NN'}^{AB}}{3h} \sum_n \frac{\langle 0 | \mathbf{A}_N | n \rangle \cdot \langle n | \mathbf{B}_{N'} | 0 \rangle}{E_0 - E_n} \quad (2.15)$$

where the factor of two arises because of presence of two equivalent energy terms which differ in that the two nuclei  $N$  and  $N'$  are permuted. The sum of the effects deriving from different mechanisms will give the total value of the coupling constant. Ramsey<sup>(5)</sup> has shown that all the cross-term contributions to the motionally-averaged coupling constant vanish and that the three parts of the perturbation can be treated separately. The reason for vanishing cross-terms between  $\hat{H}_{1b}$  and both  $\hat{H}_2$  and  $\hat{H}_3$  is that, in the absence of spin-orbit coupling, the excited states  $|n\rangle$  giving non-zero matrix elements of  $\hat{H}_{1b}$  are of the same multiplicity as the ground state (singlet in most cases), while only the excited triplet states can be coupled to the singlet ground state by the spin

dependent operators  $\hat{H}_2$  and  $\hat{H}_3$ . The general validity of this statement can be proved using the rules of vector coupling of angular momenta given by Condon and Shortley.<sup>(29)</sup> The cross term between  $\hat{H}_2$  and  $\hat{H}_3$  does not vanish because of multiplicity; the motional average is zero because the two operators involved have different angular dependence.

Upon substitution of the forms of the vector operators appearing in the Hamiltonian (2.3)–(2.5) into (2.15), the following expressions are obtained

$$J_{\text{NN}'}^{(1b)} = -\frac{8}{3h} \beta^2 h^2 \gamma_N \gamma_{N'} \sum_n \left\langle 0 \left| \sum_k r_{kN}^{-3} (\mathbf{r}_{kN} \times \nabla_k) \right| n \right\rangle \times \left\langle n \left| \sum_j r_{jN'}^{-3} (\mathbf{r}_{jN'} \times \nabla_j) \right| 0 \right\rangle / ({}^1E_n - E_o) \quad (2.16)$$

$$J_{\text{NN}'}^{(2)} = -\frac{8}{3h} \beta^2 h^2 \gamma_N \gamma_{N'} \sum_n \left\langle 0 \left| \sum_k 3r_{kN}^{-5} (\hat{\mathbf{S}}_k \cdot \mathbf{r}_{kN}) \mathbf{r}_{kN} - r_{kN}^{-3} \hat{\mathbf{S}}_k \right| n \right\rangle \cdot \left\langle n \left| \sum_j 3r_{jN'}^{-5} (\hat{\mathbf{S}}_j \cdot \mathbf{r}_{jN'}) \mathbf{r}_{jN'} - r_{jN'}^{-3} \hat{\mathbf{S}}_j \right| 0 \right\rangle / ({}^3E_n - E_o) \quad (2.17)$$

$$J_{\text{NN}'}^{(3)} = -\frac{2}{3h} \left( \frac{16\pi\beta\hbar}{3} \right)^2 \gamma_N \gamma_{N'} \sum_n \left\langle 0 \left| \sum_n \delta(\mathbf{r}_{kN}) \hat{\mathbf{S}}_k \right| n \right\rangle \times \left\langle n \left| \sum_j \delta(\mathbf{r}_{jN'}) \hat{\mathbf{S}}_j \right| 0 \right\rangle / ({}^3E_n - E_o) \quad (2.18)$$

where the summation is carried out over the excited singlet states in (2.16) and over the excited triplet states in (2.17) and (2.18). For reasons of completeness, the contribution from  $\hat{H}_{1a}$ , though very seldom calculated, may be included. It has the form

$$J_{\text{NN}'}^{(1a)} = \frac{4}{3h} \frac{e^2 h^2}{2mc^2} \gamma_N \gamma_{N'} \left\langle 0 \left| \sum_k (\mathbf{r}_{kN} \cdot \mathbf{r}_{kN'}) r_{kN}^{-3} r_{kN'}^{-3} \right| 0 \right\rangle \quad (2.19)$$

For the Fermi contact term it may be proved, using the above mentioned general formulae of Condon and Shortley,<sup>(29)</sup> that the three parts of the scalar product due to  $\hat{S}_x$ ,  $\hat{S}_y$  and  $\hat{S}_z$  contribute equally to the coupling constant.  $\hat{S}_z$  involves the  $M_s = 0$  component of the triplets, while  $\hat{S}_x$  and  $\hat{S}_y$  give non-zero matrix elements between the singlet ground state and  $M_s = \pm 1$  triplet components. Equation (2.18) may thus be further simplified by replacing  $\hat{\mathbf{S}}_k$  and  $\hat{\mathbf{S}}_j$  by their  $z$ -components and carrying out the summation over the excited triplet wavefunctions corresponding to  $M_s = 0$  only. Such a replacement means that the multiplication by  $\frac{1}{3}$  in eqn (2.13) and (2.18) should be excluded and the expression for  $J_{\text{NN}'}^{(3)}$  becomes

$$J_{\text{NN}'}^{(3)} = -\frac{128}{9} \beta^2 h \gamma_N \gamma_{N'} \sum_n \left\langle 0 \left| \sum_k \delta(\mathbf{r}_{kN}) \hat{S}_{zk} \right| n, S = 1, M_s = 0 \right\rangle \cdot \left\langle n, S = 1, M_s = 0 \left| \sum_j \delta(\mathbf{r}_{jN'}) \hat{S}_{zj} \right| 0 \right\rangle / ({}^3E_n - E_o) \quad (2.20)$$

Thus, the Fermi contact mechanism is isotropic and does not contribute directly to the anisotropy of the coupling tensor. The other mechanisms are not isotropic; the expressions for the whole coupling tensor may be of interest for them and are readily obtained by suitably replacing the scalar products in eqns (2.16), (2.17) and (2.19) by outer multiplications and excluding the factor  $\frac{1}{3}$ . Furthermore, for studies of anisotropy, the Fermi contact-spin dipolar cross term should be included and is, in fact, dominant in many cases. Substituting the appropriate operators in eqn (2.15) and replacing the scalar product by outer multiplication gives

$$J_{\text{NN}'}^{(2,3)} = -\frac{64\beta^2 h}{3} \gamma_N \gamma_{N'} \sum_n ({}^3E_n - E_o)^{-1} \times \left\langle 0 \left| \sum_k \delta(\mathbf{r}_{kN}) \hat{\mathbf{S}}_k \right| n \right\rangle \times \left\langle n \left| \sum_j r_{jN'}^{-5} (\hat{\mathbf{S}}_j \cdot \mathbf{r}_{jN'}) \mathbf{r}_{jN'} - r_{jN'}^{-3} \hat{\mathbf{S}}_j \right| 0 \right\rangle \quad (2.21)$$

The Rayleigh-Schrödinger perturbation theory eqns (2.16)–(2.21) have been given by Ramsey.<sup>(5)</sup> The main difficulty in using them for calculations is that knowledge of all excited states of the molecule under consideration is required, including continuum, which is an unreachable goal. Different approaches suitable for making the actual calculations will be presented in the next Section. Some of them use eqns (2.16)–(2.21) and a truncated set of excited state wavefunctions with varying degrees of sophistication, others use perturbational schemes of different types. The reason for deriving the general formulae as done in this Section is not dictated by a conviction that these are the most useful ones. Rather, the derivations have been presented partly for historical reasons and partly because of the straightforwardness of the theory behind them.

The variational method has also been applied in the calculation of nuclear spin-spin coupling constants. However, since all the recent applications of this method have been limited to the hydrogen molecule, the review of this theory will be saved for Section 4 on the diatomic molecules.

### 3. COMPUTATIONAL METHODS

#### 3.1. Introductory Remarks

This Section deals with general computational methods for calculation of nuclear spin-spin coupling constants, i.e. methods applicable for one-bond couplings as well as long-range couplings and in diatomic molecules as well as polyatomic molecules. Methods specially designed for the calculation of  $\pi$ -electron contributions, 'through space' couplings, etc. will be discussed in later Sections. Methods applied so far only to diatomic molecules, even if general in principle, will be reviewed in Section 4.

We begin by discussing perturbation methods within the framework of molecular orbital theory. Therefore, it may not be out of place to review briefly the different types of molecular orbital wavefunctions and methods. A somewhat arbitrary but useful classification of the MO methods used for the calculation of nuclear spin-spin coupling constants is the following, where the ordering is based on increasing accuracy:

1. Independent electron LCAO MO methods including all valence electrons; two widely used schemes of this type are those of Hoffman<sup>(30)</sup> and Pople and Santry.<sup>(31)</sup>

2. Semi-empirical self-consistent field (SCF) LCAO MO methods including all valence electrons; the iterative solution of the Hartree-Fock eqns determining the molecular orbitals, as formulated by Roothaan<sup>(32)</sup> is applied with simplifying assumptions about some of the integrals involved. Two such methods, developed by Pople and co-workers, are CNDO<sup>(33-36)</sup> (Complete Neglect of Differential Overlap) and INDO<sup>(36,37)</sup> (Intermediate Neglect of Differential Overlap). The main difference between these two methods lies in the inclusion of one-centre exchange integrals in the INDO method, which is consequently more accurate.

3. Non-empirical (*ab initio*) SCF LCAO MO methods where the Hartree-Fock eqns<sup>(32)</sup> are solved for all electrons after computing all of the integrals involved without approximations. The non-empirical calculations may be further classified depending on the type of the atomic basis set used (Slater type orbitals, STO, or Gaussian type orbitals, GTO) and the size of the basis set.

### 3.2. The Fermi Contact Mechanism: Molecular Orbital Theory

For most of the coupling involving protons and the first row atoms (with a possible exception of fluorine) the Fermi contact mechanism accounts for the dominant contribution to the coupling constants. In many cases, computational schemes have been first developed for this particular contribution and later generalized to include other mechanisms. Thus, it seems appropriate to start this review by presenting methods for the calculation of the Fermi contact contribution to the coupling constants.

Two of the early methods require special attention because they are still being applied. Though it came later chronologically, the method developed by Pople and Santry<sup>(11)</sup> is discussed first. In this method, eqn (2.20) is used and a truncated set of excited states' wavefunctions is constructed by promoting a single electron from the molecular orbital occupied in the ground state into a virtual orbital. This assumption simplifies the form of eqn (2.20) considerably and gives

$$J_{\text{NN}'}^{(3)} = -\frac{64}{9} \beta^2 h \gamma_{\text{N}} \gamma_{\text{N}'} \sum_i \sum_a ({}^3\Delta E_{i \rightarrow a})^{-1} \langle i | \delta(\mathbf{r}_{\text{N}}) | a \rangle \langle a | \delta(\mathbf{r}_{\text{N}'}) | i \rangle \quad (3.1)$$

where the many-electron integrals are reduced to one-electron matrix elements of the Dirac delta function between the occupied MOs  $i$  and unoccupied  $a$ , or the products of orbital amplitudes at the coupled nuclei. The infinite summation over the excited states is replaced by a finite sum over pairs of MOs. The term  ${}^3\Delta E_{i \rightarrow a}$  is the excitation energy corresponding to the excitation of an electron from the orbital  $i$  into  $a$ , the resulting electron configuration being a triplet. Pople and Santry<sup>(11)</sup> then introduced the LCAO MO approximation with a minimal basis set of valence shell atomic orbitals. Further, only the integrals involving a single atomic centre (one-centre integrals) have been retained, giving the following expression

$$J_{\text{NN}'}^{(2)} = -\frac{64}{9} \beta^2 h \gamma_{\text{N}} \gamma_{\text{N}'} s_{\text{N}}^2(0) s_{\text{N}'}^2(0) \times \sum_i^{\text{occ}} \sum_a^{\text{unocc}} c_{i\text{N}} c_{a\text{N}} c_{i\text{N}'} c_{a\text{N}'} ({}^3\Delta E_{i \rightarrow a})^{-1} \quad (3.2)$$

where  $s_{\text{N}}(0)$  is the amplitude at the origin of the valence shell  $s$  orbital associated with nucleus  $\text{N}$  and  $c_{i\text{N}}$  is the LCAO coefficient of this atomic orbital in the  $i$ -th MO. Further, assuming the independent electron model, the triplet excitation energies are given by the differences of the orbital energies  $\epsilon_a$  and  $\epsilon_i$  between orbitals  $a$  and  $i$  and eqn (3.2) may be written in terms of the quantity known as the atom-atom polarizability,  $\pi_{\text{NN}'}$ .

$$J_{\text{NN}'} = \frac{16}{9} \beta^2 h \gamma_{\text{N}} \gamma_{\text{N}'} s_{\text{N}}^2(0) s_{\text{N}'}^2(0) \pi_{\text{NN}'} \quad (3.3)$$

where

$$\pi_{\text{NN}'} = -4 \sum_i^{\text{occ}} \sum_a^{\text{unocc}} \frac{c_{i\text{N}} c_{a\text{N}} c_{i\text{N}'} c_{a\text{N}'}}{\epsilon_a - \epsilon_i} \quad (3.4)$$

At an even earlier date, the MO method for the calculation of the coupling constants was formulated by McConnell<sup>(7)</sup> who started with eqn (2.10) and immediately introduced the average excitation energy approximation. Providing that a suitable average denominator  ${}^3\Delta E$  can be found, the closure relation may be used for the matrix elements in the numerator, yielding an expression solely in terms of the ground state wavefunction

$$J_{\text{NN}'}^{(3)} = -\frac{2}{3h} \left( \frac{16\pi\beta\hbar}{3} \right)^2 \frac{\gamma_{\text{N}} \gamma_{\text{N}'}}{{}^3\Delta E} \times \left\langle 0 \left| \sum_k \sum_j \delta(\mathbf{r}_{k\text{N}}) \delta(\mathbf{r}_{j\text{N}'} \cdot \hat{\mathbf{S}}_k \cdot \hat{\mathbf{S}}_j \right| 0 \right\rangle \quad (3.5)$$

Assuming a singlet ground state and using a LCAO MO approximation, McConnell obtained

$$J_{\text{NN}'}^{(3)} = \frac{16\beta^2 h}{9} \gamma_{\text{N}} \gamma_{\text{N}'} ({}^3\Delta E)^{-1} P_{s_{\text{N}} s_{\text{N}'}}^2 s_{\text{N}}^2(0) s_{\text{N}'}^2(0) \quad (3.6)$$



where  $P_{s_N s_{N'}}$  is the element of the bond order matrix between the valence atomic orbitals  $s_N$  and  $s_{N'}$

$$P_{s_N s_{N'}} = 2 \sum c_{iN} c_{iN'} \quad (3.7)$$

$c_{iN}$  and  $c_{iN'}$  have the same meaning as in eqn (3.2). Actually, the atom–atom polarizability expressed in eqn (3.4) will reduce to (3.7) if the average excitation energy is introduced. The McConnell<sup>(7)</sup> formula (3.6) can thus be viewed as an approximation of formula (3.3) of Pople and Santry.<sup>(11)</sup>

Equation (3.6) has the obvious drawback of predicting a positive sign for all the coupling constants between nuclei with magnetogyric ratios of the same sign. This is not the case with eqn (3.3). The method proposed by Pople and Santry<sup>(11)</sup> is very useful for qualitative discussions and has been used for this purpose with considerable success. The applications using independent electron schemes for numerical calculations were popular in the second half of the sixties.<sup>(12)</sup> However, attempts to use eqn (3.3) and the independent electron models for quantitative discussions were severely criticized by Armour and Stone<sup>(38)</sup> who advocated use of the more correct SCF MO wavefunctions.

This brings us to a very crucial point, which may be stated in the following way: no perturbational treatment can be better than permitted by the zeroth order wavefunctions used. Equation (3.3) given by Pople and Santry,<sup>(11)</sup> is about the best possible when independent electron theory is used. The only minor modification that can be made is the inclusion of the multi-centre integrals. This procedure has been suggested by Varga and Zumdahl<sup>(39)</sup> (who also used a self-consistent charge variant of the extended Hückel theory, EHT, of Hoffman<sup>(30)</sup>) and by Pachler.<sup>(40)</sup> Still, it is questionable whether this really constitutes an improvement and whether it is consistent with the rest of the semi-empirical scheme.

The situation is different when working within the framework of the self-consistent field MO theory. In principle, eqn (3.3) may also be used here; however, in this case it contains an error due to the fact that the triplet excitation energies are no longer given by the simple differences of the orbital energies, but include also an additional term

$${}^3\Delta E_{i \rightarrow a} = \epsilon_a - \epsilon_i - (ii|aa) \quad (3.8)$$

where the symbol  $(ii|aa)$  denotes the Coulomb integral, a special case of an electron repulsion integral

$$(\kappa\lambda|\mu\nu) = \int \phi_\kappa^*(1)\phi_\mu^*(2) \frac{1}{r_{12}} \phi_\lambda(1)\phi_\nu(2) d\tau_1 d\tau_2 \quad (3.9)$$

Further, the one-centre integral approximation, present already in eqn (3.2), may no longer be valid, especially in non-empirical calculations. Thus, in order to find the simplest expression tolerably consistent with SCF MO wavefunctions we must at least revert to eqn (3.1).

The first calculation of nuclear spin–spin coupling constants using a SCF wavefunction and eqn (3.1)

was presented by Loève and Salem<sup>(41)</sup> as early as 1965. The MOs and excitation energy data were actually taken from two different non-empirical calculations using the minimal basis set for the methane molecule. Similar calculations have been carried out subsequently by other authors and will be reviewed below in the Sections dealing with applications.

In the late sixties non-empirical wavefunctions were fairly scarce and expensive to calculate. In the area involving coupling constants, there existed a need of the semi-empirical SCF schemes. The CNDO method and eqn (3.1) were first applied to the problem of nuclear spin–spin coupling by Ditchfield and Murrell<sup>(42)</sup> and a similar application of the INDO method was reported by Ditchfield.<sup>(43)</sup> In both these papers the Coulomb integrals were included but only the one-centre integrals over the Dirac delta function were retained, which is consistent with the other assumptions of the methods employed. The results of these calculations for the proton coupling constants in methane and ethene are given in Table 2 together with the non-empirical results of Loève and Salem<sup>(41)</sup> and Armour and Stone.<sup>(38)</sup>

Equation (3.1) is based on the assumption that the singly-excited triplet configurations give a satisfactory description of the excited states. This assumption, though rather obvious as a first approximation, is not very satisfactory for several reasons. First of all, the virtual orbitals obtained in a SCF calculation are a poor approximation to the orbitals for the excited states, since they are computed in the field of  $2n$  electrons instead of the correct  $2n-1$ . Second, as was pointed out by Nakatsuji<sup>(44)</sup> the expression (3.1) is not independent of a unitary transformation among the excited configurations. In practice this can mean that a transformation to the localized orbitals may cause a major change in the computed value of the coupling constant. This dependence on a unitary transformation arises when the off-diagonal elements of the Hamiltonian matrix for the excited triplet states are neglected. Neglect of these off-diagonal elements will have an additional consequence. Use of eqn (3.1) without special care may lead to results without any physical meaning for systems with high symmetry (at least one three-fold or higher axis). This was first pointed out by Pouzard *et al.*<sup>(45)</sup> and explained in terms of group theory. The spin-projected triplet wavefunctions of the form

$${}^3\Psi_{i \rightarrow a} = \frac{1}{\sqrt{2}} \{ A(\psi_i \bar{\psi}_1 \dots \psi_i \bar{\psi}_a \dots \psi_n \bar{\psi}_n) + A(\psi_1 \bar{\psi}_1 \dots \psi_a \bar{\psi}_i \dots \psi_n \bar{\psi}_n) \} \quad (3.10)$$

used in arriving at (3.1) are not necessarily bases for irreducible representations and should therefore be symmetry-projected. The errors that arise due to neglect of this projection, observed by Pouzard *et al.*<sup>(45)</sup> as differences between the  $J$ -value computed for different pairs of symmetry-related nuclei in cyclohexane ( $D_{3d}$  symmetry), were not very large. A more complete

TABLE 2. Proton coupling constants in methane and ethene obtained using sum-over-states (SOS) calculations

	CNDO <sup>(42)</sup>		INDO <sup>(43)</sup>		Non-emp. <sup>(38,41)</sup>		Exp
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	
CH <sub>4</sub>	1.4	1.7	—	−1.8	−6.1	—	−12.4
C <sub>2</sub> H <sub>4</sub> <i>gem</i>	7.3	9.0	7.8	7.6	12.9	9.3	2.5
C <sub>2</sub> H <sub>4</sub> <i>cis</i>	9.0	11.4	9.0	11.4	6.2	9.6	11.6
C <sub>2</sub> H <sub>4</sub> <i>trans</i>	17.4	24.6	23.5	27.0	14.9	20.1	19.1

<sup>a</sup> No triplet configuration interaction.<sup>b</sup> Triplet configuration interaction included.

collapse is also possible and has been noted by Schaumburg.<sup>(46)</sup> The fluorine–fluorine coupling constant computed for different pairs of fluorines in tetrafluoromethane (*T<sub>d</sub>* symmetry) varied between −113.1 and +12.1 Hz.<sup>(46)</sup> The last point may be corrected by resorting to symmetry projection of the degenerate triplet configuration. This would however not help the other deficiencies of the model, since a more general solution is required. One way to make the excited states more physical, suggested (in the context of calculations of the nuclear spin–spin coupling constants) by Armour and Stone<sup>(38)</sup> on the non-empirical level and by Ditchfield and Murrell<sup>(42,43)</sup> for CNDO and INDO methods, is to allow for mixing of the singly-excited triplet configurations (singly-excited triplet configuration interaction or, concisely, triplet CI).

The wavefunctions describing the excited states in this scheme are the linear combinations of the singly-excited singlet configurations, the coefficients being obtained by diagonalizing the Hamiltonian matrix in the basis of configurations. Following Ditchfield and Murrell,<sup>(42)</sup> we may thus write

$${}^3\Psi_n = {}^3\Psi_{i \rightarrow a} \cdot \mathbf{d} \quad (3.11)$$

where  $\mathbf{d}$  is the eigenvector matrix and  ${}^3\Psi_n$  is the new set of triplet state wavefunctions. The expression for the coupling constant becomes

$$J_{\text{NN}'}^{(3)} = -\frac{64}{9} \beta^2 h \gamma_{\text{N}} \gamma_{\text{N}'} \sum_n ({}^3\Delta E_n)^{-1} \times \sum_i^{\text{occ}} \sum_a^{\text{unocc}} \sum_j^{\text{occ}} \sum_b^{\text{unocc}} \times d_{i \rightarrow a}^n d_{j \rightarrow b}^n \langle i | \delta(\mathbf{r}_{\text{N}}) | a \rangle \langle b | \delta(\mathbf{r}_{\text{N}'}) | j \rangle \quad (3.12)$$

where  $d_{i \rightarrow a}^n$  is an element of the  $\mathbf{d}$  matrix of eqn (3.11) and  ${}^3\Delta E_n$  is the  $n$ -th eigenvalue of  $\mathbf{H} - E_0 \mathbf{I}$ . It should be noted that diagonalization of the Hamiltonian automatically guarantees the proper symmetry projection.

Expression (3.12) requires a considerably larger computational effort than eqn (3.1), because the whole Hamiltonian matrix (the diagonal elements are given by (3.8) and the off-diagonal ones consist of electron repulsion integrals of general type (3.9) with the indices  $\kappa, \lambda, \mu$  and  $\nu$  denoting the MOs) must now be constructed and diagonalized. The first stage of these

calculations cannot be avoided but the second one can be made easier; Armour and Stone<sup>(38)</sup> took into account the interaction between the singly-excited triplet configurations by writing

$$J_{\text{NN}'}^{(3)} = -\frac{128}{9} \beta^2 h \gamma_{\text{N}} \gamma_{\text{N}'} \sum_{m,n} \left\langle 0 \left| \sum_k \delta(\mathbf{r}_{\text{kN}}) \hat{S}_{zk} \right| m \right\rangle \times \langle m | (\mathbf{H} - E_0 \mathbf{I})^{-1} | n \rangle \left\langle n \left| \sum_j \delta(\mathbf{r}_{\text{jN}'}) \hat{S}_{zj} \right| 0 \right\rangle \quad (3.13)$$

which is valid for an arbitrary set of triplets  $|n\rangle$  and  $|m\rangle$  and thus obviously invariant to unitary transformations. Equation (3.12) corresponds to the case when the states  $|n\rangle$  and  $|m\rangle$  are obtained from the singly excited configurations by means of a unitary transformation  $\mathbf{d}$ , which diagonalizes the Hamiltonian. Equation (3.12) is thus a special case of (3.13). The computations implied by (3.13), with such singly-excited triplet configurations as  $|m\rangle$  and  $|n\rangle$  are simpler than those in (3.12) (matrix diagonalization is replaced by matrix inversion) but eqn (3.12) has been used more often. The effect of the triplet CI can be seen in Table 2 and is especially clear in the work of Armour and Stone.<sup>(38)</sup>

Singly-excited triplet CI offers one way to improve the description of the excited states. Other procedures have also been suggested for this purpose. One approach, applied to the problem of the nuclear spin–spin coupling constants in polyatomic molecules by Birnstock and Klöpper,<sup>(47)</sup> is to compute the excited states' orbitals  $a$  in eqn (3.1) as improved virtual orbitals, in the manner developed by Huzinaga and Arnau.<sup>(48)</sup>

Working with eqn (3.1) or (3.12) means that the infinite summation of eqn (2.21) is replaced by a sum over a finite set of discrete excited states obtained within fairly simple models. An entirely different way to handle eqn (2.21) has been suggested by Pyykkö and co-workers.<sup>(21,49)</sup> In their approach the summation is replaced by integration over momenta of the intermediate states. The formula for the coupling constant becomes

$$J_{\text{NN}'} = \frac{64}{9} \beta^2 h \gamma_{\text{N}} \gamma_{\text{N}'} B(n, Z_{\text{N}}) B(n, Z_{\text{N}'}) \int_0^\infty \Phi(k) dk \quad (3.14)$$

where  $B(n, Z)$  is the hydrogen-like relativistic correction (necessary in this case, since coupling constants

involving heavy nuclei are being calculated<sup>(21)</sup>,  $k$  is the momentum of the intermediate state and  $\Phi(k)$  is the spectral density function, defined in slightly different ways for different cases.<sup>(21,49)</sup>

The framework of the Hartree–Fock theory also provides another way of obtaining the second-order properties like the nuclear spin–spin coupling constant, which at first glance appears quite different. This is the so-called coupled Hartree–Fock (CHF) theory. Generally speaking, CHF means that the Hartree–Fock eqns for the molecular orbitals are solved in the presence of a perturbation. There are two computational schemes used for the calculation of the coupling constants that fall into this category. For the first one, like so many other developments in theory of NMR parameters, we are indebted to Pople and co-workers.<sup>(50–52)</sup> Their approach is called the finite perturbation theory (FPT) and involves the calculation of the wavefunction in the presence of a finite perturbation. In the case of the nuclear spin–spin coupling constants this involves an unnaturally large nuclear magnetic moment. In the original papers<sup>(50,52)</sup> the discussion is carried out in terms of the reduced coupling constants  $K_{NN'}$  which are related to  $J_{NN'}$  by eqn (1.2) and we follow this here.

Consider a molecule with two nuclear magnetic moments  $\mu_N$  and  $\mu_{N'}$  directed along the  $z$ -axis. In the presence of the Fermi contact interaction alone, the Hamiltonian for the molecule may be written as

$$\hat{H} = \hat{H}_0 + \mu_N \hat{H}_N + \mu_{N'} \hat{H}_{N'} \quad (3.15)$$

where

$$\hat{H}_N = \frac{16\pi\beta}{3} \sum_k \delta(\mathbf{r}_{kN}) \hat{S}_{zk}. \quad (3.16)$$

From the power expansion of the energy in the presence of the two magnetic moments, the expression for the reduced coupling constant may be written

$$K_{NN'} = \left[ \frac{\partial^2 E(\mu_N, \mu_{N'})}{\partial \mu_N \partial \mu_{N'}} \right]_{\mu_N = \mu_{N'} = 0}. \quad (3.17)$$

Using the Feynman–Hellman theorem, proved by Pople *et al.* to be valid for the SCF wavefunctions in the case at hand,<sup>(51)</sup> the second derivative of energy may be set equal to the first derivative of the expectation value of  $\hat{H}_N$  with respect to  $\mu_{N'}$ , evaluated in the presence of  $\mu_N$ .

$$K_{NN'}^{(3)} = \left[ \frac{\partial}{\partial \mu_{N'}} \langle \Psi(\mu_{N'}) | \hat{H}_N | \Psi(\mu_{N'}) \rangle \right]_{\mu_{N'} = 0}. \quad (3.18)$$

Thus, the calculation of  $K_{NN'}$  requires calculation of the wavefunction in the presence of one of the nuclear magnetic moments,  $\mu_{N'}$ . Subsequent calculation of the expectation value of  $\hat{H}_N$  and its derivative is much simpler and can easily be done for any number of magnetic nuclei in a molecule.

In the finite perturbation method of Pople *et al.*<sup>(50–52)</sup>  $\Psi(\mu_{N'})$  is computed as an unrestricted SCF

LCAO MO wavefunction. This is necessary because the presence of  $\mu_{N'} \hat{H}_{N'}$  (the matrix elements of which enter the Fock matrix with a different sign for  $\alpha$  and  $\beta$  electrons) induces a non-vanishing spin-density in the molecule. The spin-density matrix  $\rho$  may be defined as the difference between the first-order density matrices associated with  $\alpha$  and  $\beta$  electron spins.

$$\rho = \mathbf{P}^\alpha - \mathbf{P}^\beta \quad (3.19)$$

and the expectation value of  $\hat{H}_N$  appearing in (3.18) may be written in terms of  $\rho$

$$\langle \Psi(\mu_{N'}) | \hat{H}_N | \Psi(\mu_{N'}) \rangle = \frac{8\pi\beta}{3} \sum_{\lambda, \nu} \rho_{\lambda\nu}(\mu_{N'}) \langle \lambda | \delta(\mathbf{r}_N) | \nu \rangle \quad (3.20)$$

where  $\lambda$  and  $\nu$  denote the atomic orbitals. Now, the  $\mu_{N'}$  dependence of the right-hand side of eqn (3.20) is limited to the spin-density matrix. Derivation with respect to  $\mu_{N'}$  gives the reduced coupling constant

$$K_{NN'}^{(3)} = \frac{8\pi\beta}{3} \sum_{\lambda, \nu} \langle \lambda | \delta(\mathbf{r}_N) | \nu \rangle \left[ \frac{\partial}{\partial \mu_{N'}} \rho_{\lambda\nu}(\mu_{N'}) \right]_{\mu_{N'} = 0} \quad (3.21)$$

which is generally valid with any type of SCF LCAO MO procedure. Pople and associates then introduce the one-centre integral approximation, consistent with the semi-empirical CNDO and INDO methods. The matrix elements of  $\delta(\mathbf{r}_N)$  are set to zero unless  $\lambda = \nu =$  valence shell  $s$  orbital on nucleus  $N$ . This assumption reduces the double sum over atomic orbitals in eqn (3.21) to a single term

$$K_{NN'}^{(3)} = \frac{8\pi\beta}{3} s_N^2(0) \left[ \frac{\partial}{\partial \mu_{N'}} \rho_{s_N s_N}(\mu_{N'}) \right]_{\mu_{N'} = 0}. \quad (3.22)$$

The one-centre integral approximation also affects the calculation of  $\alpha$  and  $\beta$  MOs and thus the spin-density matrix. The implementation of the perturbation in the SCF scheme simply involves the addition of a quantity

$$h_{N'} = \frac{8\pi\beta}{3} \mu_{N'} s_N^2(0) \quad (3.23)$$

to the diagonal Fock matrix elements corresponding to  $s$  orbital of atom  $N'$  for  $\alpha$  orbitals; for  $\beta$  orbitals  $h_{N'}$  is subtracted from the analogous matrix elements. Substituting  $\mu_{N'}$  from (3.23) into (3.22) we obtain

$$K_{NN'}^{(3)} = \left( \frac{8\pi\beta}{3} \right)^2 s_N^2(0) s_{N'}^2(0) \times \left[ \frac{\partial}{\partial h_{N'}} \rho_{s_N s_N}(h_{N'}) \right]_{h_{N'} = 0} \quad (3.24)$$

and the last remaining problem is the calculation of the derivative in eqn (3.24). This is done using the method of finite differences. Due to the fact that  $\rho$



is an odd function of  $h_{N'}$ , only one  $h_{N'}$  value is needed for the calculation. With a suitable choice of  $h_{N'}$  the derivative can be approximated by  $\rho_{s_N s_{N'}}(h_{N'})/h_{N'}$  and the final expression for the coupling constant is given by

$$K_{NN'}^{(3)} = \left(\frac{8\pi\beta}{3}\right)^2 s_N^2(0) s_{N'}^2(0) \frac{\rho_{s_N s_{N'}}(h_{N'})}{h_{N'}}. \quad (3.25)$$

The orbital densities  $s_N^2(0)$  can be obtained from atomic Hartree–Fock calculations or can be considered as adjustable parameters. In each case they can also be made atomic charge dependent. The values given by Pople *et al.*<sup>(52)</sup> have been obtained from a least-squares fit of the calculated coupling constants to the experimental ones and are somewhat larger than the atomic Hartree–Fock values.

In recent years the finite perturbation method using an INDO approximation has been the most widely used approach for calculation of the coupling constants and many results obtained with this method will be reviewed in the Sections dealing with applications. Here, just a single set of results for the geminal coupling constant in methane is given. On the CNDO level  $^2J_{\text{HH}} = 1.60$  Hz is obtained, which goes down to  $-6.17$  Hz when one-centre exchange integrals are introduced in the INDO approximation. The experimental value is  $-12.4$  Hz and the FPT INDO value compares favourably with the sum-over-states (SOS) results obtained using eqns (3.1) and (3.12), cf. Table 2. The superiority of the FPT over the SOS methods at the INDO and CNDO levels seems to be a general and well-established result. There is, however, one disturbing point about the FPT approach. The non-empirical tests of the method performed (using a minimal STO basis set) by Ostlund *et al.*<sup>(53)</sup> yield much poorer results than those obtained using semi-empirical methods. To take just a single example, the geminal coupling obtained for methane was  $-58$  Hz. For most other cases considered by Ostlund *et al.*,<sup>(53)</sup> the signs were correct but the magnitudes were severely overestimated. Since the non-empirical calculations should be expected to be more reliable than the semi-empirical ones, this point should really be investigated in more detail, especially in view of the tremendous impact made by the semi-empirical FPT calculations. The reason for the poor quality of the results is probably the insufficient flexibility of the minimal basis set.

An alternative computational scheme of the coupled Hartree–Fock type has been proposed by Blizzard and Santry.<sup>(54,55)</sup> By analogy with FPT, expression (3.21) is the method's basic eqn. The derivative of the spin-density matrix is, however, evaluated in a different way, i.e. from the first-order correction of the molecular orbitals. Let  $\mathbf{c}_i^{(0)}$  be a column vector representing the  $i$ -th occupied MO in the space spanned by the atomic orbital basis and  $\mathbf{c}_i^{(1)}$  a column vector representing the first-order correction to  $\mathbf{c}_i^{(0)}$  due to the perturbation  $\mu_N \hat{H}_{N'}$  (compare eqns (3.15)

and (3.16)). Using standard second-order perturbation theory with

$$\mathbf{F}^{(0)} \mathbf{c}_i^{(0)} = \epsilon_i \mathbf{c}_i^{(0)} \quad (3.26)$$

as the zeroth-order eqn, the expression for  $\mathbf{c}_i^{(1)}$  becomes

$$\mathbf{c}_i^{(1)} = \left[ \sum_a (\epsilon_a - \epsilon_i)^{-1} \mathbf{c}_a^{(0)} \tilde{\mathbf{c}}_a^{(0)} \right] \mathbf{F}^{(1)} \mathbf{c}_i^{(0)} \quad (3.27)$$

$\mathbf{F}^{(0)}$  in eqn (3.26) is the Fock matrix in the absence of the perturbation and  $\mathbf{F}^{(1)}$  is the first-order correction to the Fock matrix.  $\mathbf{F}^{(1)}$  depends on the first-order correction to the density matrices for the  $\alpha$  and  $\beta$  electrons, defined in the following way

$$P_{\lambda\nu}^{\alpha(1)} \equiv \left( \frac{\partial P_{\lambda\nu}^{\alpha}}{\partial \mu_{N'}} \right)_{\mu_{N'}=0} = \sum_i (c_{i\lambda}^{(0)} c_{i\nu}^{(1)} + c_{i\lambda}^{(1)} c_{i\nu}^{(0)}) \quad (3.28)$$

Due to the dependence of  $\mathbf{F}^{(1)}$  on  $\mathbf{P}^{(1)}$ , eqn (3.27) for the first-order corrections to the orbitals must be solved iteratively. When convergence is reached, eqn (3.28) gives the sought-after value of the derivative of the spin density matrix. From the symmetry of the operator  $\hat{H}_{N'}$ , we have

$$\mathbf{P}^{\alpha(1)} = -\mathbf{P}^{\beta(1)} \quad (3.29)$$

and

$$\left( \frac{\partial \rho_{\lambda\nu}}{\partial \mu_{N'}} \right)_{\mu_{N'}=0} = 2P_{\lambda\nu}^{\alpha(1)}. \quad (3.30)$$

Further, Blizzard and Santry<sup>(54,55)</sup> introduced the INDO approximation with the same assumptions about the integrals as those of Pople *et al.*<sup>(52)</sup> The final expression for the reduced coupling constant then becomes

$$K_{NN'}^{(3)} = 2P_{s_N s_{N'}}^{(1)} \left( \frac{8\pi\beta}{3} \right)^2 s_N^2(0) s_{N'}^2(0). \quad (3.31)$$

It should be pointed out that there is no fundamental disparity between the methods of Pople *et al.*<sup>(50–52)</sup> and Blizzard and Santry.<sup>(54,55)</sup> In the former case the spin density matrix is calculated correctly to the infinite order in  $\mu_{N'}$  and then derived with respect to it at the  $\mu_{N'} = 0$  limit. In the later method the first-order spin density matrix, equal to the derivative by definition, is computed directly. The differences are of a computational nature; in this respect the self-consistent perturbation theory (SCPT) of Blizzard and Santry has the advantage of replacing the tedious and sometimes slow-to-converge unrestricted SCF procedure by a series of simple matrix multiplications.

The Blizzard–Santry approach has also been used on the non-empirical level by Ditchfield and Snyder.<sup>(56)</sup> The subject of this paper was actually the anisotropy of the coupling tensor and it will be reviewed later.